THE INORGANIC STRUCTURAL CRYSTALLOGRAPHY OF ANTIMONY TRICHLORIDE 1-HALONAPHTHALENE MOLECULAR COMPLEXES

Juan Ladislao Arroyo Cuyubamba

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THE INORGANIC STRUCTURAL CRYSTALLOGRAPHY OF ANTIMONY TRICHLORIDE·1-HALONAPHTHALENE MOLECULAR COMPLEXES

being a thesis presented by

JUAN LADISLAO ARROYO CUYUBAMBA

to the University of St. Andrews
in application for the degree of
Doctor of Philosophy

CERTIFICATE

I certify that Mr.Juan L. Arroyo C. has spent nine terms at the University of St.Andrews in research under my supervision, that he has fulfilled the conditions of Ordinance No.12 and of Resolution No.1 of the St.Andrews Court 1967 and that he is qualified to submit this Thesis in application for the degree of Doctor of Philosophy.

September 1980 Signed:

R.Hulme (Research Supervisor)
Chemistry Department,
St. Andrews.

DECLARATION

I declare that this Thesis is a record of my own work, that it is my own composition and that it has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, the University of St.Andrews, under the direction of Mr.R.Hulme.

September 1980 Signed:

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ABSTRACT

The compounds formed by $SbCl_3$ and the 1-halonaphthalene in the crystalline state may provide information on some of the factors involved in molecular complex formation.

The gradation in both the size and the electronegativity of the naphthalene substituent permits comparisons internally and externally with the parent $2SbCl_3$·naphthalene complex. Other molecular complexes are briefly surveyed.

(1:1)$SbCl_3$·1-bromonaphthalene forms triclinic crystals, $P\bar{1}$. with $a=9.08$, $b=11.98$, $c=12.72$ Å, $\alpha=113.1$, $\beta=93.6$, $\gamma=91.5^\circ$ $V=1268$ Å^3, $Z=4$. Photographic Mo data refined to $R=0.14$ for 591 reflections. The crystal structure is built up of double layers of $SbCl_3$ molecules alternating in the "c" direction with double layers of 1-bromonaphthalene molecules, tilted 25° to [010] . The $SbCl_3$ molecules form dimers, further bridged into infinite chains. The Sb atoms are in a distorted pentagonal bipyramid environment, with a bonded chlorine atom and the aromatic π-system in axial positions at 2.38 and 3.32Å. The lone pair of electrons is stereochemically inactive.

(2:1)$SbCl_3$·1-chloronaphthalene forms monoclinic crystals, Cc, with $a=16.059$, $b=9.525$, $c=11.674$ Å, $\beta=98.63^\circ$, $V=1765$ Å^3, $Z=4$. Diffractometer Mo data refined to $R=0.125$ for 1035 reflections. The structure is built up of double layers of $SbCl_3$ molecules alternating in the "a" direction with single layers of 1-chloronaphthalene molecules, tilted $\sim 25^\circ$ to [001]. $SbCl_3$ molecules form dimers, further bridged into infinite chains. Two non-equivalent $SbCl_3$ molecules are situated near to the 1-chloronaphthalene molecule (~ 3.32Å). Sb(1) is close to the ring carrying the chlorine atom whereas Sb(2) is close

to the other ring on the opposite side. The Sb atom is in a distorted pentagonal bipyramid environment, with a bonded chlorine atom and the aromatic π-system in axial positions at 2.32 and 3.32 Å respectively. Again the lone pair of electrons is stereochemically inactive.

(1:1)$SbCl_3 \cdot$1-iodonaphthalene forms triclinic crystals, P1, with $a=13.15$, $b=7.65$, $c=15.01$ Å, $\alpha=104.7^\circ$, $\beta=102.2^\circ$, $\gamma=108.5^\circ$, $V=1312$ Å^3, $Z=4$. Photographic Mo data refined to $R=0.20$ for 678 reflections having ℓ even. With ℓ odd serious streaks appear suggesting a partly disordered structure. The crystal structure is built up of double layers of $SbCl_3$ molecules alternating in the "a" direction with double layers of 1-iodonaphthalene molecules, tilted $\sim 25^\circ$ to [010]. The two $SbCl_3$ molecules are linked to one another by Sb...Cl bridging, which are part of an infinite chain. Plane-to-plane molecular stacking of 1-$C_{10}H_7I$ is observed. The Sb environment is similar to that in the 1-bromonaphthalene compound.

It seems that the $SbCl_3$:1-halonaphthalene complexes may be linked by an electron-donor-acceptor interaction where an electron donation occurs from the π-system to the antimony atom.

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APPENDIX

A Computing program to calculate the best fit of a rigid molecule in a triclinic cell.

B Observed structure amplitudes and calculated structure factors for (1:1) $SbCl_3$·1-bromonaphthalene complex.

C Observed and calculated structure amplitudes for the (2:1) $SbCl_3$·1-chloronaphthalene complex.

D Observed and calculated structure amplitudes for the (1:1) $SbCl_3$·1-iodonaphthalene complex.

1. INTRODUCTION

Molecular Complexes present the current valence theory with a challenge. The reason for their formation is not fully understood and several factors affect their formation. This thesis will be concerned with one particular type of molecular complex formed by antimony trichloride with aromatic hydrocarbon systems. The existence of complexes may be established analytically and by the construction of the appropriate phase diagram, but structural information depends upon x-ray diffraction studies of these crystalline molecular complexes.

The particular aromatic systems chosen for study are the 1-halonaphthalenes, partly because they may be compared with the $2SbCl_3$·naphthalene complex whose structure has been determined, and partly because they present a gradation both in the size and the electronegativity of the substituent. Such controlled change may make possible the understanding of some of the factors involved in complex formation, and the type of interaction which occurs between the two components of a molecular crystal.

This chapter will be concerned to outline chemical aspects of molecular complexes and to mention some structural features.

1.1 FEATURES OF MOLECULAR COMPLEXES

A molecular complex is defined as an association of molecules with definite stoichiometry. The association is customarily taken to be stronger than Van der Waals interactions between closed electronic shell structures.

Four classes of molecular complexes are known:

a) Inclusion Compounds: which are based on the tendency to form a phase of highest possible density by the inclusion of foreign molecules in order to reach a state of lowest energy content (Ketelaar, 1958,p364). In this group are the clathrates, the gas hydrates and certain compounds of urea.

b) Compounds which are held together by hydrogen bonding (Cameron, 1975). For example the 1:1 complex of urea and barbital ($CH_4N_2O \cdot C_8H_{12}N_2O_3$) (Gartland and Graven, 1974).

c) Compounds which are 'polarization bonded', in which no formal electron transfer is involved, but only dipole interaction, for example the purine-hydrocarbon systems (Claverie, Pullman and Caillet, 1966; Foster, 1969,p356).

d) Those compounds in which molecules of low ionization-potential are associated with molecules of high electron affinity to form Electron-Donor-Acceptor (EDA) complexes, also called 'charge-transfer' complexes. The present survey is mainly concerned with this class of complex.

Some authors have suggested that EDA complexes play an important role in biology particularly in hormone action (Alison and Nash, 1959; Karreman, Isenberg, et.al., 1959; Sheina, Radchenko, et.al., 1979). Others (Epstein, et.al., 1964) have thought that the formation of EDA complexes might explain the observed correlation between the electron-donor-acceptor capacity of some compounds and their carcinogenic activity. It has been suggested also that the action of certain drugs may be related to the formation of this type of compound (Foster, 1969, p335; Kill and Widdowson, 1976).

In chemistry, molecular complexes have been proposed as reaction intermediates (Kosower,1965;Foster,1969,p303; Colter and Dack, 1973),e.g. in some photochemical reactions (Foster,1969,p326;Tsujimoto, et.al., 1976; Nonhebel and Walton, 1976; Ohashi and Tsujimoto, 1976). They are thought also to participate in kinetic processes (Corriu and Coste, 1967; Kubota, 1976); in catalysis (Satchel, 1970; Brieger and Tzuu-Heng, 1976) and in the construction of semiconductor materials (Hertler, 1976; Glazov and Kiselev, 1976; Lyalikova, et.al., 1975).

In particular complexes of $SbCl_3$ with organic substrates have played an important role in similar processes (Corriu and Coste, 1967; Corriu, Coste and Guerin, 1970; Lyalikova, et.al., 1975), and have some use as model compounds for certain classes of conducting polymers (Baughman, R.H., et.al., 1979).

1.2 CHARACTERISTICS OF ELECTRON-DONOR-ACCEPTOR COMPLEXES

EDA complexes share the following features:

a) Their composition as shown in phase diagrams corresponds to integral mole ratios of the components. The complex constitutes a new phase with a structure distinct from either of the components

b) The distances separating component molecules in the crystalline state are shorter than the Van der Waals distances but greater than those of covalent bonds.

c) They have, usually, small heats of formation and definite formation constants (Prout and Kamenar, 1973).

d) The presence of a new charge-transfer band in the visible or UV spectrum of the complex which is not found in the spectrum of either component.

1.3 QUANTUM MECHANICAL TREATMENT OF ELECTRON-DONOR-ACCEPTOR COMPLEXES

It was Mulliken (1952, a, b) who formulated a quantum-mechanical explanation for the stability, spectral features and dipole moment of such complexes. Mulliken's treatment applies only to cases in which the donor and acceptor are neutral closed-shell species and both are in totally symmetrical singlet electronic states.

In the case that donor and acceptor are even-electron systems, the lowest energy wave function of the combined system Ψ_N, is:

$$\Psi_N(D \cdot A) \approx a\ \Psi_0(D,A) + b\ \Psi_1(D^+-A^-) + c\ \Psi_2(A^+-D^-) \qquad (1.3.1)$$

Where the no-bond wave function $\Psi_0(D,A)$ is an antisymmetrized product of Ψ_D and Ψ_A, and the 'dative' wave function $\Psi_1(D^+-A^-)$ represents transfer of an electron from donor to acceptor. The third term $\Psi_2(A^+-D^-)$ may arise when the donor D (a weak base) and acceptor A (a weak acid) are in their symmetrical ground states, but $c < b \leq a$ and $c \rightarrow$ zero if donor or acceptor are strong.

In the case of 'self-complexes', where both components have similar donor and acceptor properties, b=c, and,

$$\int \Psi_N^2\, d\tau = a^2 + b^2 + 2ab\,S_{01} = 1 \qquad (1.3.2)$$

Where the overlap integral $S_{01} = \int \Psi_0 \Psi_1 \, d\tau$ (1.3.3)

Apportioning the overlap term evenly the fractional amounts of no-bond and dative character in Ψ_N are (Mulliken and Person, 1969a):

$$F_{01} = a^2 + ab\, S_{01}, \qquad F_{1N} = b^2 + ab\, S_{01} \qquad (1.3.4)$$

F_{1N} is equal to the fraction of an electronic charge which has been transferred from D to A in the complex.

Regarding configurational properties of EDA complexes, Mulliken and Person (1969b) have suggested the 'principle of compromise geometry', by which the configurations of D and A in the complex are compromises between those expected in free D and A and those expected in the dative structure.

For example in the weak benzene.Cl_2 complex, the π electron removed from the π-donor benzene goes into an antibonding σ^*MO of Cl_2. Hence, by the principle of compromise geometry, the contribution of $b\Psi_1$ to Ψ_N during the formation of the complex should lead to a weakening of the internal bonding both in D and in A In practice d(Cl-Cl) changes from 2.99 to 2.98 Å. (Hassel and Strømme, 1959). The complex as a whole is nevertheless more stable than D and A separately because the internal losses are compensated by resonance stabilization due to the mixing of the dative and no-bond structures.

THE EXCITED-STATE AND CHARGE-TRANSFER SPECTRA.

Complementary to Ψ_N a corresponding excited state exists which is primarily dative in character and is given by:

$$\Psi_E \approx a^* \Psi_1(D^+-A^-) - b^* \Psi_0(D,A) + \ldots \qquad (1.3.5)$$

and, for weak complexes, $b^* \ll a^*$.

The excited state can be attained by the absorption of either UV or visible light. The transition from the ground state to the excited state which accompanies the absorption of light of appropriate wavelength corresponds to the transfer of an electron from the donor to the acceptor. Thus an intense absorption band (The charge-transfer band) corresponding to $\Psi_N \rightarrow \Psi_E$ is predicted, even for "loose" complexes. This probably accounts for the colour observed when some molecular complexes are formed.

ENERGIES OF THE NORMAL AND CHARGE-TRANSFER (CT) STATES

The energies W_N and W_E associated with the total wave function of the ground state and CT state are given by:

$$W_N = \langle \Psi_N | H | \Psi_N \rangle \quad \text{and} \quad W_E = \langle \Psi_E | H | \Psi_E \rangle \qquad (1.3.6)$$

Solving these equations after substituting for Ψ_N and Ψ_E from equations (1.3.1) and (1.3.5) gives the solution for W whose two roots are to be identified as W_E and W_N:

$$W = \left[1/(1-S_{01}^2) \right] \left\{ \tfrac{1}{2}(W_0 + W_1) - S_{01}W_{01} \pm \left[(\Delta/2)^2 + \beta_0 \beta_1 \right]^{\frac{1}{2}} \right\} \qquad (1.3.7)$$

where $S_{01} = \int \Psi_0 \Psi_1 \, d\tau$ and $W_{ij} = H_{ij} = \int \Psi_i^* H \Psi_i \, d\tau$

$$\beta_0 = W_{01} - W_0 S_{01} \qquad (\beta_0 < 0) \qquad (1.3.8)$$

$$\beta_1 = W_{01} - W_1 S_{01} \qquad (\beta_1 < 0) \qquad (1.3.9)$$

$$\Delta = W_1 - W_0 \qquad (1.3.10)$$

From (1.3.8) and (1.3.9) one can find that,

$$\beta_1 - \beta_0 = -S_{01}\Delta \text{ , and } |\beta_1| > |\beta_0| \text{ if } \Delta > 0 \text{ and } S_{01} > 0 \qquad (1.3.11)$$

The frequency of the CT band is then given by:

$$h\nu_{CT} = W_E - W_N = \left[2/(1-S_{01}^2)\right] \cdot \left[(\Delta/2)^2 + \beta_0\beta_1\right]^{\frac{1}{2}} \qquad (1.3.12)$$

and the related wave functions are:

$$\Psi_N = (\Psi_0 + \rho\Psi_1)/\left[\, 1 + 2\rho S_{01} + \rho^2\right]^{\frac{1}{2}} \qquad (1.3.13)$$

$$\Psi_E = (\Psi_1 - \rho^*\Psi_0)/\left[\, 1 - 2\,\rho^* S_{01} + \rho^{*\,2}\right]^{\frac{1}{2}} \qquad (1.3.14)$$

where $$\rho = {}^{b}/_{a} = \frac{-(W_0-W_N)}{(W_{01}-S_{01}W_N)} = -\frac{(W_{01}-S_{01}W_N)}{(W_1-W_N)} \qquad (1.3.15)$$

$$\rho^* = \frac{b^*}{a^*} = \frac{(W_{01}-S_{01}W_E)}{(W_0-W_E)} = \frac{(W_1-W_E)}{(W_{01}-S_{01}W_E)} \qquad (1.3.16)$$

Fig. 1.3.1a, indicates schematically the energies and wave functions when Δ is small.

For weak complexes the approach between D and A molecules is not much closer than the van der Waals distance, so that S_{01}^2, β_0, and β_1 are small; besides Δ is usually large so that $(\Delta/2)^2 \gg \beta_0\beta_1$. So according to Mulliken by using 'Perturbation Theory' one finds approximate energies:

$$W_N = W_0 - \beta_0^2/\Delta \quad + \text{ small correction terms} \qquad (1.3.17a)$$

$$W_E = W_1 + \beta_1^2/\Delta \quad + \text{ small correction terms} \qquad (1.3.17b)$$

The energy of the CT band is therefore,

$$h\nu_{CT} = \Delta + (\beta_0^2 + \beta_1^2)/\Delta + \ldots, \qquad (1.3.18)$$

in this case, $\rho = b/a = -\beta_0/\Delta \quad (\rho > 0 \text{ if } \Delta > 0)$ (1.3.19a)

$$\rho^* = b^*/a^* = -\beta_1/\Delta \; (\rho^* > 0 \text{ if } \Delta > 0) \qquad (1.3.19b)$$

Fig 1.3.1b shows the perturbation theory solution when $\Delta^2 \gg \beta_0 \beta_1$.

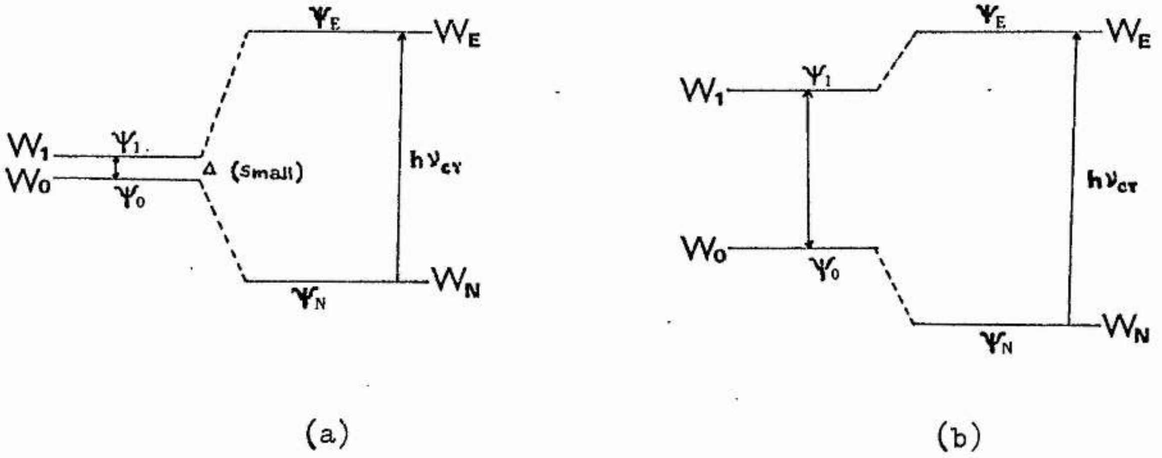


Fig 1.3.1. Energy level diagrams.

(a) For $\Delta \approx 0$ (b) Perturbation theory solution for $\Delta^2 \gg \beta_0 \beta_1$

The results of this resonance interaction are: (i) stabilization of the ground state by the mixing in of the CT state, hence the formation of a complex; and (ii) absorption of light for the transition ground state → CT-state with transfer of an electron from an orbital associated with the electron donor to an orbital associated with the electron acceptor. The size of the CT resonance interaction is proportional to the overlap integral between orbitals D and A, S_{DA}, defined by (Poleshchuk and Maksyutin, 1976):

$$S_{01} = \sqrt{2} \; S_{DA}/(1 + S_{DA}^2)^{\frac{1}{2}} \qquad (1.3.20)$$

$\Psi(D,A)$ and $\Psi(D^+-A^-)$ are sensitive to the relative orientations of the donor and acceptor, and only if $\Psi(D^+-A^-)$ is much more sensitive to the relative orientations of donor and acceptor than $\Psi(D,A)$ will the CT interaction be largely responsible for determining the structure of the complex (Prout and Kamenar, 1973). Thus the CT interaction will vary with orientation due to the dependence of S_{DA} on: (a) The distances between atomic centres on the donor and acceptor molecules. (b) The MO coefficients of the relevant donor and acceptor orbitals which may by symmetry partly or totally negate the overlap integral S_{DA} even though there is a large degree of 'overlap' between donor and acceptor molecules.

Experimentally, the orientation of D with respect to A in the complex, and the changes in the internal geometry of D or A, may be found in principle by x-ray diffraction studies of the solid complex. Theoretically, the orientation is determined by a balance of several factors within Ψ_0, such as electrostatic and dispersion attractive forces, and exchange repulsion forces (Mulliken and Person, 1969b).

ALTERNATIVES TO MULLIKEN'S THEORY

The current Mulliken's theory outlined above, has been questioned by several authors. Thus, Weiss (1942, 1943) would emphasise interaction between the ground states of the components giving compounds with ionic ground states, i.e. coulombic interaction between the partners of the complex. However Dewar and Thompson (1966) and Lefevre et.al. (1968) have argued that a more important contribution comes from dispersion and polarization forces. Other authors (Briegleb, 1961, p2ff. Herbstein, 1971; Hanna and Lippert, 1973; Sheina, Radchenko et.al., 1979; Kaplan, 1979) have supported both ideas in different degrees.

The final word is still to be said. Nevertheless, it is convenient to attempt a classification of donor and acceptor molecules.

1.4 CLASSIFICATION OF DONORS AND ACCEPTORS

Donor (D) and acceptor (A) are relative terms since particular compounds act as donors in some circumstances and as acceptors in others. Mulliken and Person (1969) have clasified electron donors and electron acceptors into increvalent and sacrificial type according to the functional and structural type. Increvalent donors are lone-pair (n) donors for which electrons are donated from an essentially non-bonding orbital with the subsequent increase of bonds without affecting the bonding in D. Sacrificial σ or π electron donors or sacrificial σ^* or π^* electron acceptors are molecules in which electrons are donated from bonding σ or π MO's or accepted by antibonding σ^* or π^* MO's respectively with the consequent weakening of the intramolecular bonding of the D or A. Increvalent electron acceptors (v) are molecules with a vacant valence shell orbital. See Table 1.4.1.

TABLE 1.4.1

MAJOR CLASSES OF ELECTRON-DONOR AND ACCEPTOR MOLECULES[a]

SYMBOL	STRUCTURE TYPE SITE OF DONOR/ACCEPTOR ACTION	NATURE OF DONOR/ ACCEPTOR ACTION	EXAMPLES
	ELECTRON DONORS		
n	valence-shell lone pair	increvalent	Amines, ethers, halides, etc.
$b\sigma$	σ bonding electrons	sacrificial	Aliphatic hydrocarbons and RX
$b\pi$	π bonding electrons	sacrificial	Aromatic and unsaturated hydrocarbons
	ELECTRON ACCEPTORS		
v	vacant valence-shell	increvalent	BCl_3, Ag^+, etc. or compounds of B.
$a\sigma^*$	σ^*antibonding electrons	sacrificial	X_2^b, XY, HX, RX
$a\pi^*$	π^* antibonding MO	sacrificial	Unsaturated and aromatic hydrocarbons fortified with electron withdrawing groups

[a] After Mulliken and Person (1969b)

[b] X, Y represent any halogen atom.

Much of this classification is debateable and uncertain. What is unambiguous is the relative arrangement of molecules in crystal structures, which therefore provide test data with which to evaluate interpretations and classifications of EDA complexes. Thus a review of some EDA type crystal structures is relevant at this point.

1.5 CRYSTAL STRUCTURES OF DONOR-ACCEPTOR COMPLEXES

Most of the geometrical configurations in the solid state have been determined by x-ray diffraction technique. Following Prout and Kamenar (1973), complexes of $n-\sigma^*$, $n-\pi^*$, $\pi-\sigma^*$ and $\pi-\pi^*$ types are considered here.

1.5.1 CRYSTAL STRUCTURES OF $n-\sigma^*$ TYPE

In the majority of the structures of this kind of complex, the donor is a nitrogen atom of an amine or aromatic nitrogen heterocycle; oxygen, sulphur or selenium atoms may act similarly. The electron acceptors include the halogens, halogen-rich halo-alkanes, and the antimony (III) halides.

e.g. Trimethylamine-iodine (Strømme, 1959); 1,4-dioxane with bromine (Hassel and Hvoslef, 1954) and (1:2) 1,4-dithiane antimony triiodide (Bjørvatten,1966).

The structure of $(CH_3)_3N \cdot I_2$ consists of isolated molecules in which the nitrogen is bound to iodine. d(N···I) is 2.27Å, which is 1.4Å less than the sum of Van der Waals radii and only about 0.3Å greater than the sum of covalent radii. d(I-I) is 2.83Å, 0.17Å longer than in a free I_2 molecule. The nitrogen atom has a fairly regular tetrahedral coordination and the N···I-I system is linear. The second iodine atom is involved in intermolecular binding by Van der Waals forces only.

In the case of 1,4-dioxane·Br_2, the most significant feature is the formation of halogen-bridges between pairs of oxygen-donor atoms. d(O···Br) is 2.71Å equatorial and the O···Br-Br···O system is approximately linear. D(Br-Br) 2.31Å. Fig. 1.5.1a.

In 1,4-dithiane·SbI_3 , each Sb atom is bound to 2 sulphur atoms of different molecules and two such 'antimony bridges' link neighbouring dithiane molecules together, resulting in endless chains of SbI_3 and dithiane molecules. $d(Sb\cdots S)$ 3.27 and 3.34Å $d(Sb-I)$ at 2.78, 2.75 and 2.77Å, are all significantly longer than the value (2.72Å) in SbI_3 itself, which supports the idea that Sb in SbI_3 may act as an acceptor towards n donors. Fig. 1.5.1b.

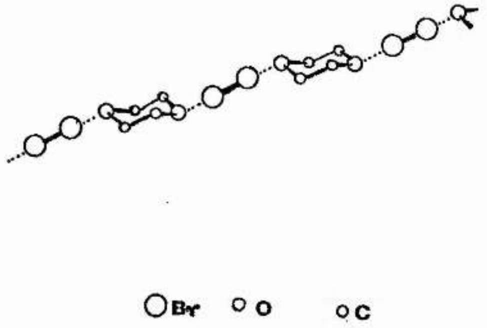


Fig 1.5.1a Structure of the 1,4-dioxane-bromine complex.

(After Hassel and Hvoslef, 1954)

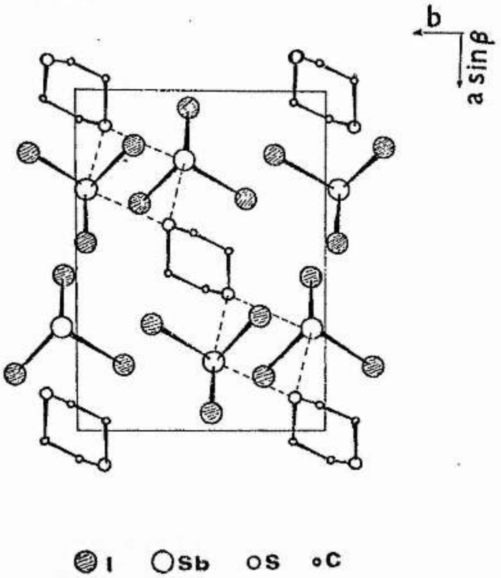


Fig 1.5.1b Structure of SbI_3-1,4-dithiane complex

(After Bjφrvatten, 1966).

1.5.2 CRYSTAL STRUCTURES OF $\pi - \sigma^*$ TYPE

This kind of complex is formed when a π donor (usually an aromatic hydrocarbon) interacts with a σ^* acceptor (a halogen molecule or halogen-rich halo-alkane).

Representative examples are the 1:1 complexes of benzene with bromine and chlorine (Hassel and Strφmme, 1958, 1959), and of p-xylene with carbon tetrabromide (Strieter and Templeton, 1962).

The benzene-Br_2 complex is formed with Br-Br bond co-incident with the perpendicular through the centroid of the benzene ring plane (Fig. 1.5.2). The Br atom is 3.36Å out of the c plane and $d(Br-Br)$ is 2.28Å the same as that found in the free molecule.

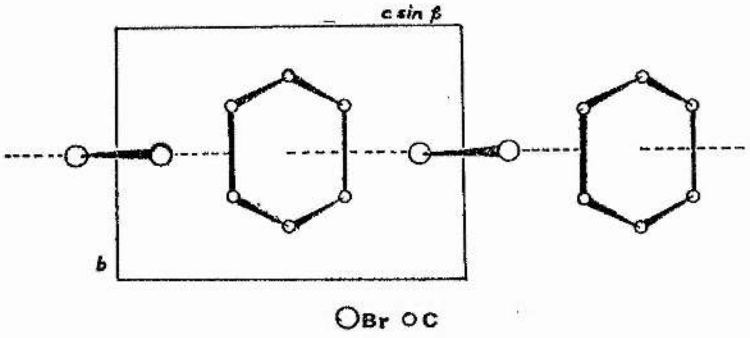


Fig 1.5.2 Structure of the benzene-bromine complex (After Hassel and Strφmme, 1958).

1.5.3 THE CRYSTAL STRUCTURES OF n-π^* TYPE

This type of complex is formed by the interaction of an n-donor (a lone-pair electron donor) with a π acceptor (aromatic hydrocarbon with electron withdrawing substituents). Few examples have been reported in the literature. The 1:1 complex of $N_2O_4 \cdot 1,4$-dioxane (Groth and Hassel, 1965) has been classified under this type by Prout and Kamenar (1973), assuming that the π^* orbital of the oxygen makes the more important contribution (Fig. 1.5.3a). A second example is that of triethylphosphate-benzotrifurazan (Cameron and Prout, 1968). In this complex the phosphate P=O group lies along the perpendicular to the ring plane at its centroid and the oxygen atom is only 2.49Å above the ring. (Fig. 1.5.3b)

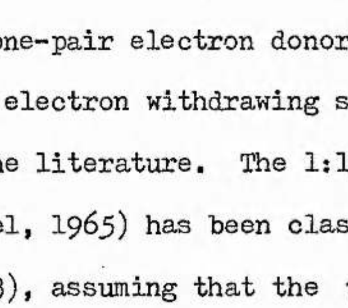


Fig 1.5.3a Structure of $N_2O_4 \cdot 1,4$-dioxane (After Groth and Hassel, 1965).

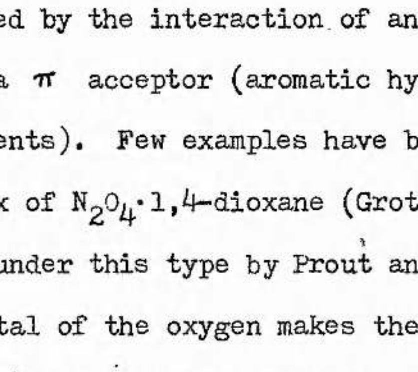


Fig 1.5.3b Molecular Arrangement of the structure of triethylphosphate-benzotrifurazan complex (After Cameron and Prout, 1968).

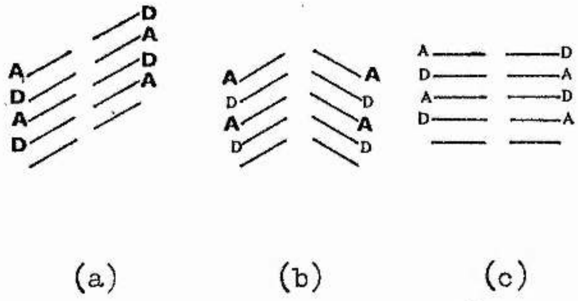


Fig 1.5.4 Typical donor-acceptor stacks in $\pi-\pi^*$ complexes.

(After Prout and Wright, 1968).

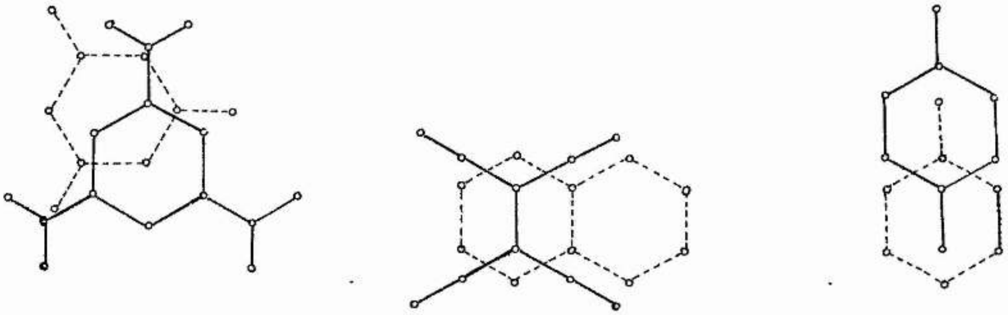
1.5.4 THE CRYSTAL STRUCTURE OF $\pi - \pi^*$ COMPLEXES

The π-electron-donor molecules cover a wide group of aromatic hydrocarbons, substituted hydrocarbons and heterocycles. Likewise the π-electron acceptor molecules can be classified into several groups (Herbstein, 1971): (a) olefinic compounds: e.g. Tetracyanoethylene (TCNE) and hexacyanobutadiene. (b) substituted aromatic compounds: substituted benzenes and some polynitronaphthalenes, and (b) substituted aromatic ketones and quinones.

Most of the donor and acceptor molecules in $\pi - \pi^*$ EDA complexes of known structure are planar. They crystallize in plane-to-plane stacks of donor and acceptor molecules occurring alternately (Prout and Wright, 1968) as shown in fig. 1.5.4.

A common feature in $\pi - \pi^*$ EDA Complexes is disorder, possibly associated with twinning phenomena. This may be due to either regular or irregular faults in the molecular packing within the stack(s).

Some examples of $\pi - \pi^*$ complexes are 1,3,5-triaminobenzene·TNB (Iwasaki and Saito, 1970); Naphthalene·TCNE (Williams and Wallwork, 1967); and p-benzoquinone·phenoquinone (Sakurai, 1968) as illustrated below.



(a) 1,3,5-TAB·TNB

(b) Naphthalene·TCNE

(c) p-benzoquinone·phenoquinone

Fig 1.5.5

1.6 MOLECULAR COMPLEXES OF $SbCl_3$

1.6.1 BONDING AND STRUCTURE OF $SbCl_3$

The crystal structure of $SbCl_3$, determined first by Lindqvist and Niggli (1956) and later confirmed by Lipka (1979), belongs to the orthorhombic space group Pnma with cell dimensions a = 8.111(2), b = 9.419(1) and c = 6.313(1)Å; and Z = 4. Least squares refinement lead to R = 0.045 for 963 independent reflections obtained with Mo$k\alpha$ radiation.

The molecules of $SbCl_3$ have pyramidal geometry with two equivalent Sb-Cl bonds of 2.368(1)Å and a third $Sb-Cl_3$ of 2.340(2)Å. The bond angle opposite the short bond is 90.58(2)° while the other two are at 95.70(5)°.

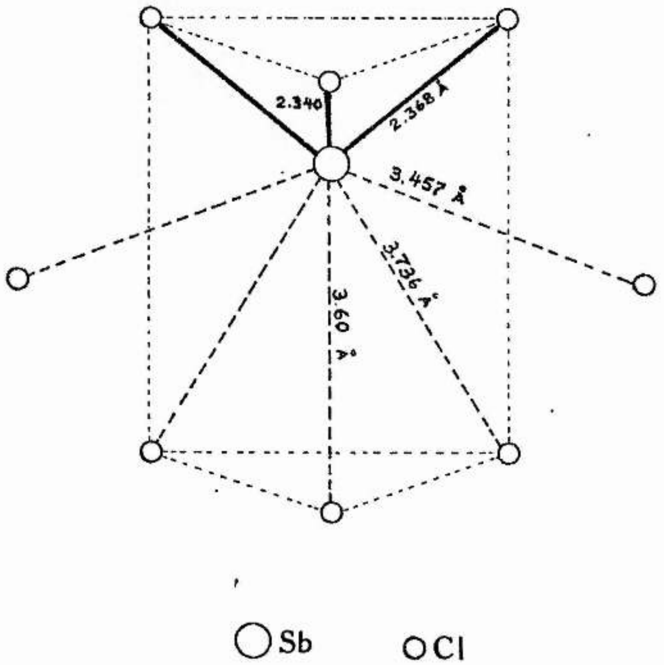
The $SbCl_3$ molecules pack to give some intermolecular Sb···Cl contacts which are shorter than the sum of the Van der Waals radii (4.0Å). This suggests that the coordination number of the Sb atom has increased to eight, as shown below.

Fig 1.6.1

Crystal structure of

$SbCl_3$.

(After Lipka, 1979).



'Bonding' is primarily between the three p electrons of antimony and a p electron from each chlorine (Kolditz, 1967). Mutual repulsion results in valence angles greater than 90°.

1.6.2 DONOR AND ACCEPTOR PROPERTIES OF $SbCl_3$

$SbCl_3$ is structurally analogous to the similar halides of group V, all of which are pyramidal (see Table 1.6.2), with a lone pair of electrons at the apex.

TABLE 1.6.2

BOND ANGLES OF THE PYRAMIDAL GEOMETRY FOR THE TRIHYDRIDES AND TRIHALIDES OF GROUP V[(a)]

	N	P	As	Sb
H	107.8	93.3	91.8	91.3
F	102.1	97.8	96.2	88.2
Cl	$106.8_2^{(c)}$	100.3	98.5	90.6 , 95.7 (b)
Br		99.0(2),101.3(2)(e)	99.6	α 97.4 95.5 93.6 β 97.5 92.8(d)
I		102.0	100.2	95.8(f)

(a) Gillespie (1972).

(b) Lipka (1979).

(c) Hartl H., et.al., (1975).

(d) α-$SbBr_3$ (Cushen & Hulme (1964)).
β-$SbBr_3$ (Cushen & Hulme (1962)).

(e) Enjalbert P., et.al. (1979).

(f) Trotter & Zobel (1966).

However, $SbCl_3$ has less tendency to utilize its unshared pair of electrons in donor-acceptor complexes than the lighter elements in the group (Kolditz, 1967). In a few compounds like $Ni(CO)_3SbCl_3$ and $Fe(CO)_3(SbCl_3)_2$, Wilkinson (1951) has inferred an electron-donor behaviour.

Many authors have reported that in molecular complexes of $SbCl_3$ with organic molecules, $SbCl_3$ behaves as an electron acceptor. This has been confirmed by different means.

Thus, $SbCl_3$ behaves as an electron acceptor towards Nitrogen, Oxygen and Sulphur atoms e.g. The geometry around the antimony atom in the crystal structure of $SbCl_3.C_6H_5NH_2$ (Hulme and Scruton, 1968) is distorted trigonal-bipyramidal with one chlorine and the N atom occupying the axial sites. The lone pair of electrons of the antimony together with two chlorines are in the equatorial position. Further expansion occurs in the case of $SbCl_3.2C_6H_5NH_2$ (Scruton, 1965), where the sixth site is occupied by the lone pair (see Table 1.6.4a). Also for the complex of (1:1) $SbCl_3$·1,4-dithiane (Kiel and Engler, 1974) the Sb atom is in a distorted octahedral geometry. Interaction with two S atoms in cis positions and two chlorine atoms complete the equatorial sites; the axial positions are occupied by the lone pair of electrons and one chlorine atom. The complex (1:1) $SbCl_3$. terephthaldehyde (Baker and Williams, 1978) is an example of interaction with an oxygen as donor. Sb atom is in a distorted pentagonal bipyramidal environment with its lone pair of electrons in axial position (see Table 1.6.4a).

The acceptor property towards π -electron donor systems has been found in several compounds. Some examples are $2SbCl_3$· naphthalene (Hulme and Szymanski, 1969); $2SbCl_3$· p-xylene (Hulme and Mullen, 1976); $2SbCl_3$· phenanthrene (Demaldé, et.al., 1972); $2SbBr_3$· pyrene (Bambieri, et.al. 1972); $2SbCl_3$· diphenyl (Lipka and Mootz, 1978a), where the basic feature of the interaction of $SbCl_3$ and the organic molecule in their crystal structure is that the Sb and two chlorine atoms are in a plane parallel to the plane of the aromatic ring. Furthermore, the direction of Sb and the third chlorine atoms is approximately perpendicular to the plane of the ring; and, the lone pair in most of the cases is in an equatorial position.

Poleshchuk et.al. (1979) have carried out a 'quantum-chemical' calculation of the charge-transfer and charge distribution for complexes of (1:1) $SbCl_3.C_6H_5NH_2$ and (1:1) $SbCl_3$·benzene. In both cases they have confirmed the electron-acceptor behaviour of Sb in $SbCl_3$.

However, in many crystal structures of the compounds shown in Table 1.6.4a,b, the lone pair of electrons of the Sb atoms were not located; instead an interaction with chlorine atoms from other $SbCl_3$ molecules (often forming bridges) have been found. In most of the cases the distances of these interactions lie between the sum of the Van der Waals radii and the sum of the covalent radii. This seems to suggest that, at least in some cases, the Sb atom acts in two ways simultaneously: as an acceptor and as a donor.

1.6.3 DONOR AND ACCEPTOR PROPERTIES OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons are regarded mainly as π electron donors and they can be divided into two groups:

(a) UNSUBSTITUTED AROMATIC HYDROCARBONS

Benzene and naphthalene act as electron donors to form molecular complexes with inorganic and many organic acceptors, e.g. the molecular complexes of benzene with $SbCl_3$ (Poleshchuk, et.al., 1979) and naphthalene with $SbCl_3$ (the crystal structure of which was determined by Hulme and Szymanski, 1969), have been found.

Naphthalene, pyrene, anthracene and phenanthrene, equally form molecular compounds with polynitrobenzenes (Sinomiya, 1940a). In each case the hydrocarbons acts as π-electron donors (Shostakovski, et.al., (1973).

(b) SUBSTITUTED AROMATIC HYDROCARBONS

Electron-donating substituents enhance donor strength and electron withdrawing ones diminish it.(Herbstein, 1971).

Qualitative study of the effect of substituents in aromatic hydrocarbons on their capacity to form molecular complexes has been carried out by Sinomiya (1940b). In particular, he studied the effects of substituents in positions 1 and 2 of naphthalene in compounds formed with various polynitrobenzenes. Taking into account both the nature and position of the substituent he arrived at the following sequence for the ability to favour molecular complex formation: $NH_2 > CH_3 > OH > C_2H_5 > OCH_3 > Cl > Br > OC_2H_5 > H > COOH > COOCH_3 > OC_6H_5 > CN > COOC_6H_5 > NO_2$. He concludes that substitution in position 1 always favours molecular complex formation while the reverse is sometimes true for substituent in position 2.

Park (1969) for the particular case of complexes of $SbCl_3$ with organic molecules concluded that in general $SbCl_3$ molecules are coordinated with π-donors rather than n-donors. In most of the cases, according to his conclusion, $SbCl_3$ seems to prefer delocalized electron density in the aromatic ring rather than localized electron density at one atom. This is in some contrast to the conclusion of other authors. Thus, Hulme and Mullen (1976), found the particular atom carrying a methyl group to be most closely associated with Sb in the (1:1) $SbCl_3 \cdot$ p-xylene complex. Also Baker (1976) has found an Sb...O interaction for molecular complexes of $SbCl_3$ with some aromatic hydrocarbons containing carbonyl groups.

1.6.4 CRYSTAL STRUCTURE OF MOLECULAR COMPLEXES OF $SbCl_3$ WITH ORGANIC MOLECULES

In general the stronger CT complexes tend to be between donors and acceptors that are both increvalent (i.e. n-v or π- v types which increase the number of bonds). See Section 1.4. With this in view, molecular complexes of $SbCl_3$ with organic compounds may be clasified into these two groups, n-v type complexes are formed when the donor atoms are the nitrogen of an aromatic amine, aromatic nitrogen heterocycles, oxygen or sulphur atoms, and probably ion Cl^-. (See Table 1.6.4a) π - v type complexes mostly involve aromatic hydrocarbons as donors. The basic feature of these structures is that the Sb and two chlorines are in a plane parallel to that of the aromatic ring, with the third Sb-Cl bond perpendicular to and away from it, (see Table 1.6.4b.

TABLE No. 1.6.4a

CRYSTAL STRUCTURE OF m $SbCl_3 \cdot n$ ORGANIC COMPOUND
COMPLEXES WITH NITROGEN, OXYGEN, SULPHUR AND ION Cl^- AS DONORS.

ORGANIC COMPOUND AND STOICHIOMETRY (m:n)	R FACTOR AND OTHER REMARKS	ACCEPTOR INTERATOMIC PARAMETERS:		INTERMOLECULAR CONTACTS		RELEVANT GEOMETRICAL FEATURES	REFERENCE
		Sb - Cl(Å)	Cl-Sb-Cl(°)	d(Sb...D)(Å),	ANGLES(°)		
ANILINE (1:1)	0.136 for 637 Refns. Low T. Photog. Mok$_\alpha$	1 2.510 2 2.322 3 2.335	1,2 86.8 1,3 86.7 2,3 96.1	Sb...N 2.525	Cl_1-Sb...N 166.3	Sb in distorted trigbipyramid. N & Cl axial; lone pair in equatorial. Infinite chains.	HULME & SCRUTON (1968)
ANILINE (1:2)	0.136 for 459 Refns. Low T. Photog. Mok$_\alpha$	2.36	1,2 86.1 1,3 90.2 2,3 90.2	Sb...N 1 2.64(4) 2 2.64(4)	Cl-Sb-N 1,1 166.1 2,1 166.1 N-Sb-N 1,2 102.8	Sb in distor. octahedr. Two N from 2 diff. molec. in equatorial cis posit; lone pair in sixth site. Infinite chains.	SCRUTON (1965)
DIACETYLBENZENE (1:1)	0.051 for 2489 Refns. Diffract. Mok$_\alpha$	1 2.36 2 2.39 3 2.37	1,2 89.5 1,3 93.4 2,3 93.2	Sb...O 1 2.67 2 2.81 Sb...Cl 3.21	Cl - Sb-O 1,2 170.7 2,1 167.5 O - Sb-O 1,2 101.6	Sb in distor. Octahedr. Two O from 2 DAB molec. in equatorial cis posit., coord. AX6 type lone pair no located. Infinite chains.	BAKER & WILLIAMS (1978)
DIPHENYLAMMONIUM-CHLORIDE (1:1)	0.049 for 1771 Refs. Diffractometer. Mok$_\alpha$	1 2.388 2 2.358 3 2.374	1,2 92.0 1,3 95.5 2,3 93.5	Sb...Cl^- 4 3.04 5 3.13 2' 3.42		Sb in distor. Octahedr. with Cl^-; lone pair no located. $SbCl_3$ & anion-cation chains are bridged by Cl^- giving Sq. tubes.	LIPKA & MOOTZ (1978)

TABLE No. 1.6.4a (cont.)

TEREPHTHALDEHYDE TEPTD (1:1)	0.062 for 1693 Refns. Diffractometer. Mok$_\alpha$	1 2.345 2 2.391 3 2.345	1,2 94.4 1,3 91.3 2,3 89.4	Sb...O Cl -Sb...O 1 2.932 1,1 78.5 2 2.934 3,1 74.3 Sb...Cl 3.507	Sb in distor. pentag. bipyramid. Two O from 2 TEPTD in equatorial posit. Lone pair in axial. Infinite chains.	BAKER & WILLIAMS (1978)
1,3,5-TRIACETYL-BENZENE TAB (1:1)	0.039 for 2235 Refns. Diffractometer. Mok$_\alpha$	1,1 2.323 1,2 2.368 1,3 2.350 2,4 2.327 2,5 2.310 2,6 2.377	1,2 97.1 1,3 92.1 2,3 93.4 4,5 93.1 4,6 89.3 5,6 95.9	Sb_1...O Sb_2...Cl 1,1 3.040 2.2 3.323 1,2 2.694 2.3 3.320 1,3 3.023 2,2 2.85	Both Sb in distor. Octahedr. Sb_1 coord. to 3 O from 3 TAB molec. Lone pair no located. Sb_2 coord to 2Cl & O. Lone pair no located. Infinite chains.	BAKER & WILLIAMS, (1978)
1,4-DITHIANE (1:1)	0.060 for 2426 Refns. Diffractometer. Mok$_\alpha$	1 2.420 2 2.386 3 2.441	1,2 91.2 1,3 94.6 2,3 90.3	Sb...S 1 3.135 2 3.065	Sb in distor. Octahedr. Two S from diff. dithiane in equator. sites. Lone pair in the 6th site. Infinite chains.	KIEL & ENGLER, (1974)
1,4-DITHIACYCLO-MEPTANE (1:1)	0.034 for 1028 Refns. Diffractometer. Mok$_\alpha$	1 2.40 2 2.36 3 2.39	1,2 94.3 1,3 94.0 2,3 92.1	Sb...S S -Sb-S 1 3.23 1.2 87.6 2 3.13 1.2' 112.9 2' 3.40	Sb in distor. Octahedr. 3 S from 3 diff mokec. Lone pair no located. Infinite chains.	SCHMIDT et.al., (1979)
1,3,5-TRITHIAN (1:1)	0.032 for 524 Refns. Diffractometer. Mok$_\alpha$	2.375	92.9	Sb..S S-Sb-S 3.258 54.7	Sb in distort. Octahedr. 3 S from 3 diff trithian. Infinite chains.	LINDEMANN et.al., (1977)

TABLE No. 1.6.4a (cont.)

PYRIDINE (2:1)	0.149 for 285 Refns. Photog. Mokα	1,1 2.36 1,2 80.8 1,2 2.37 1,3 97.8 1,3 2.68 2,3 82.0 2,4 2.64 4,5 81.2 2,5 2.31 4,6 73.8 2,6 2.33 5,6 81.4	Sb...N Cl...Sb...Cl 2.49 1.4 106.9 Sb...Cl 2.4 94.5 1,4 2.79 2,3 3.21	Sb$_1$ in distor. Octahedr. Lone pair no located. Sb$_2$ in distor. trigon. bipyramid. Lone pair in equatorial. Infinite layers py-"Sb$_4$Cl$_{12}$" (tetramers).	MULLEN (1970)
PYRIDINE (2:3)	0.110 for 329 Photog. Mokα	1,1 2.258 1,2 77.7 1,2 2.405 1,3 105.5 1,3 2.395 2,3 95.6 2,4 2.141 4,5 97.3 2,5 2.513 4,6 100.4 2,6 3.003 5,6 159.4	Sb...N N-Sb$_2$-N 1 2.270 1,2 170.4 2 2.487 N-Sb$_2$-Cl 1,4 90.4	Sb$_1$ in distor. Octahedr. Lone pair in axial site. The Sb$_2$ is attached to 2py in trans position Infinite chains.	MULLEN (1970)

TABLE 1.6.4b

CRYSTAL STRUCTURE OF m $SbCl_3 \cdot n$ ORGANIC COMPOUND

2. COMPLEXES WITH AROMATIC π-ELECTRON DONORS.

ORGANIC COMPOUND AND STOICHIOMETRY (m:n)	R FACTOR AND OTHER REMARKS	ACCEPTOR INTERATOMIC PARAMETERS		INTERMOLECULAR CONTACTS		RELEVANT GEOMETRICAL FEATURES	REFERENCE
		Sb – Cl(Å)	Cl – Sb-Cl(°)	Sb...D(Å)	ANGLES(°)		
DIBENZYL (2:1)	0.138 for 169 Refns. 2D photog Cuk$_\alpha$	1,1 2.31 1,2 2.32 1,3 2.40 2,4 2.32 2,5 2.36 2,6 2.28	1,2 96.0 1,3 92.3 2,3 92.3 4,5 97.7 4,6 90.2 5,6 95.2	Sb...Cl 5 3.37 2 3.27		Sb in dist. trig. bipyrad. One Cl and interact. with π-syst. in apical sites. Lone pair in equatorial. $SbCl_3$ forms dimer; plane parallel to benzene to benzene ring. Alternating layers.	HURSTHOUSE (1965)
DIBENZYL (4:1)	0.196 for limited Refs. Photog. Mok$_\alpha$	1 2.34 2 2.32 3 2.25	1,2 92.7 1,3 91.0 2,3 95.6	Sb...ring-plane 3.40		Possibly Sb in trigon. bipyramid. Sb & 2Cl in a plane parallel to plane-ring on either side; Cl_3 perpendicular and away from it. Lone pair in equat. Alternating layers.	HURSTHOUSE (1965)
DIPHENYL (2:1)	0.051 for 3306 Refns. Diffractometer. Mok$_\alpha$	1,1 2.367 1,2 2.382 1,3 2.369 2,4 2.355 2,5 2.353 2,6 2.342	1,2 93.48 1,3 94.32 2,3 91.41 4,5 93.88 4,6 96.36 5,6 93.03	Sb...ring-plane 1,1 3.26 2,2 3.08 Sb...Cl 1,1 3.44 2,1 3.46		Sb in a distor. Octahedr. Each $SbCl_3$ points to a phenyl ring. Lone pair no located. $SbCl_3$ forms dimer. Alternating layers.	LIPKA & MOOTZ (1978a)
DIPHENYLAMINE (2:1)	0.060 for 2829 Refns. Diffractometer. Mok$_\alpha$	1,1 2.377 1,2 2.356 1,3 2.357 2,4 2.380 2,5 2.382 2,6 2.365	1,2 92.4 1,3 95.2 2,3 93.2 4,5 92.2 4,6 94.3 5,6 91.7	Sb...ring-plane 1,1 3.08 2,2 3.09 Sb...Cl 2,1 3.351 2,5 3.499		Sb in distor. Octahedr. Two $SbCl_3$ point to a phenyl ring each. Lone pair no located. $SbCl_3$ forms dimer. Alternating layers.	LIPKA & MOOTZ (1978b)

TABLE 1.6.4b (cont.)

NAPHTHALENE (2:1)	0.091 for 2566 Refns. Diffractometer. Mok_α	1 2 3	2.348 2.347 2.367	1,2 1,3 2,3	91.59 94.41 94.70	Sb...ring-plane 3.20 Sb...C 1 3.36 2 3.39	Sb in distor. trigon. bipyramid. 2Cl & Lone pair in equatorial sites. Interact. with π-syst. and Cl_3 in axial. Alternating layers.	HULME & SZYMANSKI (1969)
PHENANTHRENE (2:1)	0.038 for 4013 Refns. Diffractometer. Mok_α	1,1 1,2 1,3 2,4 2,5 2,6	2.350 2.349 2.359 2.338 2.398 2.359	1,2 1,3 2,3 4,5 4,6 5,6	92.0 94.4 95.1 92.2 93.7 92.4	Sb...ring-plane 1,1 3.27 2,3 2.94 Sb...Cl 2,3 3.49 2,5 3.26 1,6 3.41 1,1 3.55	Possibly Sb in distor. Octahedr. Each $SbCl_3$ points to a rind. 1Cl & interact. with π-syst. in axial sites. Lone pair no located. $SbCl_3$ form dimer. Alternating layers.	DEMALDE et.a (1972)
STILBENE (4:1)	0.139 for 1938 Refns. Low T. Photog. Mok_α	1,1 1,2 1,3 2,4 2,5 2,6	2.35 2.39 2.36 2.36 2.42 2.36	1,2 1,3 2,3 4,5 4,6 5,6	94.07 91.49 94.67 91.77 93.47 95.85	Sb...ring-plane 1,1 3.40 2,2 3.40	Possibly Sb in distor. Octahedr. Sb & 2Cl in a plane parallel to ring-plane. Each phenyl ring is 'sandwiched' by $2SbCl_3$. lone pair no located. Alternating layers.	HURSTHOUSE (1965)
P-XYLENE (2:1)	0.110 for 920 Refns. Low T. Photog. Mok_α	1 2 3	2.304 2.320 2.369	1,2 1,3 2,3	94.1 92.8 93.1	Sb...ring-plane 3.09 Sb...Cl 3.24	Possibly Sb in distor. Octahedr. $SbCl_3$ points to the ring. Lone pair in equatorial site. $SbCl_3$ forms dimer. Alternating layers.	HULME & MULLEN (1976)

1.7 DISORDER PHENOMENA IN CRYSTALS

It has been stated (Bernal, 1959 and Refs. there; Jagodzinski, 1963), that as a general rule all crystals are disordered to a certain degree. In particular disorder phenomena often occur in solid-state molecular compounds. One of the features of the crystal chemistry of some π-molecular compounds is the order-disorder transformation due to changes in temperature or due to growth faults (Herbstein, 1971). Little consideration has been given to the relation between this feature and the nature of bonding, stability and structure in these compounds. Therefore, it is important to study this associated phenomena as it may lead to a better understanding of the nature of some molecular complexes.

The following survey is a brief introduction to disorder phenomena in crystals and their relation to the diffraction pattern.

1.7.1 TYPES OF DISORDER

Two general types of disorder may occur in crystals (Wooster, 1964; Jagodzinski, 1964; Herbstein, 1971). The first type is a thermodynamic disorder, where the equilibrium degree of order varies with temperature and pressure. At elevated temperatures no crystal is perfectly ordered because of the thermal vibration of the atoms and molecules or reorientation of the molecules.

The second general type is non-equilibrium in nature. This is associated with lattice defects which are observable in the diffraction pattern. The lattice distortions normally observed in crystals are due to growth faults which are "frozen-in" during crystallization. This type of disorder does not change with temperature. Here the imperfection can involve substitution as well as displacement disorder.

1.7.2 BRIEF INTRODUCTION TO THE DIFFRACTION OF X-RAYS BY AN IDEAL AND A DISORDERED CRYSTAL

The position of lattice point of a periodic three-dimensional lattice may be defined by the vector:

$$\hat{t}_n = \hat{t}_{n_1 n_2 n_3} = n_1\hat{a} + n_2\hat{b} + n_3\hat{c} \qquad (1.7.1)$$

where n_1, n_2, n_3 are integers and $\hat{a}$, $\hat{b}$, $\hat{c}$ define the unit cell translations. A lattice may be expressed by an array of δ functions$^{(1)}$ of the type $\delta(\hat{t}-[n_1\hat{a} + n_2\hat{b} + n_3\hat{c}])$, in which n_1, n_2 and n_3 take on all allowed values corresponding to each lattice point.

The lattice function, $Z(\hat{t})$, is defined as:

$$\sum_{n_1 n_2 n_3} \delta(t_n - [n_1\hat{a} + n_2\hat{b} + n_3\hat{c}]) \qquad (1.7.1a)$$

In which the summation signifies that for every allowed value of n_1, n_2, n_3 all lattice points are generated.

In reciprocal space a reciprocal lattice vector, $\hat{r}^*$, is given by

$$\hat{r}^* = \hat{s} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^* \qquad (h,\ k,\ l \text{ integers})$$

MATHEMATICAL EXPRESSION OF THE DIFFRACTION OF X-RAYS BY CRYSTALS

A perfect crystal is built up by successive equal parallel displacements of the three dimensional unit cell. The structure factor

---

(1) A δ function at the point x relative to x_o is expressed as $\delta(x-x_o)$, which equals unity at $x=x_o$ and zero for all other values of x. A δ function is thus the mathematical description of a point or of a phenomenon at a point.

(see p 68) for such crystals can be expressed (Woolfson, 1970, p80) by:

$$F_{hkl} \text{ (or } F(\hat{s})) = \sum_{j=1}^{N} f_j \exp(\, 2\pi i \hat{s}.\hat{r}_j) \qquad (1.7.2)$$

Where $\hat{r}_j = x_j \hat{a} + y_i \hat{b} + z_j \hat{c}$, defines the atomic position of the jth atom with atomic scattering factor f_j. The summation is extended over all N atoms in the unit cell.

In a molecular crystal, where molecules have individuality, it is of interest to express the structure factor, $F(\hat{S})$ as a function of the transforms of the different molecules referred to their centers (J. and M. Amorós, 1968, p82). Thus with P molecular centers at $\hat{r}_p$ and related atomic coordinates, $r_{j,p}$ (for Jp atoms relative to the centre, P) we have:

$$F(\hat{S}) = \sum_{p=1}^{P} \sum_{j=1}^{J} f_j \exp\left[\, 2\pi i \hat{S}.(\hat{r}_{j,p} + \hat{r}_p)\right] \qquad (1.7.3)$$

Equation (1.7.3) may be rewritten as:

$$F(\hat{S}) = \sum_{p=1}^{P} F_p(\hat{S}) \exp(\, 2\pi i \hat{S}.\hat{r}\ ) \qquad (1.7.3a)$$

where $F_p(\hat{S}) = \sum_{j=1}^{J_p} f_j \exp(\, 2\pi i \hat{S}.\hat{r}_{j,p})$, is the contribution of the pth molecule to the total structure factor $F(\hat{S})$.

As the intensity for a molecular crystal involves imaginary quantities, the complex conjugate of $F(\hat{S})$, i.e. $F^*(\hat{S})$ will be involved in the expression for the intensity given by:

$$I(\hat{S}) = F(\hat{S}).F^*(\hat{S}) \qquad (1.7.4)$$

Replacing values for $F(\hat{S})$ of eq. (1.7.3a) in eq. (1.7.4), then performing the respective summation, eq. (1.74) becomes:

$$I(\hat{S}) = \sum_{=1}^{P} I_p(\hat{S}) + \sum_{p=1} \sum_{p'=1} F_p(\hat{S}) F_{p'}(\hat{S}) \exp\left[2\pi i \hat{S}.(\hat{r}_p - \hat{r}_{p'})\right] \tag{1.7.4a}$$

Where $I(\hat{S})$ is the total intensity due to the contribution of the p and p' molecules in the cell and $I_p(\hat{S}) = F_p(\hat{S}).F_p^*(\hat{S})$.

An example will illustrate this. Adipic acid, $HO_2.C-(CH_2)_4CO_2H$, crystallizes in the monoclinic cell with space group $P2_1/a$, Amorós, (1968), p 83 . The unit cell contains two centrosymmetric molecules in special positions. One molecule has a center at the origin, and the second has a center of symmetry at $\frac{1}{2}\frac{1}{2}0$. Considering the projection of the structure on (010), the contribution of the second molecule to the structure factor can be calculated from eq. (1.7.3a):

$$F_2(h0l) = F_1(h0l)\exp\left[2\pi i\hat{s}.\hat{r}_p\right] = F_1(h0l)\exp\left\{2\pi i\left[h\hat{a}^* + l\hat{c}^*\right]\left[\frac{\hat{a}}{2} + \frac{\hat{b}}{2}\right]\right\} \tag{1.7.5}$$

where $F_1(h0l)$ is the contribution of the first molecule.

In the unit cell both molecules diffract together, therefore the total structure factor will be given by:

$$F_{h0l} = F_1(h0l) + F_2(h0l) = F_1(h0l)\left\{1 + \exp\left[2\pi i\left(\frac{h}{2}\right)\right]\right\} \tag{1.7.5a}$$

as $\hat{a}^* . \hat{a} = 1$

$\hat{a}^* . \hat{b} = 0$

$\hat{a}^* . \hat{c} = 0$ etc.

THE DIFFRACTION OF X-RAYS BY A DISORDERED CRYSTAL

Under the general classification of disorder which occurs in crystals stated earlier, we consider here cases where the disorder is an orientational one, this occurs when the molecules are statistically distributed in certain molecular sites with different orientations. The Bragg intensities are sentitive to this kind of disorder but are not altered in position. The intensity may in the extreme be zero due to interference and so may suggest pseudo absences and symmetry corresponding to an "average structure".

Another form of disorder associated with diffuse scattering around Bragg angles may arise because of static defects in the crystal lattice in one, two and three-dimensions. Thus Jagodzinski (1963) identifies one-dimensional disorder as a disorder in the stacking sequence of layers, as one Laue condition fails to be fulfilled A statistical displacement of rows of unit cells from the ideal position correspond to a two-dimensional one. A three-dimensional occurs when by insertion or depletion of an atom, ion or a group of them; the structure is locally swollen or contracted.

GENERAL MATHEMATICAL EXPRESSION FOR DIFFRACTION BY DISORDERED CRYSTALS

The electron density of an atom can be expressed as

$$\rho(\hat{r}) = \int_{v^*} F_{hkl} \exp(-2\pi i\hat{s}.\hat{r})dv^* \qquad (1.7.6)$$

where F_{hkl} is the structure factor and v^* the reciprocal volume.

$\hat{r} = x\hat{a} + y\hat{b} + z\hat{c}$ expresses the atomic position

By definition also:

$$F_{hkl} = F(\hat{S}) = \int_{v} \rho(\hat{r}) \exp(\ 2\pi i\hat{S}.\hat{r})dv \qquad (1.7.7)$$

which is the Fourier Transform of (1.7.6); conversely equation (1.7.6) is the Fourier Transform of (1.7.7).

The convolution, ($*$), of two functions $f(\hat{x})$ and $g(\hat{x})$ is defined by (Guinier, 1963):

$$Y(\hat{x}) = f(\hat{x}) * g(x) = \int f(\hat{R})\, g(\hat{x}-\hat{R})d\hat{R} \qquad (1.7.8)$$

a particular property is:

$$P(\hat{x}) = f(\hat{x}) * f(-\hat{x}) = \int f(\hat{R})f(\hat{x} + \hat{R})d\hat{R} \qquad (1.7.9)$$

A Patterson function in terms of $\rho(\hat{r})$ can be calculated using eq. (1.7.9):

$$P(\hat{r}) = \int \rho(\hat{R})\, \rho(\hat{r} + \hat{R})d\hat{R} = \rho(\hat{r}) * \rho(-\hat{r}) \qquad (1.7.10)$$

where $\hat{r}$ represent atomic position of an atom A

$\hat{R}$ represent any other atomic position of atom A or B.

At the origin, $\hat{r} = 0$, $P(0) = \int \rho^2(\hat{R})d\hat{R} = \int |F(\hat{S})|^2 d\hat{S}$

(1.7.11)

For an imperfect crystal, for which it is possible to define an average periodic lattice; the electron density of the crystal can be expressed by (Cowley, 1975):

$$\rho(\hat{r}) = \langle \rho(\hat{r}) \rangle + \Delta\rho(\hat{r}) \qquad (1.7.12)$$

Where $\langle \rho(\hat{r}) \rangle$ is the electron density distribution for the average lattice, defined to be time independent and periodic. $\Delta\rho(\hat{r})$ represents the deviation from the average lattice, which is non-periodic, (this could be time dependent or not).

By definition the averaging process involving $\langle \Delta\rho \rangle = 0$.

From eq. (1.7.12) and using expression (1.7.10) we may write the Patterson function as:

$$P(\hat{r}) = \left\{ \langle \rho(\hat{r}) \rangle + \Delta\rho(\hat{r}) \right\} * \left\{ \langle \rho(-\hat{r}) \rangle + \Delta\rho(-\hat{r}) \right\} \text{ or}$$

$$P(\hat{r}) = \left\{ \langle \rho(\hat{r}) \rangle \underset{(1)}{*} \langle \rho(-\hat{r}) \rangle \right\} + \left\{ \langle \rho(\hat{r}) \rangle \underset{(2)}{*} \Delta\rho(-\hat{r}) \right\} +$$
$$\left\{ \Delta\rho(\hat{r}) \underset{(3)}{*} \Delta\rho(-\hat{r}) \right\} + \left\{ \Delta\rho(\hat{r}) \underset{(4)}{*} \langle \rho(-\hat{r}) \rangle \right\}$$

$$(1.7.13)$$

The electron density of a collection of atoms may be written as:

$$\rho(\hat{r}) = \sum_{l,m,n} \rho_o(\hat{r}) * \delta\left\{ \hat{r} - (l\hat{a} + m\hat{b} + n\hat{c}) \right\} \qquad (1.7.14)$$

Where $\rho_o(\hat{r})$ is the electron density in the unit cell.

The delta function $\delta\left\{ \hat{r} - (l\hat{a} + m\hat{b} + n\hat{c}) \right\}$ defines the lattice.

$\hat{r} = x\hat{a} + y\hat{b} + z\hat{c}$ is the atomic position.

Eq. (1.7.14) can be expressed also as:

$$\rho(\hat{r}) = \rho_o(\hat{r}) * \sum_{i} \delta\left\{ \hat{r} - \hat{r}_i \right\} \qquad (1.7.15)$$

In eq. (1.7.13), in terms of spatial averaging, the second term of the equation may be written by using (1.7.15) as:

$$\rho_o(\hat{r}) * \sum_{r} \delta(\hat{r} - \hat{R}_n) * \Delta\rho(-\hat{r}) = 0 \qquad (1.7.16)$$

Where $\hat{R}_n$ is a lattice vector of the average lattice.

The convolution of $\Delta\rho(-\hat{r})$ with $\sum \delta(\hat{r} - \hat{R}_n)$ represents the superposition of the function $\Delta\rho(-\hat{r})$ with the lattice vector shifts. There is, thus an averaging of $\Delta\rho(-\hat{r})$ values at every point of the unit cell and by definition is zero. The same principle can be applied to the convolution of the fourth term.

Therefore eq. (1.7.13) is reduced to:

$$P(\hat{r}) = \left\{ \langle \rho(\hat{r}) \rangle * \langle \rho(-\hat{r}) \rangle \right\} + \left\{ \Delta\rho(\hat{r}) * \Delta\rho(-\hat{r}) \right\} \tag{1.7.17}$$

The Fourier transform of eq. (1.7.17) will give:

$$I(\hat{s}) = \left| \overline{F}_{hkl} \right|^2 + \left| \Delta F_{hkl} \right|^2 \tag{1.7.18}$$

which is the expression for the total scattering power by disordered crystals. $\overline{F}_{hkl}$ and ΔF_{hkl} are the Fourier Transforms of $\langle \rho(\hat{r}) \rangle$ and $\Delta\rho(\hat{r})$ respectively.

In eq. (1.7.18) $|\overline{F}_{hkl}|^2$ will be periodic and therefore will give sharp reflections. But since $\Delta\rho(\hat{r})$ is not periodic, $|\Delta F_{hkl}|^2$ will represent a continuous distribution of intensity between the reciprocal lattice points and will produce diffuse scattering in the diffraction pattern.

1.7.3 THE STRUCTURE FACTOR FOR TWO CASES OF ORIENTATIONAL DISORDER

(a) Abrahams and Lipscomb (1952), give an example of orientational disorder in the structure of thiophene, H_4C_4S. The structure has 4 molec/unit cell, and was interpreted in space group Bmab (in standard orientation, Cmca, No.64), which has the following space-group diagram:

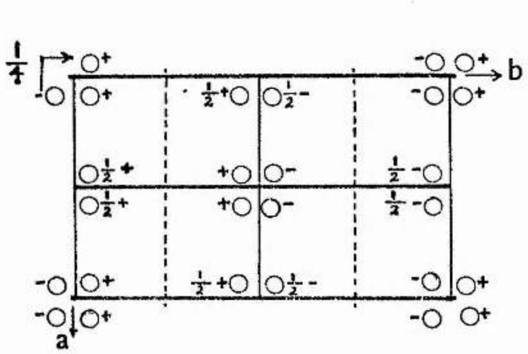


Fig 1.7.1

Bmab space group.

In order to accomodate the 4 molecules in 16 general positions, the following explanation is given: Each molecule could occupy any one of four different orientations around a common position (see fig. 1.7.2), so that the center of gravity of the disordered molecule lies at the special positions, 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

The general positions are related to each other by two perpendicular mirror planes mutually normal to the molecular plane. One mirror plane is parallel to a and the other parallel to the axis [011], the angle made by the molecular plane with the b axis is 47.8°.

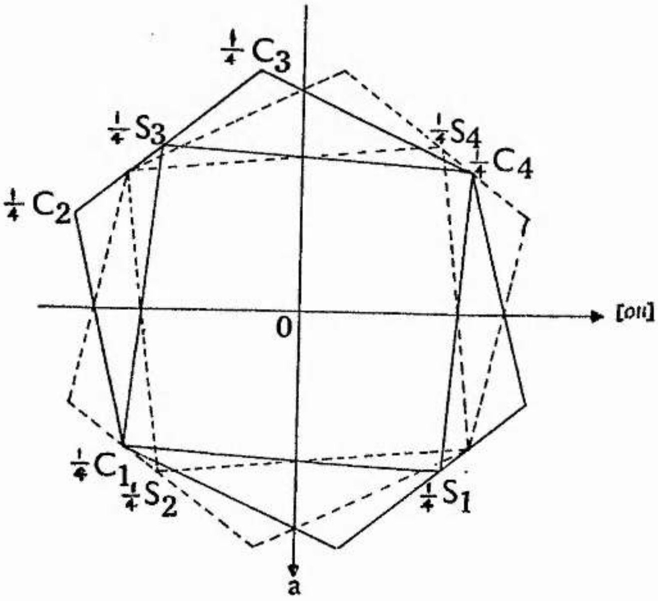


Fig 1.7.2

Schematic representation of the disorder of a molecular orientation in crystal of thiophene. (Abraham and Lipscomb, 1952).

The observed diffraction corresponds to a statistical distribution of the molecules equally over these four positions, so that on average there appears to be a quarter molecule in each orientation.

The contribution of the ith atom in a particular orientation of the thiophene molecule will be given by:

$$F_1\,(hkl) = \sum_{j}^{4} \sum_{i=1}^{5} (f_i/4) \cos 2\pi(hx_{i,j}+ky_{i,j}+lz_{i,j}) \qquad (1.7.19)$$

Where f_i is the atomic scattering factor of the ith atom, and $hx_{i,j} + ky_{i,j} + lz_{i,j}$, defines the position of the ith atom in the jth orientation.

The total structure factor F(hkl), will be given by:

$$F(hkl) = \sum_{P=1}^{4} F_1(hkl) \exp\left[\, 2\pi i\hat{s}.\hat{r}_p \right] \qquad (1.7.20)$$

Where $\hat{s} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^*$, (hkl integers), and $\hat{r}_p = x_p\hat{a} + y_p\hat{b} + z_p\hat{c}$, defines the center of the molecule. x_p , y_p and z_p are the fractional coordinates of the centers and $\hat{a}$, $\hat{b}$, and $\hat{c}$ are the cell unit translations.

(b) The second example of a disordered structure is that of chloropentamethylbenzene, (Charbonneau and Trotter, 1968). The crystals were interpreted as monoclinic, space group $P2_1/m$ with two molecules per unit cell. The space group can be represented by the following diagram:

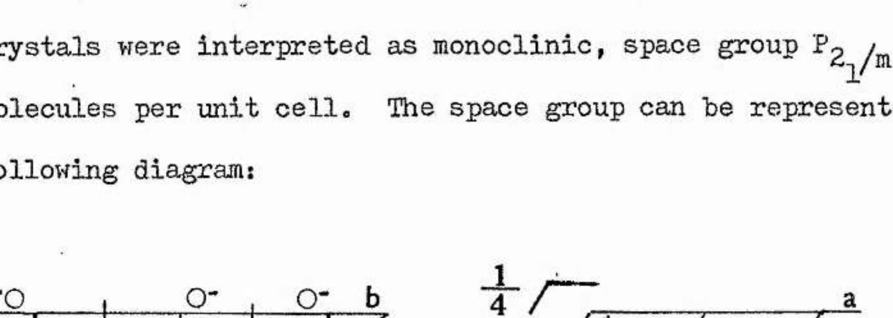


Fig 1.7.3

Diagram of space group $P2_1/m$.

According to the space group considered, there are four general equivalent positions per unit cell where we can accommodate molecules of chloropentamethylbenzene. The fact that there are only two molecules in the cell suggests the presence of disorder to simulate a pseudocentric structure.

In the structure analysis, the three-dimensional Patterson function did not show any outstanding peaks corresponding to Cl-Cl vectors, but an interpretation was possible in terms of a composite molecule corresponding to six positions for the chlorine atom on the benzene molecules, lying exactly in the mirror plane of the space group ($P_{2_1/m}$) at $y = \frac{1}{4}$.

Therefore, the total structure factor can be calculated in the following steps:

(i) The partial contribution from the two aromatic rings of carbons can be represented by:

$$F_1(hkl) = \sum_{j=1}^{12} f_c \exp(2\pi i\hat{s}.\hat{r}_j) \qquad (1.7.21)$$

where f_c represents the atomic scattering factor for the carbon atoms; and $\hat{r}_j = x_j\hat{a} + j_i\hat{b} + z_j\hat{c}$ is the atomic position and $\hat{s} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^*$ for hkl integers.

(ii) The partial contribution from the substituents of the benzene will be given by:

$$F_2(hkl) = \sum_{k=1}^{12} \left(\frac{1}{6} f_{Cl} + \frac{5}{6} f_c\right) \exp(2\pi i\hat{s}.\hat{r}_k) \qquad (1.7.22)$$

where f_{Cl} is the atomic scattering factor for the clorine atom. Therefore the total structure factor, (excluding H atoms), will be represented by:

$$F_{hkl} = F_1(hkl) + F_2(hkl) = \sum_{j=1}^{12} f_C \exp(2\pi i\hat{s}.\hat{r}_j) + \sum_{j=1}^{12} \left(\frac{1}{6} f_{Cl} + \frac{5}{6} f_C\right) \exp(2\pi i\hat{s}.\hat{r}_k) \qquad (1.7.23)$$

This disorder makes possible a centrosymmetric structure so that F_{hkl} reduces to

$$F_{hkl} = \sum_{j=1}^{6} f_C \cos 2\pi(hx_j+ky_j+lz_j) + \sum_{k=1}^{6} (\tfrac{1}{6} f_{Cl}+\tfrac{5}{6}f_C) \cos 2\pi(hx_k+ky_k+lz_k) \qquad (1.7.24)$$

A projection of the structure along b is illustrated in fig. 1.7.4:

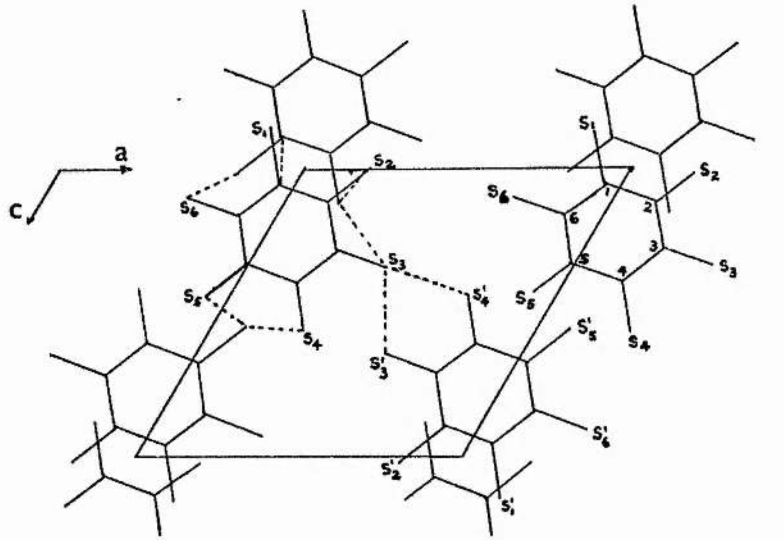


Fig. 1.7.4

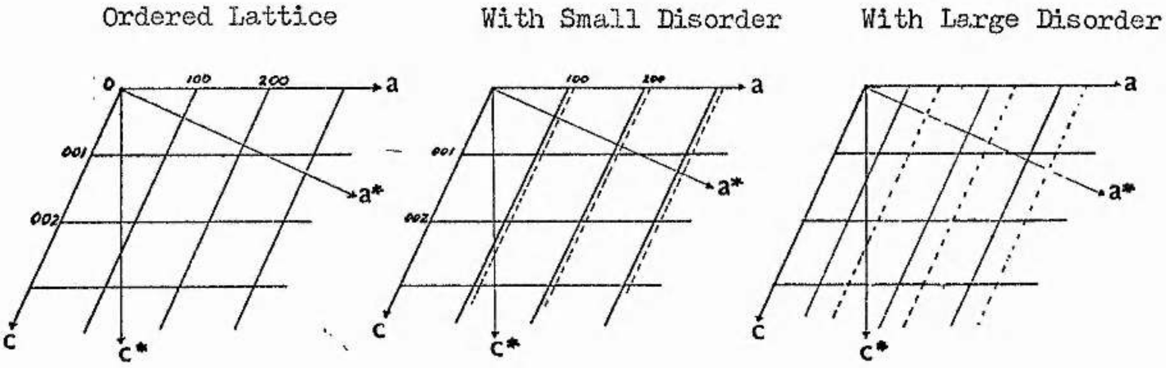
Projection of the structure of chloropentamethylbenzene along b.

S_i, i=1,2,...,6., are the substituents represented by a pseudo-atom with scattering factor $(\frac{1}{6} f_{Cl} + \frac{5}{6} f_C)$.

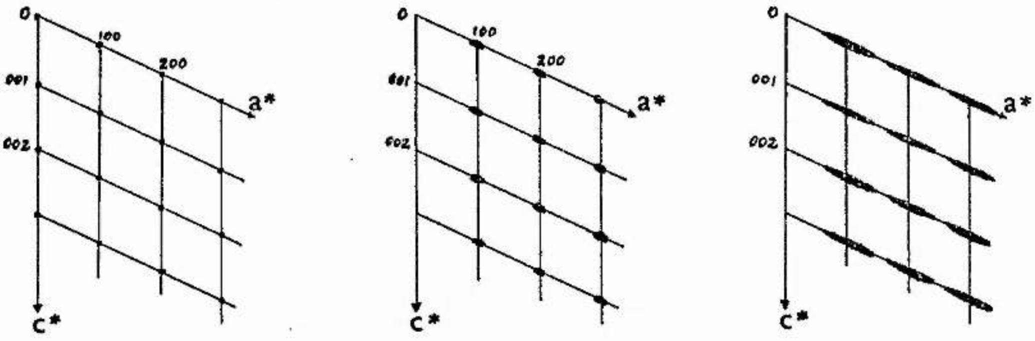
1.7.4 DIFFRACTION PATTERN FOR ONE DIMENSIONAL CASE OF DISORDER IN THE CRYSTAL LATTICE.

A Qualitative Illustration.

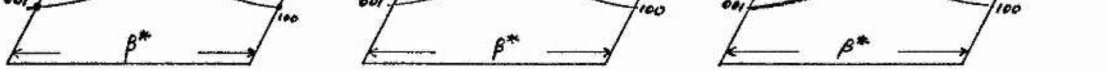
In the case of statistical arrangement of parallel layers having ordered cell dimensions in b and c, only one Laue-condition fails to be valid; according to the diffraction theory diffuse streaks along a^* are to be expected in reciprocal space (see fig. 1.7.5abc). The diffuseness depends strongly on the degree of disorder.



(a) Real Lattice



(b) Undistorted Reciprocal Lattice



(c) Distorted Reciprocal Lattice (Weissenberg)

Fig 1.7.5 Real and Reciprocal Lattice or a Crystal

An example of this kind of disorder may be given by a crystal of cobalt, (Lipson, 1942). It was reported that for hkl reflections, sharp reflections will occur when:

$$h - k = 3n \qquad n = 0,1,2,\ldots,n$$

$$\text{and} \qquad l = 2m \qquad m = 0,1,2,\ldots,m.$$

Diffuse spots occur when these conditions are not satisfied and they consist of streaks elongated parallel to the z-axis.

The distribution lattice which produces this diffraction pattern can be deduced from these results (Wooster, 1964). Fig. 1.7.6 shows a lattice net for crystal of cobalt. The hexagonal unit cell is represted by $A_0A_1A_2A_3$.

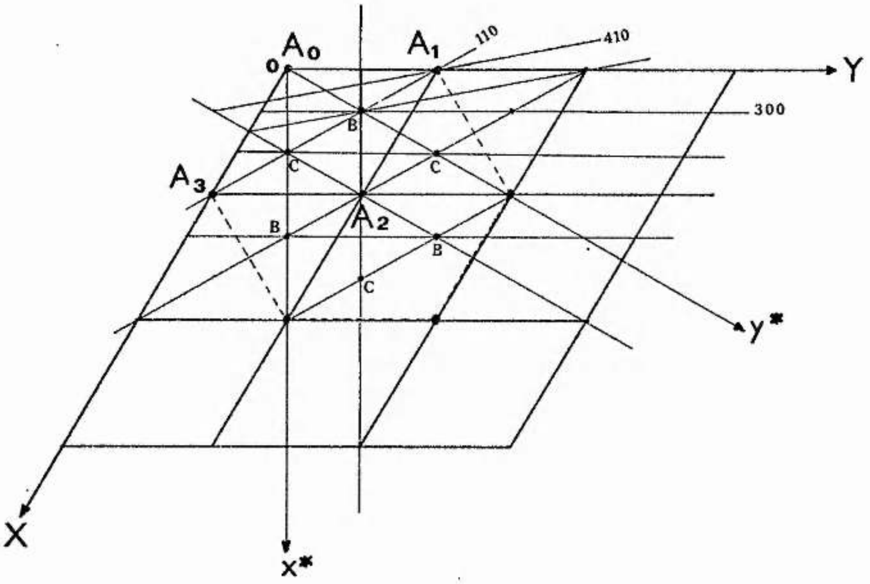


Fig 1.7.6

Lattice net for normal and disordered cobalt structure.

(After Wooster, 1964)

According to the rules mentioned above, sharp reflections will occur for planes 300,030,110,410,520, etc. The fact that l = 2m means that the length in the z-axis direction of the distribution lattice is half the height of the original unit cell (i.e. c/2).

At room temperature cobalt forms a hexagonal close-packed arrangement (i.e., two layers of atoms, symbolized by ABAB... or ACAC...), therefore atoms lie on A and B only (or on A and C only). The B or C points being occupied only at the points c/2 above the A points. If the points were occupied in the sequence ABCABC... (a cubic close-packed arrangement), the layers A, B and C being identical with one another, then we obtain a cubic close packing. The fact that the diffuse spots are elongated along z-axis means that the crystals of cobalt consist of parallel layers of atoms which are arranged sometimes in a hexagonal and sometimes in a cubic close-packed manner.

In many cases the disorder is a multiple one, where there is a mixture of the different types of disorder mentioned above or associated with other defects, such as the twinning phenomena, substitution disorder, etc. that is the case of the disorder found in crystals of wollastonite, $CaSiO_3$ (Jeffrey, 1953).

2. METHODS FOR STUDYING MOLECULAR COMPLEXES IN THE SOLID STATE.

In studying crystalline molecular complexes of $SbCl_3$ with organic compounds, the following methods were used:

(a) Melting-point-composition diagrams to detect of compound formation and stoichiometry,

(b) chemical and physico-chemical analysis to confirm the stoichiometry, and

(c) x-ray diffraction to determine the spatial relationships between the components.

2.1 DETERMINATION OF MELTING POINT-COMPOSITION DIAGRAMS.

The study of the equilibria of systems containing more than one component is based on the phase-rule developed by Gibbs:

$$f + p = c + 2$$

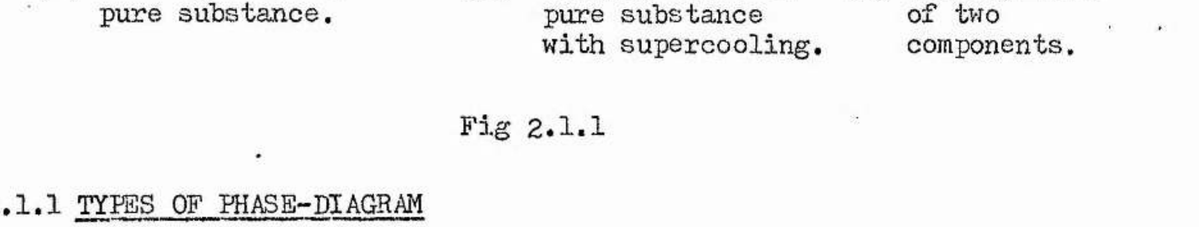
where f is the number of independent variables which must be specified to characterize the equilibrium system of c independent components in p phases.

At equilibrium (Fig. 2.1.2a), a simple binary (c=2), two-phases (p=2) system has f=2 so that to characterize the equilibrium system two independent variables need to be specified. i.e. two of temperature, T, pressure, p, and mole fraction composition x_i. The choice of two of these fixes the other. If we choose the pressure to be fixed (say 1 atm), then temperature and composition must be uniquely related, and one can plot a temperature vs. composition curve for equilibrium mixture of the two components.

Experimentally, the determination of equilibrium curves is usually carried out by taking the cooling curves (temperature vs. time) of mixtures of various compositions and noting the initial and the final solidification temperatures. These, plotted for several compositions, constitute the phase diagram.

When a pure (one-component) substance is allowed to cool without phase change its temperature falls at an exponentially decreasing rate as represented in the ideal cooling curves (Fig. 2.1.1a). In practice fig. (2.1.1b) is often observed, due to supercooling, but ideality may be approached by cooling slowly with adequate stirring. More complex curves (fig. 2.1.1c) may be observed if compound formation occurs.

The temperature of the system can be measured by means of thermocouples (for high temperatures) or ordinary thermometers for the relatively low temperatures.



(a) Cooling curve of pure substance.

(b) Cooling curve of pure substance with supercooling.

(c) Cooling curve of two components.

Fig 2.1.1

2.1.1 TYPES OF PHASE-DIAGRAM

When the two components of a binary system are completely miscible in the liquid state, the following types may be distinguished:

a) COMPLETE MISCIBILITY IN THE SOLID STATE

Here the components form a solid solution which exhibits characteristics similar to liquid solutions. On structural grounds such solid solutions may arise either by atom substitution or by atom occupation of interstitial positions within the host structure.

A typical diagram where complete miscibility occurs in the solid state is shown in Fig. 2.1.2a for the copper-nickel system.

b) A SIMPLE EUTECTIC SYSTEM

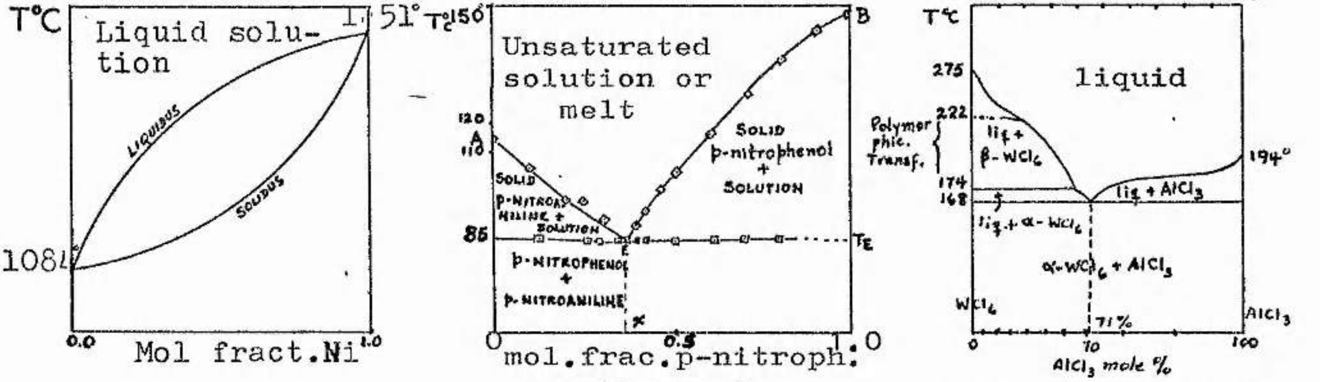
This is characterized by the fact that upon cooling, the mixed constituents, A and B, of a system yield only pure A or pure B as solid phases. An example occurs in the p-nitrophenol-p-nitroaniline system (Palepu and Moore, 1978) as shown in Fig. 2.1.2b.

c) EUTECTIC SYSTEM WITH POLYMORPHOUS COMPONENT

The effect of polymorphism in one of the components is to cause a "break" in the liquidus curve (Mckie and Mckie, 1974,p515). An example for $AlCl_3$-WCl_4 system (Korshunov and Gol'din, 1961) is shown in Fig. 2.1.2c. This feature is also found in the $SbCl_3$-sulphur system (Lipka, 1979a).

d) PARTIAL MISCIBILITY IN SOLID STATE WITH EUTECTIC

When two constituents A and B of a system are partially miscible in the solid state to form stable solid solutions, the standard diagram is modified to that shown in Fig. 2.1.2d. The points D and E represent the limits of solutions of α, α'-dipyridyl in diphenyl and of diphenyl in α, α'-dipyridyl respectively. (Kitaigorodsky, 1973, p.96).



Phase diagram for Cu-Ni system

(a)

p-nitrophenol-p-nitroaniline system.

A simple eutectic system at constant pressure.

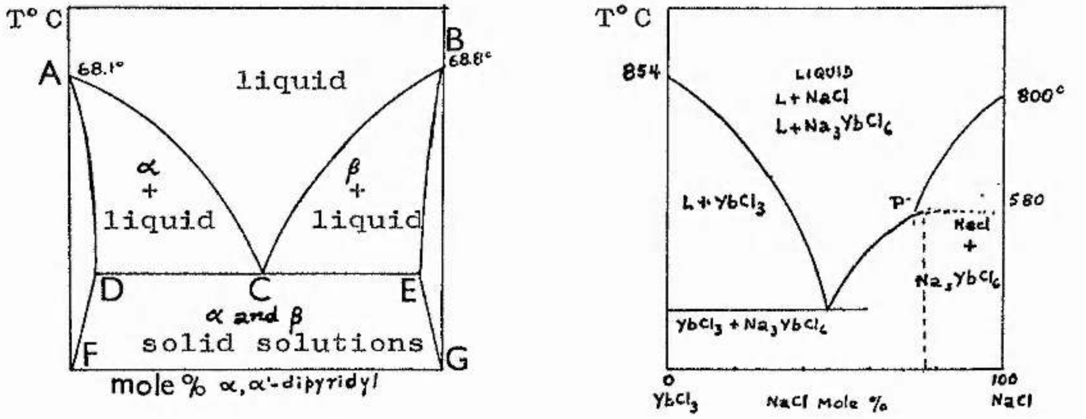
(After Palepu & Moore, 1978).

(b)

Phase diagram of the $AlCl_3.WCl_6$ system

(After Korshunov & Gol'din, 1961)

(c)



Phase diagram of the Diphenyl- α, α'-dipyridyl system.

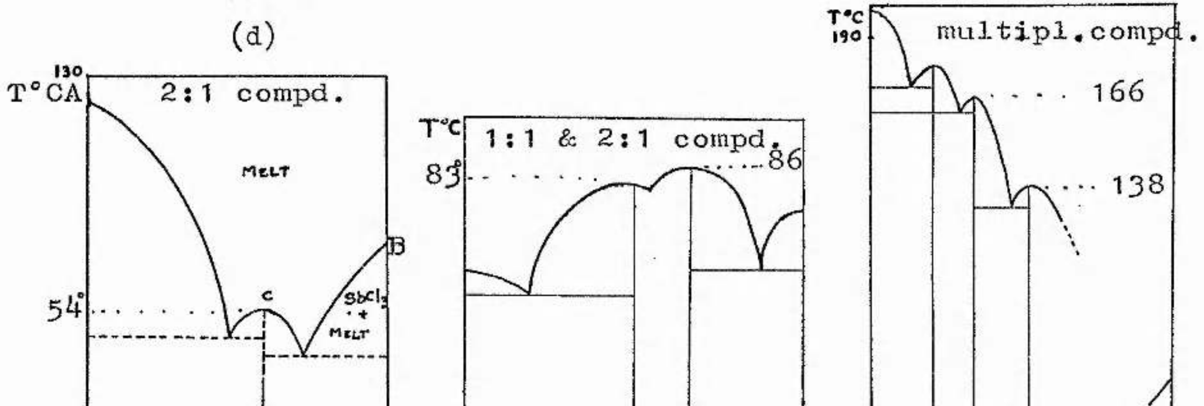
(After Kitaigorodsky, 1973) p.96.

(d)

$YbCl_3$-NaCl system

(After Drobot, Korshunov & Borodulenko, 1968).

(e)



$SbCl_3$-Triphenylamine system

(After Lipka, 1979 a)

(f)

$SbCl_3$-Diphenylamine system

(Ibid, 1979 a)

(g)

$SbCl_3$-Aniline hydrochloride system

(ibid, 1979 a)

(h)

Fig 2.1.2 Phase Diagram for Different Systems.

e) FORMATION OF COMPOUND WITH CONGRUENT MELTING POINT

When component A and B are melted together in suitable proportions, a definite compound crystallizes on cooling. Such a compound is said to have a congruent melting point. Three typical examples are shown in Fig. 2.1.2f,g,h. In the simplest case it can be considered that the diagram is made up of two diagrams of the simple eutectic type placed side-by-side.

f) EUTECTIC SYSTEM WITH AN INCONGRUENTLY MELTING INTERMEDIATE COMPOUND

A binary compound A.B is said to melt incongruently if at a certain temperature it dissociates into a liquid and a solid phase of different composition. Thus in the $NaCl-YbCl_3$ system (Fig. 2.1.2e), an incongruent melting compound ($Na_3.YbCl_6$) is formed (at 75% mole NaCl). The 'reaction point', P, is at 580°C. The liquid phase corresponding to P is at 70 mole % NaCl.

2.2 COMPONENT ANALYSIS

Various methods of analysis may be used in quantifying components of molecular complexes of $SbCl_3$ with organic molecules. Titration vs KIO_3 or atomic absorption for Sb(III); Ultra-violet, Infra-red and Nuclear Magnetic Resonance for the organic component. Selection of a suitable method depends upon such factors as interference, convenience, speed and accuracy.

2.2.1 QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS BY NMR

Certain nuclei possess a spin angular momemtum which is described by a nuclear spin quantum number, I, which can take the value n/2, n=1,2,....

When a nucleus which has a magnetic moment is placed in a magnetic field, B, it takes up one of a number of quantized orientations with respect to that field. Each nuclear orientation has an associated energy level, the lowest corresponding to the orientation in which the nuclear magnetic moment is most closely aligned with the field.

For a nucleus with $I = \frac{1}{2}$, two values for the nuclear spin angular momentum, $m_1 = \pm\frac{1}{2}$, indicate the allowed orientations of the nuclear magnetic moment vector in an external magnetic field. The value $+\frac{1}{2}$ corresponds to alignment of the vector with the applied magnetic field and $-\frac{1}{2}$ opposed to it. The first is the more stable state of lower energy (α) ; the second is the less stable state of higher energy (β).

The energy difference between the two states (α & β) will be given by:

$$\Delta E = 2 \mu B_0 = h\nu \qquad (2.2.1)$$

where μ is the resolved part of the magnetic dipole moment $\vec{\mu}$ in the direction of the applied homogeneus magnetic field, B_0, ($\sim 10^4$ gauss) (Drago, 1965).

There are two allowed transitions: (a) $\alpha \rightarrow \beta$ which corresponds to an absorption of energy and (b) $\beta \rightarrow \alpha$, which correspond to induced emission. The difference in energy between these two states is very small relative to kT (Boltzman's constant and temperature), so that at room temperature the states are very nearly equally populated, and the observation of transitions between them necessitates the use of intense fields and of a resonance effect. Thus for NMR with frequencies in the Radio Frequency region ($\nu = 4.3 \times 10^6$ Hz.), the excess population of spins in the lower state is only about 1 in 10^5.

Obtaining an NMR signal affects the populations of the spins states, but this is compensated by thermal relaxation of the nuclear spins.

Absorption intensity of electromagnetic radiation is then plotted against the change in the applied field strength. For a given nucleus the field strength and NMR frequency are linearly proportional, so that an NMR spectra may be measured in either field or frequency units.

CHEMICAL SHIFTS

When a molecule containing the nuclei under observation is placed in the magnetic field, the electrons within the molecule shield the nuclei from the external applied field. That is, the field at the nucleus, is not equal to the applied field. This difference, called the nuclear shielding, is proportional to the applied field.

The chemical shift, δ , is thus defined as the nuclear shielding divided by the applied field. It is always measured with respect to suitable reference (Me_4Si for the proton):

$$\delta = \frac{(B_{reference} - B_{sample})}{B_{reference}} \times 10^6 \text{ ppm} \qquad (2.2.2)$$

Eq.(2.2.2) can be written also as:

$$\delta = \frac{(\nu_{sample} - \nu_{reference})}{\text{Oscillation frequency (Hz)}} \times 10^6 \text{ ppm} \qquad (2.2.2a)$$

$\delta = 0$ for TMS (tetramethylsilane), increasing downfield. Occasionally $\tau = 10 - \delta$ is used.

INTENSITY OF ABSORPTION AND SPIN-SPIN SPLITTING

One of the most useful aspects of Proton NMR is the fact that the integrated NMR signal obtained is directly proportional to the number of hydrogen nuclei producing it. This is particularly important in quantitative analysis (Abraham and Loftus, 1978,p150).

Another phenomenom, observed in NMR spectra, is the occurrence of spin-spin splitting. Thus the proton spectrum of dichloroacetaldehyde ($CHCl_2CHO$), consists of four peaks - each of the two expected peaks corresponding to different protons (δ values) is split by the influence of the neighbouring proton. Thus does not however affect the quantitative use of NMR spectra.

APPLICATION OF NMR IN QUANTITATIVE ANALYSIS

Whatever the split, the total integrated absorption is directly proportional to the number of H atoms whatever their environment (Pasto and Johnson, 1969). Thus, the analysis of mixtures (Cerfontain, et.al., 1974), may be accomplished, provided that the absorptions of H atoms in one molecule are distinct from the absorptions due to H atoms in the others.

EXPERIMENTAL EXAMPLES

a) The composition of a mixture of three known components, 2-propanol, N-methyl-2-pyrrolidone and water has been determined (Chamberlain, 1974).

The spectrum consists of six well-separated bands, with band overlap only in the case of the exchangeable hydrogen (band f). See Fig. 2.2.1.

The procedure consists in identifying the bands and assigning them, by reference to their δ values, to the particular hydrogen atoms associated with the parent components. Then, from the peak-areas the composition may be found.

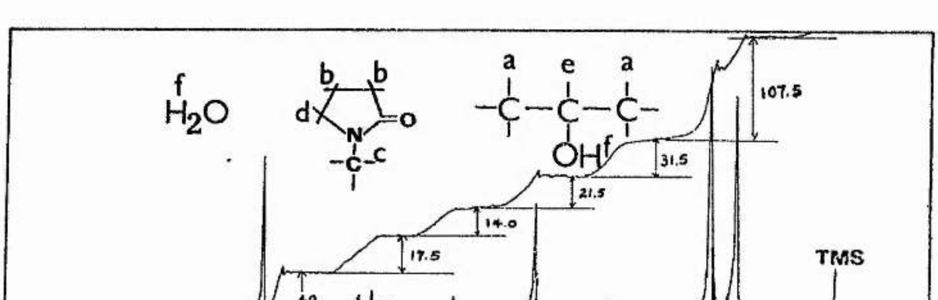


Fig 2.2.1 NMR spectrum of mixture for quantitative analysis.

b) DETERMINATION OF 1-CHLORONAPHTHALENE IN A COMPOUND USING AN INTERNAL STANDARD (MeI).

The stoichiometry of a molecular complex may be determined if the weight of one component is known. This may be achieved by adding a known weight of an internal reference whose peaks are not near those of the organic material being determined. The weight is then obtained from the integrated peak ratios. A typical spectrum of $1\text{-}C_{10}H_7Cl$ recorded in a Varian EM-360 60MHz NMR-spectrometer is shown in Fig. 2.2.2.

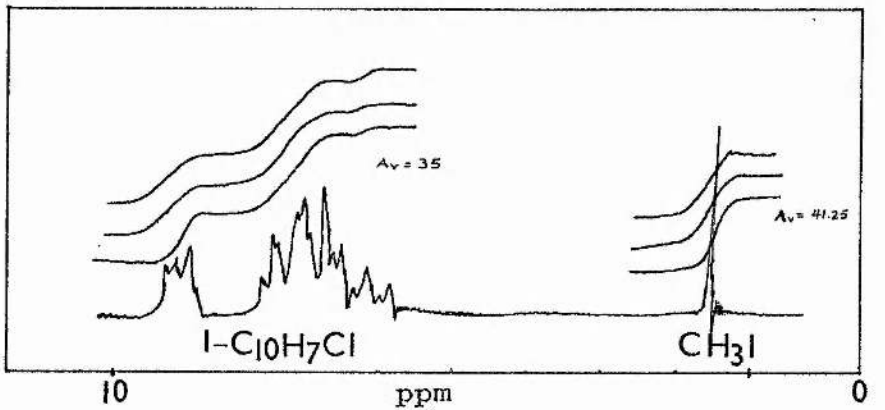


Fig 2.2.2

NMR spectrum of $1\text{-}C_{10}H_7Cl$ and CH_3I
(Internal standard) in CCl_4.

Carbon tetrachloride (CCl_4) was found to be a suitable solvent because this compound neither reacts with the components in the sample to be analyzed nor produces a peak in the NMR spectrum being used.

Results of analysis for $1\text{-}C_{10}H_7Cl$ with and without $SbCl_3$ present in the sample are shown in Table 2.3.2. Each sample was diluted up to 10ml in CCl_4.

TABLE 2.2.3

RESULTS OF ANALYSIS FOR 1-$C_{10}H_7Cl$ (α) BY NMR

(Taking MW α = 162.6 and CH_3I=141.9)

Presence of $SbCl_3$	Wt. Ratio α/CH_3I	Peak Area Ratio α/CH_3I	Moles of CH_3I x10^{-3}	Moles of (1) α x 10^{-3}	Wt. of α (g)	% ERROR
No	0.2602/0.4550 = 0.5719	41.25/35.0 = 1.178	= 3.20	1.616	0.2628	+1.0
Yes (0.7300g)	0.2608/0.4548	55.0/47.5 = 1.158	3.20	1.588	0.2582	-1.0

(1) Moles α = Peak area Ratio x 3/7 x Moles of CH_3I.

2.2.2 QUANTITATIVE ANALYSIS OF Sb(III) BY TITRATION AGAINST KIO_3

Potassium Iodate is a powerful oxidising agent (Vogel, 1978). In solutions of moderate acidity (~ 0.1 M HCl) it is reduced to iodine. e.g.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Whereas in more strongly acid solutions (~ 6M HCl) reduction occurs to I^{+I} .

$$IO_3^- + 6H^+ + 2I^- + 3Cl^- \longrightarrow \begin{array}{c} 3ICl \\ \downarrow\!\uparrow {\scriptstyle Cl^-} \\ 3ICl_2^- \end{array} + 3H_2O$$

However the optimum acidity for reasonably rapid reaction varies somewhat from one reductant to another.

APPLICATION TO THE ANALYSIS OF Sb(III)

In 3.0-4.5M HCl, Sb^{III} may be estimated according to the equation

$$IO_3^- + 2Sb^{III}Cl_3 + 6H^+ + 8Cl^- \rightleftharpoons ICl_2^- + 2(Sb^V Cl_6^-) + 3H_2O$$

Typically 7ml of 4M HCl is added to 0.02g $SbCl_3$ for titration with 0.025M KlO_3 using CCl_4 or Chloroform as indicator (violet colour of iodine oxidised to colourless ICl at equivalent point), to a final volume, including washings of 25 ml.

Test results of analysis are given below.

TABLE 2.3.2

RESULTS OF TEST ANALYSIS FOR $SbCl_3$

Weight of $SbCl_3$(g)	Vol. 0.025M KlO_3 employed (ml)	Experimental Weight of $SbCl_3^{(\pm)}$ (g)	ERROR (%)
0.0209	1.822	0.0208	-0.43
0.0209	1.822	0.0208	-0.43
0.0721	6.300	0.0719_8	-0.17

(±) Based on $KlO_3 \equiv 2\ SbCl_3$

$$\therefore \quad 1\text{ ml } 0.025\text{ M} \equiv \frac{2\times228.5}{40{,}000} = 11.425\text{ mg.}$$

2.3 STRUCTURAL DETERMINATION (SINGLE CRYSTAL X-RAY DIFFRACTION).

X-ray diffraction is one of the most important methods in the study of molecular complexes in the solid state, and the main one to provide information about the spatial arrangement of the atoms.

A crystal is a periodic three-dimensional array of atoms which act as a three-dimensional diffraction grating for x-rays of wavelength comparable to the interatomic distances and interplanar spacing within it. When a beam of x-rays of wavelength, λ, passes through the crystal, the x-rays at angle incidence θ to the hkl plane are diffracted. The diffracted beams from successive planes will mutually interfere unless they are in phase according to the Bragg relationship:

$$n\lambda = 2d_{hkl} \ \mathrm{Sin}\theta \qquad (2.3.1)$$

Where d_{hkl}, the interplanar spacing is directly related to the dimensions of the unit cell and the Miller indices of the reflecting planes.

As $\sin\theta \propto 1/d$, interpretation of a diffraction pattern is facilitated by refering to the reciprocal lattice (Buerguer, 1966, p.107f; Jeffery, 1971, p.24), where the hkl plane is represented by a reciprocal lattice point λ/d_{hkl} from the origin.

2.3.1 CRYSTAL STRUCTURE ANALYSIS - INTRODUCTION

A suitable single crystal must be selected for structural analysis. Some factors which need to be considered to obtain good diffraction photographs are: (a) Stability: according to the stability of the crystal under normal conditions one decides whether it is necessary to employ a special device or not, e.g. to avoid decomposition of the molecular compounds of $SbCl_3$ with moisture, the crystal must be sealed off in a Lindemann tube. (b) Size and shape of the crystal. Ideally the crystal should be spherical, and, in order to keep absorption errors below 10%, it should have an optimum size of $2/\mu$ mm, where μ is the linear absorption coefficient (Buerguer, 1966, p.179). (c) Singularity, the selected crystal must, if possible, have clean outlines with no other adhering crystals. (d) Freedom from twining (Buerguer,1960,p53; Glasser, 1977 ,p69).

SINGLE CRYSTAL CAMERAS

All single crystal diffraction cameras have certain features in common. The crystal is bathed in a narrow beam of approximately parallel collimated x-rays, usually monochromatic. The undiffracted beam is caught in a lead trap to minimise film blackening. The diffracted beam is recorded on a film protected from light.

The selected crystal is mounted on a set of arcs with angular and linear movements attached to the goniometer head. Adjustments of the arcs and slides enables one to orient a prominent axis of the crystal suitable for the chosen recording method.

2.3.2 CELL PARAMETERS AND SPACE GROUP DETERMINATION

There are several methods of evaluating the unit cell parameters (a,b,c, α , β , and γ).

(a) The Oscillation Method (Buerguer,1966,p188;Woolfson,1970,p134;McKie and McKie,1974,p214) permits determination of one dimension for the layer spacings: e.g. using x-rays of wavelength, λ ,

$$c = \frac{\ell\lambda}{\sin\left[\tan^{-1}\left(\frac{Y}{2R}\right)\right]} = \frac{\ell\lambda}{\zeta_c} \qquad (2.3.2)$$

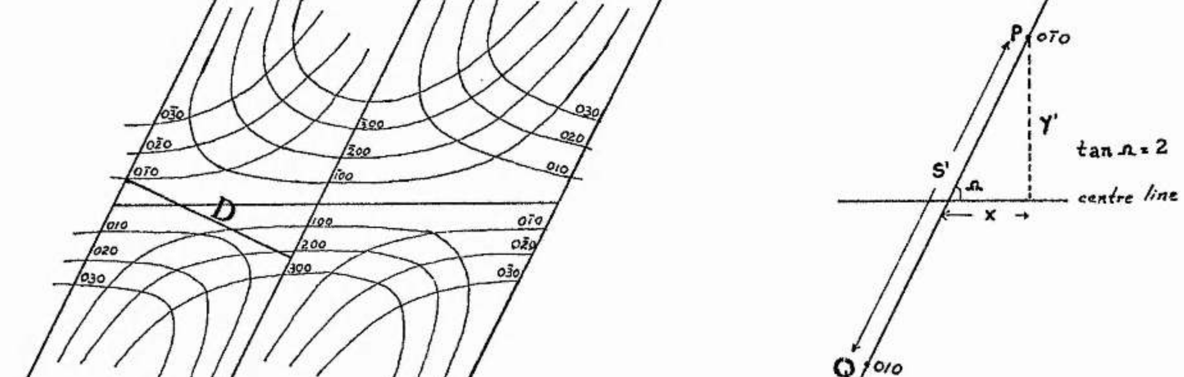
Where ℓ is the index of the layer-line considered. Y is the separation in mm between corresponding layer-lines and R is the radius of the camera (usually 2R=57.296 mm).

The process of determining the remaining cell parameters from an oscillation photograph is tedious (Mckie and Mckie, 1974, p.226; Glasser, 1977, p.90).

(b) The Weissenberg Method

This is a more convenient method (Woolfson,1970,p141; Jeffery, 1971, p.188f), both in terms of assigning indices to the plane generating a particular reflection and for determining cell parameters. There is the additional advantage that it enables one to collect information from one complete layer at one time without the overlap difficulty inherent in a simple oscillation procedure. Other layers are screened off.

A typical zero-layer weissenberg photograph obtained by synchronous movement of film and crystal oscillation is shown in fig. 2.3.4a.



(a.) Zero-layer Weissenberg photograph.

(b) Diagram of the b axis on the zero-layer Weissenberg photograph.

Fig 2.3.4

Some cell parameters can be calculated directly from a zero-layer Weissenberg photograph (Buerguer, 1964, p.377ff; Jeffery, 1971, p.264). From figs. 2.3.4a,b., where γ' is in mm.

$$d^*_{010} = kb^* = 2\sin\theta = 2\sin(Y'/2R)$$

Since $Y' = s'/\sqrt{5}$ and usually $2R = 57.296$ mm.

$$\xi_b = d^*_{0k0} = 2\sin(s'/\sqrt{5}) \qquad (2.3.3)$$

where $s'/\sqrt{5}$ is in degrees, and $\gamma'/2R$ in radians.

The reciprocal angle γ^* can be calculated from the relation:

$$\gamma^* = D \times \sqrt{5} \qquad (2.3.3a)$$

Where D is the separation (in mm) between the two reciprocal axes given the construction that $\tan \Omega = 2$.

So far only c, ξ_a, ξ_b and γ^* have been determined. To evaluate the remaining constants one must find α and β from an upper layer equi-inclination photograph about the same axis using the method of "angular lag" (Buerguer, 1942).

The basis of the "angular lag" calculation is the location of the upper-layer origin with respect to the rotation axis. This is defined in terms of two shifts δa and δb, parallel to the lattice axes.

According to the Buerguer's procedure, δa and δb are evaluated from measurements which involve low-index reflections from two superposed Weissenberg films of the zero- and first layers. Direct cell angles then can be calculated from:

$$-\tan\alpha = \frac{n\zeta_c}{\delta_a} \quad \text{or} \quad -\tan\beta = \frac{n\zeta_c}{\delta_b} \qquad (2.3.4)$$

Where ζ_c is evaluated from an oscillation photograph (about c).

This procedure suffers from two practical disadvantages. It requires two precisely superposed Weissenberg films of the zero and first layers and the measurements are made on low-index reflections which may be weak and unobservable.

A second approach has been developed by Hulme (1966). This treatment involves the measurement of angles between general hkl reflections, which complemented by other constants obtained from oscillaton and zero-layer Weissenberg photograph permits calculation of the rest of the cell constants either graphically or analytically using a least-square computer program. The graphical procedure is illustrated below (Fig. 2.3.5).

This procedure is free from the disadvantages present in the Buerguer's method and is still useful when split-film casettes are employed in low temperature work. Accuracy is best using reflections with $\theta \leq 20^\circ$ having interangles ϕ_n in the 60-120° range.

Another procedure has been described by Herbert (1978). Here measurements are made on festoons representing either axes of the reciprocal lattice or lattice lines runing parallel to these axes.

For a crystal rotating about the b axis, $\delta_{c,o}$ is calculated from:

$$\delta_{c,o} = \cos \mu_n (1-\cos \chi_{n,o}) \qquad (2.3.5)$$

where μ_n is the equi-inclination angle of the nth layer, and $\chi_{n,o}$ is the distance between the symmetrically distributed points s_1 and s_1' in axis as is shown in Fig. 2.3.6.

When a reciprocal-lattice line parallel to the axes is used, e.g. s_2, s_2' $\delta_{c,o}$ is obtained from:

$$\delta_{c,o} = \delta_c = \cos\mu_n \ (1-\cos\chi_{n,1}) - c^* \sin\beta^* \qquad (2.3.6)$$

where c^* and β^* can be obtained from the zero-layer Weissenberg photograph. Then cell angles can be calculated from

$$-\tan\alpha = \frac{n\,\zeta_b}{\delta_{c,o}}, \ \text{etc.}$$

ζ_b is calculated from an oscillation photograph.

This procedure has two main disadvantages. It is sensitive to errors when festoon extrapolation has to be performed, especially if the reciprocal spacing are large: and, this method is not applicable when a split-film casette is employed.

An oscillation, a zero Weissenberg and an n-layer Weissenberg photograph thus yield c, ξ_a, ξ_b, γ^* and α, β.

The cell parameter $a = \lambda/\xi_a \sin\beta \sin\gamma^*$ 2.3.7a

$b = \lambda/\xi_b \sin\gamma^* \sin\alpha$ 2.3.7b

and $\gamma = \cos^{-1} (\cos\alpha\cos\beta - \sin\alpha\sin\beta\cos\gamma^*)$ 2.3.7c

so that all parameters have been determined.

Since ξ and ζ are proportional to s' (in Weissenberg photograph) and y (in oscillation photograph) respectively, better accuracy may be obtained by measurement of the highest observable reflection in the axis or highest layer-line distance respectively. However factors such as the divergence of the incident x-ray beam and the progressive reduction in angle between the diffracted beam and the surface of the film as the reflections increase the use of the highest reflections does not make much difference. In general measurement of layer-line spacing in oscillation photograph or from a Weissenberg photograph yield unit cell dimensions of accuracy about 1% and angles with an error of about 0.5°.

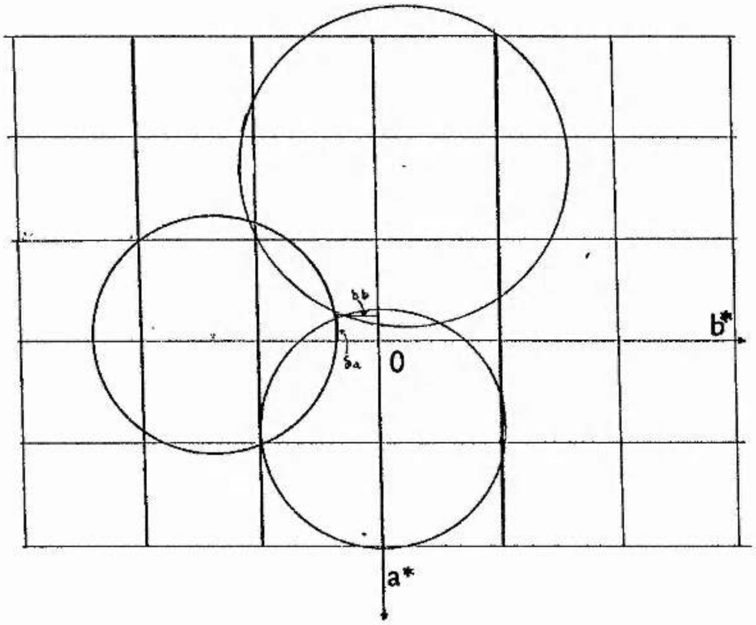


Fig 2.3.5

Angular lag method for calculation of cell parameters: Graphical evaluation of δ_a and δ_b ,and hence α and β ,for the following pair of reflections:

111 - $1\bar{1}1$: 91.50°
$1\bar{1}1$ - $\bar{1}\bar{2}1$: 83.50°
$\bar{1}\bar{1}1$ - $\bar{3}11$: 75.50°.

(Data for $SbCl_3$.1-chloronaphthalene compound, triclinic setting).

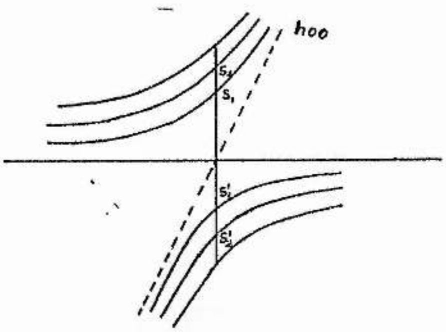


Fig 2.3.6 Schematic drawing of an upper-layer equi-inclination Weissenberg photograph about b.

(c) A Method Without Reciprocal Lattice Distortion

An undistorted picture of the reciprocal lattice (RL) may be obtained using two methods (De Jong-Boumann, 1938; Buerguer, 1944). The common feature of these methods is the mechanical linkage coupling the movement of a flat film casette and the rotation of the arcs carrying the crystal (the "dial" axis) which is measured on a dial. Such coupling fulfils the requirement for recording an undistorted reciprocal lattice i.e. A principal axis of the crystal is always kept perpendicular to the film, so that the film remains parallel to a set of RL layers during movement.

When a layer is to be photographed, unwanted reflections from other layers of the RL are excluded by positioning of a layer screen having an annular slit such that only reflections from the cone subtended at the crystal by the chosen layer are allowed to reach the film.

The scale of the undistorted picture of the RL depends on the crystal-to-film distance, M, so that typically 1cm = 1 r.l. unit.

The basic feature of the De Jong-Boumann camera is that the relative position of crystal, screen and the rotation axis of the film are unchanged (see fig. 2.3.6a). The upper-layer is brought into the recording position by altering the angle of incidence of the x-ray beam, and the position of the film.

In the precession method, the crystal is set initially with a principal axis parallel to the x-ray beam. This axis is then tilted (to be perpendicular to the film) to make an angle μ with the x-ray beam and caused to precess about it, so that the axis travels around the beam on the surface of a cone of semi-vertical angle μ . The layer screen attached to the arcs and the film similarly inclined, follow the motion of the crystal axis (fig. 2.3.6b).

Upper layers are recorded by changing the position (and sometimes the size) of the layer screen and the film position (Buerguer, 1964,p76).

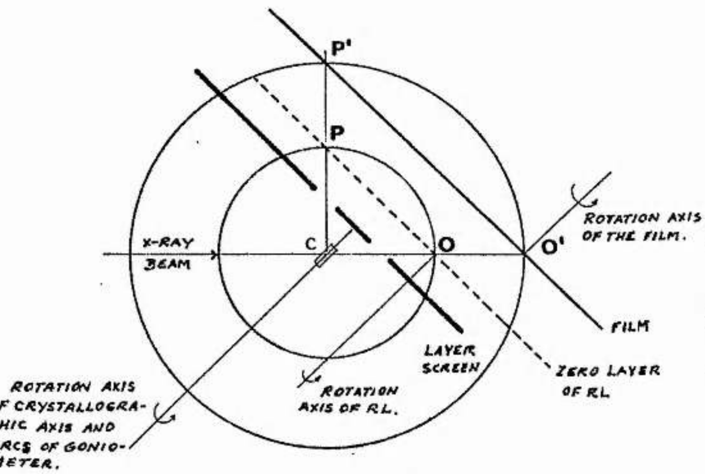


Fig 2.3.6a

The de Jong-Boumann camera
for zero-layer
(After Glasser, 1977 ,p78).

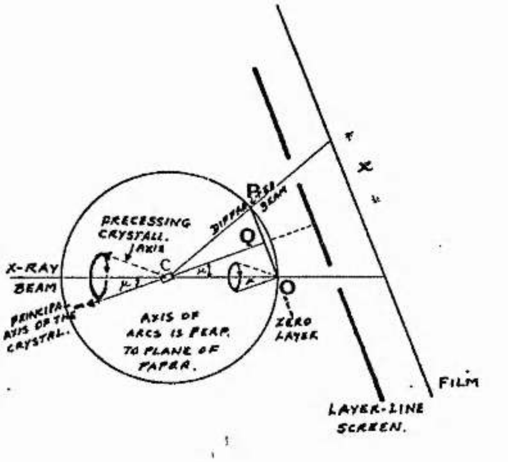


Fig 2.3.6b

Arrangement of a
Precession Camera

Evaluation of Lattice Parameters (Buerguer, 1964,p83ff).

From a photograph obtained rotating the crystal about the c-axis, a^* , b^* and γ^* can be determined by measurement of the row spacing and the angle between them, respectively.

In a similar way from a second photograph obtained rotating about the a-axis, b^* , c^* and α^* can be found.

The difference between the corresponding dial settings is the angle β . The rest of the parameters can be evaluated from the following equations.

$$\beta^* = \cos^{-1}(\cos\alpha^*\cos\gamma^* - \sin\alpha^*\sin\gamma^*\cos\beta) \qquad (2.3.8)$$

$$\cos\alpha = (\cos\beta^*\cos\gamma^* - \cos\alpha^*)/(\sin\beta^*\sin\gamma^*) \qquad (2.3.9)$$

$$\cos\gamma = (\cos\alpha^*\cos\beta^* - \cos\gamma^*)/(\sin\alpha^*\sin\beta^*) \qquad (2.3.10)$$

$$a = \lambda/(a^*\sin\beta\sin\gamma^*);\ b = \lambda/(b^*\sin\alpha\sin\gamma^*) \qquad (2.3.11)$$

$$c = \lambda/(c^*\sin\alpha\sin\beta^*) \qquad (2.3.12)$$

(d) Accurate Determination Of Cell Constants Using An X-Ray Diffractometer

Best accuracy in parameters evaluation by any of the above procedures requires appropriate choice of θ range (or reflections), and is usually improved by subjecting some dozen independent measurements to a Least Square treatment. Such an approach is particularly relevant when evaluating cell parameters using a diffractometer (Jeffery, 1971, p.170; Manual of Instruction for 2-circle x-ray diffractometer STADI 2).

2.3.3 THE SPACE GROUP

In any object there may be some points which are related to others by rotation of the object about an axis or its reflection in a plane. A particular combination of such symmetry elements, each acting at the same point is known as the point group. In space, an object may be related to others by additional translational symmetry elements (screw axes and glide planes), which are not restricted to passing through a single point. There are 230 possible combinations of symmetry elements involving translations (Vol. I of International Tables for x-ray Crystallography, 1952), which are known as space groups.

Translational symmetry elements are revealed by the 'systematic absences' caused in the diffraction pattern by destructive interference. Recognition of these absences often leads to complete determination of the space-group which describes the intra spatial relationship of atoms or molecules. In some cases ambiguity may arise depending, for example, upon whether or not there is a centre of symmetry. Thus the systematic absences for Cc and C2/c are the same. Some physical features (pyro and piezo electricity) however occur only in non-centrosymmetric crystals i.e. in space group Cc. Statistical examination of reflection intensities (Howells, E.R., et.al, 1950; Lipson and Cochran, 1966 p.46) or packing consideration may also help to discriminate between possible alternatives.

2.34 CRYSTAL DENSITY AND CELL CONTENTS

The observed density, D_o, can be determined in various ways. Normally it is measured by using a mixture of liquids whose composition can be varied until the crystals neither sink nor float. Then by comparison with the liquid density that of the crystal is established.

This density (D_o) is related to the number of moles in the cell (Z), the volume of the cell (V) and the "Mol. Weight" (M) by the expression:

$$Z = \frac{V D_o}{1.660 M} \qquad (2.3.13)$$

Which may be variously used to calculate Z, M or the density. Where V in $\AA^3$, D_o in $M_g\ m^{-3}$ and M in g/mol.

2.3.5 MEASUREMENT AND CORRECTIONS OF INTENSITY

There are two methods for recording intensities.

(a) THE PHOTOGRAPHIC METHOD

Intensities are usually measured from multiple films taken in one of the moving film cameras. The Weissenberg method is the most usual, because of the large volume of reciprocal space accessible to it, the applicability of multiple film technique in collecting data without further difficulty and the uncomplicated nature of the Lorentz factor correction. The methods used for intensity measurements by photographic means may be clasified (Jeffery, 1971) as:

i) Eye estimation against a standard scale, preferably made from a reflection of the crystal concerned.

ii) Photometry of non-integrated reflections. This may be necessary if minimum exposure times are required for any reason.

iii) Photometry of integrated reflections produced by an integrating Weissenberg camera. This involves increasing the exposure time to obtain reflections with a uniform central area whose optical density is proportional to the integrated intensity.

Suitable film blackening, corresponding to the region of linear proportionality to intensity is ensured by selection of the appropriate member of the multiple film pack.

(b) THE COUNTER METHOD

X-ray photons may either cause ionisation or scintillation. These two facts are the basis of the construction of counters. In the first case, the electrons ejected as a result of the ionisation process may be collected to give an electrical signal in a suitable circuit. Counters like the 'ionisation chamber', the 'proportional' and 'Geiger-Muller' counters (operating at ~ 100, 500 and 1000 v. respectively) belong to this group.

In the second case, with scintillation counters, light emitted by a photoactive solid due to the scintillation phenomenon may be intercepted by a photocathode which releases electrons to be subsequently amplified.

Both Proportional and Scintillation counters can provide energy discrimination as the electrical pulses are proportional to the energy of the photon, in contrast to the Geiger-Müller tube and ionisation chamber where this is not the case.

The counting of photons is subject to "response" and "dead time" errors in the counter (for which corrections may be made), but the proportinnality to the intensity of the diffracting x-ray beams also involves background corrections.

The corrected integrated intensity will be given by:

$$I_o(hkl) = N_c - \frac{t_c}{2t_b}(B_1 + B_2) \qquad (2.3.14)$$

Where N_c is the total count at the peak in a scan of time t_c; B_1 and B_2 are the backgrounds, each obtained in a time t_b.

In practice, $I_o(hkl)$ is rejected when $I_o(hkl) < S \times \sigma(I)$ or when $|B_1 - B_2| > D \times I_o(hkl)$. Where $\sigma(I) = \sqrt{N_c} + \frac{t_c}{2t_b}\left(\sqrt{B_1} + \sqrt{B_2}\right)$ (2.3.15)

S is normally 2 or 3 and D can take values of 0.100, 0.200, ..., etc.

CORRECTIONS TO THE INTENSITY

Measured intensities ($I_o(hkl)$) require corrections for:

(a) The 'Lorentz Factor' (L). Due to crystal non-ideality x-rays are diffracted over an angular range. The L factor corrects for the relative time during which different reflections can occur.

The correction has the form:

$$L^{-1} = \frac{\text{Sin } 2\theta\ (\sin^2\theta - \text{Sin}^2\mu)^{\frac{1}{2}}}{\sin\theta} \qquad (2.3.16)$$

Where θ is the Bragg angle and μ is the equi-inclination angle for data obtained in a Weissenberg type geometry (International tables for x-ray Crystallography Vol. III p. 266).

(b) The 'Polarization Factor' (p). - which allows for the state of polarization of the incident and diffracted beams. This can be expressed in the following way:

i) For rotation and Weissenberg cameras (Buerguer, 1960, 175ff.):

$$p^{-1} = \frac{2}{(1 + \cos^2 2\theta)} \qquad (2.3.17)$$

ii) With monochromatized radiation as in the present work.

$$p^{-1} = \frac{2}{\cos^2 2\theta' + \cos^2 2\theta_{mon}\ (1-2\sin^2\mu)^2} \qquad (2.3.18)$$

Where $\theta' = \tan^{-1}\left[\frac{(\text{Sin}^2\theta - \text{Sin}^2\mu)^{\frac{1}{2}}}{\cos\theta}\right]$ and θ_{mon} is the Bragg angle for the monochromator.

Since L and p are both geometrical factors they are combined into a single Lp factor and the observed $I_o(hkl)$ is multiplied by $(Lp)^{-1}$.

(c) Absorption (A). In addition to being scattered x-rays are absorbed by matter, i.e. the electromagnetic radiation energy is converted to thermal energy (Woolfson, 1970). Thus the parts of a crystal far from the x-rays source are irradiated by a beam which is less intense than that incident on the near parts. This reduces the total reflected energy below the theoretical value. The factor A by which it is reduced is given by $A = \frac{1}{v}\int e^{-\mu L} dv$, where μ is the linear absorption coefficient, L is the path length in the crystal of a beam diffracted from the volume element dv, and v is the volume of the crystal. The observed intensity must be multiplied by A^{-1} to give the theoretical value.

In certain circumstances it is difficult to apply this correction. Thus in the present case the absorption correction was ignored because the crystal was sealed in a Lindemann-glass tube and was coated with hydrolysis products. Absorption can be minimised by using an optimum size of crystal (cf. 2.3.1) and the optimal orientation of the Lindemann tube with respect to the x-ray beam.

(d) Extinction

"Primary Extinction", arises when x-rays scattered by different domains within the crystal destructively interfere.

'Secondary Extinction', occurs when a reflected beam, encounters another set of planes in the reflecting position, so that a proportion suffers a second reflection.

Primary extinction is significant only if the "mosaic" blocks are large (Darwin, 1922; Taylor et.al., 1956); secondary extinction may be important even when they are small if there are enough blocks in parallel orientation.

Both primary and secondary extinction weaken the observed intensity of the diffracted beam relative to the ideal. Both effects become more important as the fraction of energy that passes into the diffracted beam increases, and the errors are therefore most serious for the strongest reflections. These effects are not easy to eliminate, but may be minimised by using small crystals.

In crystal structure refinement, it has been recognized that reflections affected in large degree by extinction must either be discarded or corrected for the effect (Azaroff, et.al. 1974). This is done by examination of observed and calculated F's. If reflections at low angles with large Fc values have Fo consistently lower than Fc they are assumed to be affected by extinction, and they are excluded or given zero weights or corrected by an appropriate correction factor (Taylor, et.al., 1956).

2.3.6 THE STRUCTURE FACTOR, F(hkl)

The intensity of an x-ray beam reflected by a plane is dependent on the types of atoms diffracting (the atomic scattering factor $f_{i\theta}$), their positions (x_j, y_j, z_j) and the Miller indeces of the plane (hkl). This dependence is sumarised in the structure factor:

$$F(hkl) = \sum_{j=1}^{N} f_j \exp 2\pi i \, (hx_j + ky_j + lz_j) \qquad (2.3.19)$$

F(hkl) is complex, and may be written as:

$$F(hkl) = A(hkl) + iB(hkl) \qquad (2.3.20)$$

where $A(hkl) = \sum_{j=1}^{N} \cos 2\pi (hx_j + ky_j + lz_j)$ (2.3.21)

$$B(hkl) = \sum_{j=1}^{N} \sin 2\pi (hx_j + ky_j + lz_j)$$

Its modulus or structure amplitude will be given by:

$$\left| F(hkl) \right| = (A^2(hkl) + B^2(hkl))^{\frac{1}{2}} \qquad (2.3.22)$$

which has an associated phase angle:

$$\alpha_{hkl} = \tan^{-1} (B(hkl)/A(hkl)) \qquad (2.3.23)$$

EFFECT OF THERMAL VIBRATION ON THE STRUCTURE FACTOR

The thermal motion of the atoms, has the effect of 'smearing out' the atoms so causing a certain amount of destructive interference in the radiation diffracted by the atoms.

This reduces the value of the atomic scattering factor f_j by the factor, D, causing the intensity to fall off more rapidly with θ.

For a spherically symmetric (isotropic) vibration,

$$D = \exp\left[-\overline{B}\,(\sin^2\theta)/\lambda^2\right] \qquad (2.3.24)$$

where $\overline{B} = 8\pi^2\,\overline{u}^2$, $\overline{u}^2$ is the mean square displacement of the structure from its rest position and it is determined by the statistical method used to obtain a scale factor (Wilson, 1942).

If the vibration is asymmetric (anisotropic),

$$D = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \qquad (2.3.25)$$

where $$U_{11} = \frac{\beta_{11}}{2\pi^2 a^{*2}}, \qquad U_{22} = \frac{\beta_{22}}{2\pi^2 b^{*2}} \qquad U_{33} = \frac{\beta_{33}}{2\pi^2 c^{*2}} \qquad (2.3.25)$$

$$U_{12} = \frac{\beta_{12}}{2\pi^2 a^* b^*}$$ ..., etc., are elements of a matrix U.

The temperature factor is usually refined by least-squares procedures along with the other structure parameters.

RELATION OF STRUCTURE FACTOR TO THE INTENSITY

The observed diffracted intensity is related to the structure factor by the following expression:

$$\left|F(hkl)\right|^2 = \frac{1}{K}\quad\frac{1}{(Lp)_{hkl}}\;I_o(hkl) \qquad (2.3.26)$$

Where K can be evaluated statistically by means of the Wilson plot (Wilson, 1942), $\sin^2\theta/\lambda^2$ vs. $\log(\langle I_\theta\rangle/\Sigma_\theta)$.(*)

The observed structure amplitude:

$$\left|Fo(hkl)\right| = \left(\left|F(hkl)\right|^2\right)^{\frac{1}{2}} \qquad (2.3.27)$$

(*) $\langle I_\theta\rangle$ is the mean intensity in a range around θ
$\Sigma_\theta = \sum_{i=1}^{n} f_i$ at centre range θ

From eq. (2.3.19), when the structure, i.e. atomic positions x_j, y_j, z_j are known, values of F(hkl) can be calculated (Fc (hkl)). Comparison with the corresponding observed quantities, Fo(hkl) constitutes a test of the correcteness of the atomic positions.

In practice we do not know the atomic positions. However, since the intensities are related to the structure amplitudes, $|Fhkl|$ by the expression (2.3.26), they can provide information so that the crystal structure can be solved.

An initial "trial structure" can be obtained from packing considerations (i.e. by considering the accommodation of the number of atoms or molecules in the unit cell according to the space group, so that they do not overlap). Alternatively one may solve a Patterson function (referred to later) when packing considerations alone are not enough. In either case the obtained structure may be used in the calculation of the structure factor, F_c(hkl) and in the computation of the electron density.

2.3.7 THE ELECTRON DENSITY AND PATTERSON FUNCTION

Because the electron density within a crystal is single valued, finite and continuous it may be expressed as a three-dimensional Fourier series:

$$\rho(x,y,z) = \frac{1}{v} \sum_{h} \sum_{k} \sum_{l} F(hkl) \exp\left[-2\pi i(hx + ky + lz)\right] \quad (2.3.28)$$

which is the Fourier Transform of the structure factor F(hkl). In reality the sum extends over all observed reflections, v is the volume of the unit cell.

The maxima in the function $\rho(x,y,z)$, the electron density, at point x,y,z, are at or very near to atomic positions.

Once a trial structure is established by one of the above methods, a Fourier synthesis for the electron density using the observed amplitudes $|F_o(hkl)|$ with signs (or phases) taken from the calculated structure factors, $F_c(hkl)$, can be evaluated, from which improved atomic parameters may be deduced or positions of missing atoms located.

THE PATTERSON FUNCTION

One method for determining a trial structure involves the evaluation of a function derived by Patterson (1934):

$$P(u,v,w) = \frac{1}{V}\sum_h \sum_k \sum_l |F(hkl)|^2 \cos 2\pi(hu + kv + lw) \quad (2.3.29)$$

which is particularly helpful if heavy atoms are present.

The function can be computed directly from the observed $|F_o(hkl)|^2$ without any knowledge or assumptions about the signs of phases of the structure factors, $F(hkl)$.

Eq. (2.3.29) is obtained from the product of the electron densities $\rho(x,y,z)$ and $\rho(x+u, y+v, z+w)$.

Physically the function $P(u,v,w)$ is large whenever both $\rho(x,y,z)$ and $\rho(x + u, y + v, z + w)$ are large i.e. when both (xyz) and $(x + u, y + v, z + w)$ correspond to atomic sites. Hence $P(u,v,w)$ is a vector map showing interatomic separations, u,v,w starting from the origin. It is always centrosymmetric. The magnitude of the vector peak is proportional to the product of the atomic number of the pair of atoms concerned.

There are several methods for deducing atomic positions from a vector map, e.g. by simple inspection, by superposition, or by calculation of the minimum function (Buerguer, 1959 ,p239).

2.3.8 REFINEMENT OF THE STRUCTURE

A convenient measure of the agreement between observed and calculated structure factors is a quantity called the 'reliability index' or 'residual' defined by:

$$R_1 = \frac{\sum \left| |F_o(hkl)| = |F_c(hkl)| \right|}{\sum |F_o(hkl)|} \quad \text{or } R_w = \frac{\sum w \, \Delta F(hkl)}{\sum w \, F_o(hkl)} \quad (2.3.30)$$

where $F_o(hkl)$ and $F_c(hkl)$ are the observed and calculated structure factors.

The process of refinement is, then, a procedure to make the value of R as low as possible.

There are several methods for improving agreement between $F_o(hkl)$ and $F_c(hkl)$ once an approximate structure has been found.

a) FOURIER METHODS

These involve the computation of electron density or difference maps. The process of refinement by this method starts with some model of the crystal structure which is usually known partially or imperfectly. From the Electron Density map computed atomic coordinates can be improved and it may reveal the position of other atoms not included in calculating the structure factors. The process is repeated until the coordinates no longer change, and all atoms have been included.

This method is relatively insensitive once the coordinates are approximately correct for the following reasons: Firstly because adjustment of the temperature factor is ignored when an electron density is computed; secondly because a series termination error is introduced when an infinite series is approximated by a finite one; and thirdly, because nearby atoms may not be resolved in the electron density map.

Furthermore it is usually a time consuming (Buerguer, 1960, p.590) process to define the exact centre of a peak, and the computed electron density is regarded as a 'hybrid' between that of the true structure and that of the assumed one.

One way to avoid some of the problems is to use (F_o-F_c) as the Fourier coefficient. This produces a difference map which consists essentially of the true E.D., with the E.D. due to the assumed structure subtracted. If the assumed structure is correct, the difference map should be zero everywhere, but in practice random errors in the observed data make this only approximately true even for fully refined structures. If an atom is slightly misplaced (Fig. 2.3.7), its assumed position will lie on a steep gradient in the difference map not far from the zero contour, with a large negative region to one side of it and a large positive one to the other. To improve the coordinates a shift proportional to the gradient at the assumed position and towards the positive region is made.

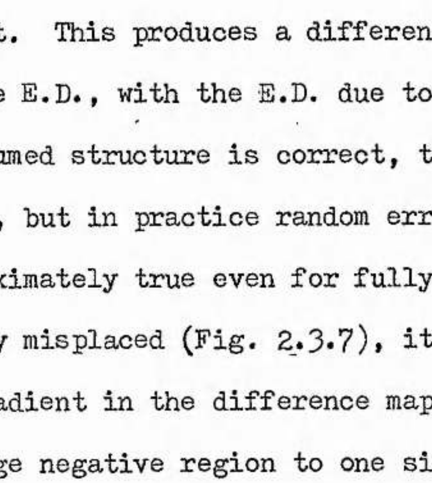


Fig 2.3.7

The relationship between the assumed position Pa, the true position Pt and the difference synthesis.

If an atom is completely misplaced, the difference map will show a large negative region at its assumed position, with corresponding positive regions to which it might be moved.

b) PARAMETER SHIFT METHOD

Bhuija and Stanley (1963) describe a structure in terms of j parameters whose initial values $u_1, u_2, \ldots, u_j$ give a residual $R = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$ The true structure will correspond to the minimal value of R.

Assuming that all the parameters are independent, we may vary each parameter systematically from $u_j - n\,\Delta u_j$ to $u_j + n\,\Delta u_j$ in 2n steps of Δu_j, calculating R at each step. Initially the steps can be quite large. The first parameter is shifted to the value which gives the lowest residual and the other parameters are treated in turn in the same way. In this way the value of R can be systematically reduced.

The advantage of this method is that scale and thermal parameters may be improved. Also it may be used to move atoms away from false positions, because the increment, Δu_j, can be adjusted to be appropriate to the circumstances. This is not likely to happen with the other methods considered here. Therefore the parameter-shift method can be used to advantage in the early stages of a refinement.

c) THE LEAST-SQUARES METHOD OF REFINEMENT

This is probably the most satisfactory method of refinement of structures once the approximate coordinates are known with sufficient accuracy. It consists in varying systematically the atomic parameters and the scale factors so as to minimize the quantity(1):

$$R_2 = \sum_{i=1}^{n} w_i (s_j \, |F_o|_i - |F_c|_i)^2 = \sum_{i=1}^{n} w_i (\Delta F)^2 \qquad (2.3.31)$$

Where the sum is taken over all independent structure amplitudes, w_i is the weight alloted to an observation and s_j is the scale factor.

Each w is to be taken as the inverse of the variance, $\sigma_i^2\,(F_o)_i$ of F_o. In practice only relative weights can be estimated in advance depending on the method used to collect the data (Lipson and Cochran, 1966, p340ff).

(1) In most expressions, hkl have been omitted for simplicity.

Thus, for film data, Hughes (1941) has suggested:

$$W \propto 1/ |F_o|^2 \qquad \text{for} \quad |F_o| \geqslant 4 |F_{min}|$$

$$W \propto 1/16 \, |F_{min}| \qquad \text{for} \quad |F_o| \leq 4 |F_{min}|$$

where $|F_{min}|$ is the minimum observable $|F_o|$.

In the present work $w = sF_o/F_{av}$ or $w = F_{av}/sF_o$ whichever is < 1, where F_{av} is the average of the observed F_o.

For data recorded by the counter method w_i is commonly set equal to $1/\sigma^2(I)$, where $\sigma(I)$ can be estimated statistically from eq.(2.3.15). Also the approximation suggested by Cruickshank et.al. (1961): $w \propto (a + |F_o| + c|F_o|^2)^{-1}$ is often used, where a and c are about $2F_{min}$ and $2/F_{max}$. respectively. Such parameters permit the even distribution of error over various ranges of $|F_o|$ magnitude and sin θ value.

The correctness of a weighting scheme used may be tested statistically. e.g. By an analysis of $w(\Delta F)^2$ as a function of scattering angle and of $|F_o|$ magnitude when both should correspond to an essential constant magnitude

Let $|F_c(hkl)|$ be the calculated structure factor which can be expanded using Taylor's series and expressed as:

$$|F_c(hkl)| = |F_c(hkl)| + \sum_i \frac{\partial |F_c(hkl)|}{\partial p_i} \, \delta p_i + \dots \qquad (2.3.32)$$

Where δp_i is the change in the ith parameter p_i.

From (2.3.31) and (2.3.32) we express as (Lipscomb and Jacobson, 1972, p68),

$$R = \sum_j w_j(s_j|F_o| - |F_c|)^2 = \sum_j w_j \left[s_j |F_o| - |F_c| - \sum_i C_{ij} \, \delta p_i \right]^2 \qquad (2.3.33)$$

Where $C_{ij} = \partial |F_c| / \partial p_i$.

Differentiating(2.3.33) with respect to the p_ith parameter gives:

$$\partial R / \partial p_i = 2 \sum_j w_j \left[|\Delta F| - \sum_j c_{ij} \, \delta p_i \right] c_{ij} = 0 \quad (2.3.34)$$

Since this is the condition for a minimum in R relative to some particular δp_i, it can be expressed as a set of linear simultaneous equations:

$$\begin{aligned}
&\sum_j w_1 c_{1j}^2 \, \delta p_1 + \sum_j w_1 c_{1j} c_{2j} \, \delta p_2 + \dots + \sum_j w_1 c_{1j} c_{kj} \, \delta p_k = \sum_j w_1 c_{1j} \Delta F_j \\
&\sum_j x_2 c_{2j} c_{1j} \, \delta p_1 + \sum_j w_2 c_{2j}^2 \, \delta p_2 + \dots + \sum_j w_2 c_{2j} c_{kj} \, \delta p_k = \sum_j w_2 c_{2j} \Delta F_j \\
&\quad \vdots \qquad\qquad\qquad\qquad \vdots \qquad\qquad\qquad\qquad\qquad \vdots \qquad\qquad\qquad\qquad \vdots \\
&\sum_j w_k c_{kj} c_{1j} \, \delta p_1 + \sum_j w_k c_{kj} c_{2j} \, \delta p_2 + \dots + \sum_j w_k c_{kj}^2 \, \delta p_k = \sum_j w_k c_{kj} \Delta F_j
\end{aligned}$$

$$(2.3.35)$$

$$\sum_{j=1} \left\{ \sum_k w_k c_{kj} c_{kj'} \right\} \delta p_j = \sum_j w_k c_{kj'} \Delta F_j \qquad (2.3.36).$$

These are the normal equations which can be expressed in matrix form as:

$$\hat{M} \cdot \hat{p} = \hat{E} \Rightarrow \hat{p} = \hat{M}^{-1} \cdot \hat{E} \qquad (2.3.36a)$$

Eq. (2.3.35) can be solved simultaneously. The c_{kj}'s have been assumed to be constant in this approach, but their values are different once a new parameter p'_k is obtained from the above equations. Hence the whole process is repeated with these new values of p_k as starting values, until the changes in p_k are well within their probable errors.

One often does not use the full matrix in the solution of the normal equations but rather approximations in order to save storage space or computing time when a high speed computer is being used.

Thus the off-diagonal coefficients in the normal equations (2.3.35) may be neglected if they fulfil certain conditions (International Tables for x-ray Crystallography, Vol. II). This approximation is known as the 'off-diagonal approximation'. Each parameter correction is then given by an equation of the type:

$$\hat{M}_{jj} \cdot \hat{\delta}\hat{p}_j = \hat{E}_j \tag{2.3.37}$$

From which values of $\hat{\delta}p_j$ and the variance can be calculated using the equations (Lipson and Cochran, 1966):

$$\begin{aligned} \hat{\delta}\hat{p}_j &= \hat{M}_{jj}^{-1} \cdot \hat{E}_j \\ \sigma^2(\hat{p}_j) &= \hat{M}_{jj} \sum w_j(\Delta F)^2/(s-m) \end{aligned} \tag{2.3.38}$$

where s (the number of observations) and m (number of parameters involved) are the number of matrix elements in the row and column respectively.

A second approximation consists in decomposing the matrix M (of order 9N x 9N) into N3 x 3 and N6 x 6 submatrices, where N is the number of atoms in the asymmetric unit. Each submatrix corresponds to a set of 3 or of 6 simultaneous equations for the correction to the parameters of one atom and can be treated independently of the others. The problem is then reduced to solving N matrices of order 3 and N or order 6. This is the 'block-diagonal' approximation (Cruickshank, et.al., 1961).

Additional simplification can be achieved by using a rigid-body least-squares refinement. In this case the rigid molecule atomic coordinates are expressed in terms of six parameters: the coordinates x,y,z of a point in the molecule and the angles θ, ϕ, Ψ defining the orientation of the rigid molecule with respect to an orthogonal coordinate system.

Refinement by the least-square procedure has in general the added advantage of refining scale and thermal parameters and allowing individual reflections to be weighted in proportion to the experimental errors in the observations.

ACCURACY OF COORDINATES AND BOND-LENGTH-ANGLES

When a crystal structure has been solved and refined, the final solution appears as a set of fractional coordinates for each atomic site from which bond-distances and angles and other distances can be calculated. The accuracy of these quantities will depend on the accuracy of the atomic coordinates and on the accuracy of the unit cell parameters.

Thus, the variance of the length l_{12} of a bond between two atoms is given by the relation (Lipson and Cochran, 1966, p.355):

$$\sigma^2(l_{12}) = \sigma^2(x_1) + \sigma^2(x_2)$$

where x_1 and x_2 are the atomic coordinates measured in the direction of the bond. If the atoms are related by a mirror plane or a centre of symmetry:

$$\sigma(l_{12}) = 2\,\sigma(x_1)$$

The accuracy of an angle (say β) at an atom (2), between bonds l_{12} and l_{23}, will be given by:

$$\sigma^2(\beta) = \frac{\sigma^2(x_1)}{l_{12}^2} + \frac{l_{13}^2}{l_{12}^2\,l_{23}^2}\,\sigma^2(x_2) + \frac{\sigma^2(x_3)}{l_{23}^2}$$

In this expression x_1 and x_3 are measured in directions perpendicular to l_{12} and l_{23} respectively and x_2 is measured in the direction of the centre of the circle passing through the three atoms.

3. INTRODUCTION TO THE EXPERIMENTAL STUDY OF $SbCl_3$·1-HALONAPHTHALENE COMPLEXES.

Because of high deliquescence property of antimony trichloride, most of the experimental work was carried out in a dry box. The box which is made from transparent perspex includes a microscope for preliminary examination of crystals and an electrical-heating system for sealing off Lindemann glass tubes. In every case Phosphorus pentoxide was used as drying agent.

Carbon tetrachloride and chloroform were used as solvents. Both of then were purified by distillation after being dried over P_2O_5.

The antimony Trichloride (HW Laboratory Reagent) was purified by recrystallisation from dry chloroform. 1-Chloronaphthalene (BDH Laboratory Reagent), and 1-Bromonaphthalene (HW GPR) were used without further purification. 1-Iodonaphthalene was synthesised (p. 101) and redistilled before use.

Crystallisation of the molecular complexes was carried out in small test tubes of 5 ml. capacity.

Crystalline aggregates for microscopic examination were extracted and were kept with their mother-liquor on the microscope slide. The aggregates were crushed prior to examination to select a crystal which seemed to be single.

A suitable single crystal was put in a Lindemann tube and was carefully sealed off using the electrical heater.

Some of the remaining crystals were dried by pressing between filter paper and after weighing dissolved in carbon tetrachloride to be used for the quantitative analysis of the components.

4. STUDY OF THE (1:1) $SbCl_3$.1-BROMONAPHTHALENE COMPLEX

4.1 THE PHASE DIAGRAM FOR THE $SbCl_3$.1-$C_{10}H_7Br$ SYSTEM

The phase diagram, determined by Menschutkin (1912), shows antimony trichloride to form a 1:1 compound with 1-Bromonaphthalene. In order to confirm this conclusion a phase diagram was constructed (see p. 42). The result is shown in fig 4.1 (Table 4.1) and confirms formation of a 1:1 compound.

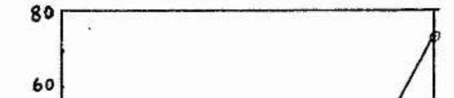


Fig.4.1 $SbCl_3$- 1-Bromonaphthalene system.

Table 4.1

% Mol $SbCl_3$	T^oC
15	-9.0 ± 1
20	5.0 ± 1
30	17.0 ± 2
34.9	20.0 ± 2
40.0	23.5 ± 0.5
44.8	23.5 ± 1.0
50.0	24.0 ± 1.0
60.0	15.0 ± 1.0
70.0	19.0 ± 1.0
76.8	26.0 ± 1.0
100.0	73.0 ± 0.5

4.2 PREPARATION AND ANALYSIS OF THE COMPLEX

Crystals of $SbCl_3$ were dissolved in 10-15% excess of 1-bromonaphthalene at about 40°C. Slow cooling of the system yielded a variety of yellow ill-formed crystals.

Analysis for Sb(III) was carried out by titration vs. 0.025M KIO_3 and 1-bromonaphthalene was determined by the NMR technique described in Chapter 2. Results of such analysis are shown in Table 4.2

Table 4.2

Sample Wt. (g)	Vol. 0.025 KIO_3 (ml)	% $SbCl_3$ (w/w)	NMR REF.(*) wt. (g)	NMR Integrated Height. Ref. Compd.	% 1-$C_{10}H_7Br$ (w/w)	Mole Ratio $SbCl_3$:1-$C_{10}H_7B_9$
0.1925	8.80	52.2	0.1873	52.50 40.66	47.1	1.01:1.00
0.1824	8.55	53.6	0.1744	53.50 41.50	46.4	1.05:1.00
0.2275	10.50	52.7	0.1679	38.50 40.00	48.0	1.00:1.00

(*) NMR reference compound was CH_3I.

4.3 PRELIMINARY INFORMATION AND UNIT CELL DETERMINATION

A crystal which appeared to be single was sealed off in a Lindemann tube (Ø=0.25mm). Optical examination through crossed polars showed straight extinction. The crystal must be non-cubic therefore and one of the crystallographic axes may coincide with the direction of extinction.

Oscillation and Weissenberg photographs were taken, using Cuk$_\alpha$ Nickel filtered x-radiation, with the crystal oscillating about "c", the length of the crystal corresponding to the extinction direction. The asymmetry of these photographs showed that the crystal belonged to the triclinic system. Approximate cell parameters (see Table 4.3) were evaluated directly from measurements of the oscillation and Weissenberg films, but others involved computation using a least square angular lag program as stated in Chapter 2. More accurate parameters were obtained after careful resetting of the crystal, when Zr filtered MoK_α radiation was used.

Table 4.3

a) MEASURED CELL PARAMETERS FOR CRYSTALS OF $SbCl_3$. 1-$C_{10}H_7Br$

(Using Mo K_α, Zr filtered Radiation)

n	Y (mm)	tanϕ=Y/2R	ϕ (°)	Sin ϕn	ζ_c=Sinϕn/n	ζ mean
5	16.67±0.02	0.29089	16.20909	0.27931	0.05586(7)	
4	13.13±0.02	0.22922	12.91031	0.22343	0.05586(8)	
3	9.75±0.01	0.17017	9.65751	0.16776	0.05592(6)	
2	6.42±0.02	0.11199	6.38993	0.11129	0.05565(18)	
1	3.22±0.02	0.05614	3.21321	0.05605	0.05605(36)	0.05587(10)

n	s' (mm)	θ^{o}=s'/2	2 sin θ_n	ξ =2sinθn/n	ξ (mean)
6	22.35±0.01	11.175	0.38762	0.06460±0.00003	b* 0.06460(3)
6	27.30±0.02	13.65	0.47198	0.07866±0.00006	
4	18.10±0.00	9.05	0.31458	0.07865± 0.0000	
2	9.00±0.01	4.50	0.15692	0.07846±0.00009	a* 0.07859(10)

2R = 57.296mm

Y is the separation in mm between corresponding layer-lines in the oscillation photograph.

For s' see fig. 2.3.4b (p. 55)

ANGLE	ANGLE MEASURED	MEAN ANGLE
γ^*	86.87°	86.83°±0.04
	86.76°	
	86.87°	

b) MEASURED AND CALCULATED CELL PARAMETERS FOR CRYSTALS OF $SbCl_3 \cdot 1\text{-}C_{10}H_7Br$ (using Mok$_\alpha$ Zr filtered and Cuk$_\alpha$ Ni filtered)

DIRECT (Å and °)		PARAMETER	RECIPROCAL (RLU and °)	
Mok$_\alpha$	Cuk$_\alpha$		Mok$_\alpha$	Cuk$_\alpha$
9.078(10)	9.104	a	0.07859(10)	0.1698
11.975(20)	11.919	b	0.06460(10)	0.1410
12.721(50)	12.677	c	0.06084	0.1328
113.08(3)*	113.33 *	α	66.91	66.56
93.60(3)*	93.30*	β	86.40	86.08
91.50(5)	90.74	γ	86.83(4)	87.77
1267.98 Å^3	1260. Å^3	V	$7.886\text{x}10^{-4}$	$7.936\text{x}10^{-4}$
		ζ_c	0.05587(20)	0.1216

* By angular procedure (see p. 56).

The crystals neither sank nor floated in 1,2-dibromoethane so that D_o=2.18 Mg m^{-3} for the density of the complex. Hence Z=3.8(≈ 4) for $SbCl_3$. 1-$C_{10}H_7Br$ (M=435.1) leading to Dc=2.30 Mg m^{-3}.

Confirmation of the triclinic system followed from the systematic calculation of various distances and angles within the cell, which gave no evidence for higher symmetry. The space group must therefore be P1 or $P\bar{1}$.

Intensity data were collected from a particular crystal (about 0.1 x 0.1 x 0.2 mm) using zirconium filtered MoK_α radiation on a multiple film pack. Layers 0 to 6 oscillating about 'c' were recorded on an integrating Weissenberg camera.

The intensities of the reflections were measured visually, and were corrected for Lorentz and Polarisation effects but not for absorption or extinction ($\mu_{MoK_\alpha} \approx 61.0\ cm^{-1}$). This gave a set of 691 structure amplitudes.

4.4 DETERMINATION OF THE STRUCTURE

A three-dimensional Patterson map was computed using all the hkl reflections. The vector map showed the following highest peaks:

Table 4.3

Patterson Coordinates and Relative Height of Peaks Within half cell (a,b, c/2).

No.	U	V	W	Height
1	0.500	0.135	0.067	820
2	0.000	0.000	0.180	750
3	0.581	0.518	0.000	683
4	0.194	0.314	0.415	483

Interpretation of the vector map was carried out assuming the space group, $P\bar{1}$. Considering four formula units of $SbCl_3 \cdot C_{10}H_7Br$ in the unit cell, there are 4 antimony, 4 bromine, 12 chlorine and 40 carbon atoms (if we ignore the H atoms).

Thus one would expect 60x59 = 3540 peaks in P(u,v,w). Because Sb-Sb vectors will be the greatest of the set (unless there is overlapping), the rest of peaks can be ignored initially in the interpretation of the vector map. There are 12 expected Sb-Sb vectors in the cell or 6 vectors within the half cell. Not all of these can be identified. (See Table 4.3).

Since there are two non-equivalent Sb atoms within the cell $Sb(1)(x_1,y_1,z_1)$ and $Sb_2(x_2,y_2,z_2)$, one of the vector peaks could be due to the $Sb_{(2)}(x_2,y_2,z_2) - Sb_{(1)}(-x_1,-y_1,-z_1)$ vector, and a second peak due to the $Sb_2(x_2,y_2,z_2)-Sb_{(1)}(x_1,y_1,z_1)$ vector. The coordinates of each vector peak in terms of (x,y,z) will be given by Peak (1) $(x_2+x_1,\ y_2+y_1,\ z_2+z_1)$ and Peak (2) $(x_2-x_1,\ y_2-y_1,\ z_2-z_1)$. From these two peaks (1 and 3 in Table 4.3), two asymmetric antimony atoms could be deduced by the half of the sum and half of the difference of the vector coordinates. In this way coordinates of Sb(1) and Sb(2) were calculated. Attempted interpretations involving the rest of peaks in Table 4.3 gave no satisfactory results.

A three-dimensional electron density map was then computed using all the observed amplitudes with signs calculated from the Sb (1) atom at $x_1=0.541$ $y_1=0.327$, $z_1=0.034$ and the Sb(2) atom at $x_2=0.041$, $y_2=0.192$ and $z_2=\overline{0.034}$. This showed an improved position of the Sb atoms and two additional peaks which were interpreted as due to the bromine atoms at Br(1) (0.151, 0.503, 0.397) and

Br(2) (-0.345, 0.044, 0.391). A second three-dimensional electron density synthesis was computed in a similar way with signs calculated from two Sb atoms and two bromine atoms. This revealed the position of five chlorine atoms which gave resonable bond distances and angles corresponding to 5/3 molecules of $SbCl_3$. At this stage the R_1 factor was 0.31.

A three-dimensional difference synthesis using coordinates of two antimony, two bromine and five chlorine atoms showed the position of the sixth chlorine atom. Another 3D-difference synthesis was calculated using improved positions for all antimony, bromine and chlorine atoms in order to locate individual carbon atoms. This was difficult, but from the map and from packing considerations approximate positions for the bromonaphthalene molecules (assumed rigid) were deduced.

4.5 REFINEMENT OF THE STRUCTURE

The Stanley parameter shift method[a] was first used for a mixture of free atoms (2Sb+6Cl) and two idealised rigid bromonaphthalene molecules. (Taken as a bromine atom linked to an idealised naphthalene molecule i.e. Br-C (1.90 Å), C-C (1.397 Å) and C-C-C (120°) (Chem.Soc., 1958). The input coordinates of the rigid molecules in the xy plane were taken in Å units relative to a chosen center referred to an orthogonal set of axes, (X=x, Y in xy plane, Z perpendicular to xy plane), and the rigid molecules were subjected to angular rotations θ_x, ϕ_y, Ψ_z, about these three axes. The bromine atoms were chosen to be the origins of the rigid molecules. The initial origins and rotation angles were respectively, Br(1) (0.1509, 0.5011, 0.3956),

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(a) Computing Program 'SHSTAN' written by R. Hulme.

Br(2) (0.6546, 0.044, 0.3913) (5.0 , 180.0°, 100.0°) and (2.0° 180.0° 100.0°). After three rounds of refinement, the positions of the rigid molecules in relation to the orthogonal axes were (5.0°, 190°, 95.0), and (10°, 190°, 105.0°) with centers at Br(1) (0.1495, 0.5036, 0.3978) and Br(2) (0.6478, 0.0007, 0.3896). The R_1 factor was 0.22.

The process of refinement was then continued by using an off diagonal least squares procedure(‡). This procedure allowed isotropic least squares refinement of antimony and chlorine atoms and refinement of the orientations of the two independent idealised bromonaphthalene molecules defined in a similar way to the rigid molecules in the shift procedure.

After four rounds the overall R_1 factor dropped to 0.19, but it was observed that the R factor corresponding to the hk4 reflections was excessively high in relation to the remaining data. After several unsuccessful attempts to improve the fourth layer it was realised that the corresponding photographs were of poor quality and further refinement omitted all (∼95) hk4 reflections. In addition five misindexed reflections on other layers were detected and eliminated.

A number of consecutive refinements reduced R_1 to 0.139 for 591 reflections. At this stage position and temperature factor shifts for the antimony and chlorine atoms were all quite small, e.g. the shifts were less than 0.001 Å. For the bromonaphthalene molecules the center and orientation shifts were also small, but the temperature factors for some of the carbon atoms were rather large. This suggested that the bromonaphthalene molecule might be distorted

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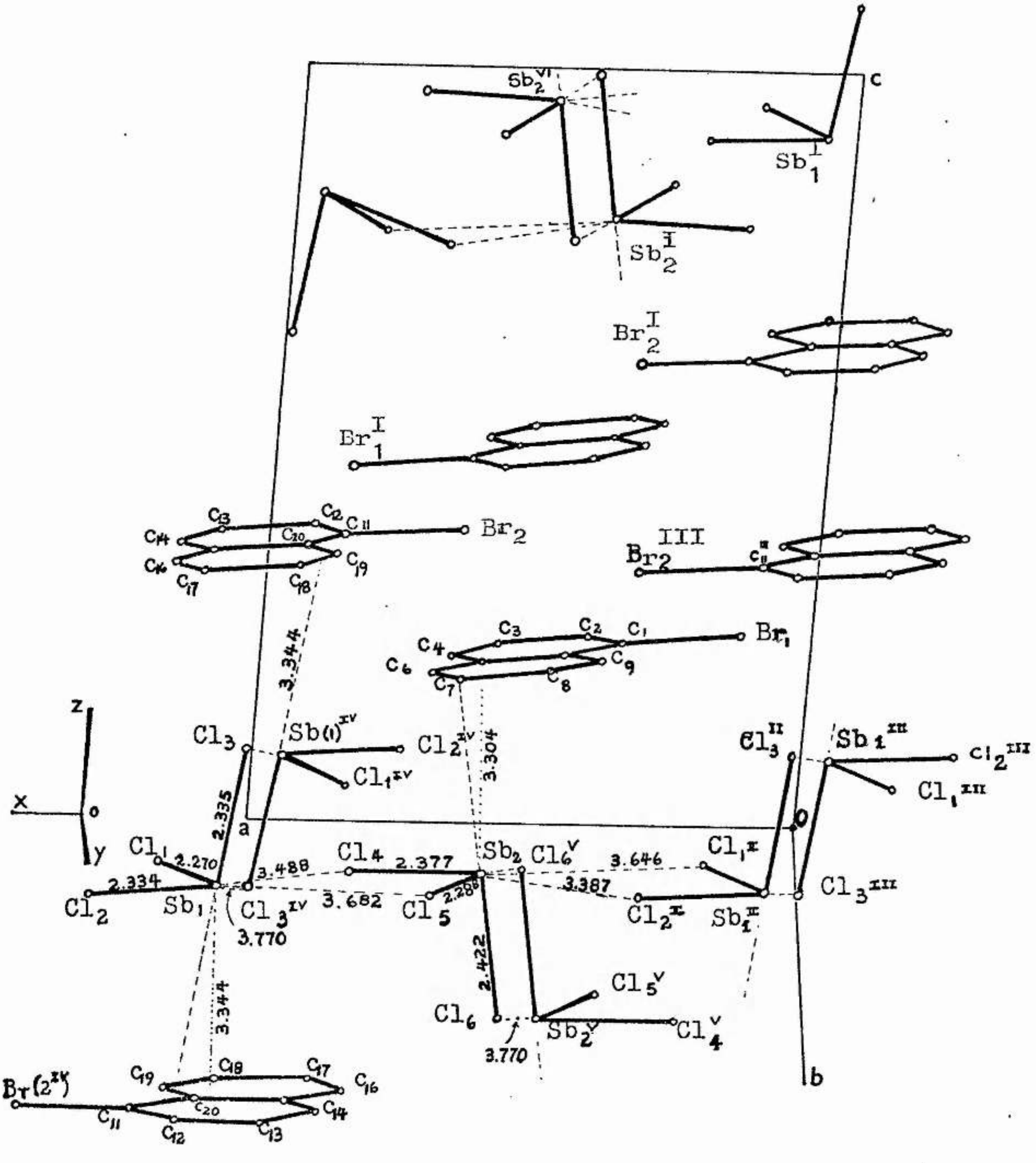
(‡) Computer Program, "Partial Rigid Three Bodies Least Squares", or' PAR3BLES' written by R. Hulme.

from ideality.

When all the atoms were freed for a final round of least squares refinement, it was found that all the resulting parameter shifts were less than the corresponding standard deviations although some lengthening of four C-C bonds and shortening of the others in the aromatic rings were observed.

The final R_1 factor for 591 independent observed reflections was 0.138. The final position and thermal parameters of the atoms are listed in Table 5.4. A table of observed structure amplitudes and calculated structure factors is shown in appendix B.



(a)

Fig.4.4. A view of the structure from a point between b and c close to [011]. The atom notation and dimensions were added to the figure for clarity. (Plotted using Comp. Prog. PAMOLE).

TABLE 4.4

Fractional Atomic Triclinic Coordinates and

Thermal Parameters ($\AA^2$) with e.s.d.'s in Parentheses

(for atom numbering see fig 4.4 (p.89))

Atom	x	y	z	B'
Sb_1	1.0499(5)	0.1871(6)	-0.0284(8)	1.770(0.36)
Sb_2	0.5548(5)	0.3129(6)	0.0308(8)	1.761(0.36)
Cl(1)	1.1652(20)	0.3747(25)	0.0622(34)	5.000(1.745)
Cl(2)	1.2752(18)	0.0955(22)	-0.0664(32)	3.300(1.581)
Cl(3)	1.0185(21)	0.1530(26)	0.1381(35)	6.150(1.947)
Cl(4)	0.7941(17)	0.4114(21)	0.0639(29)	2.150(1.481)
Cl(5)	0.6467(17)	0.1254(21)	-0.0582(30)	1.950(1.484)
Cl(6)	0.5067(23)	0.3518(28)	-0.1414(38)	7.850(2.139)
Br(1)	0.1458(8)	0.5053(10)	0.3969(14)	4.300(0.649)
Br(2)	0.6449(8)	0.0008(10)	0.3850(13)	3.880(0.629)
C(1)	0.3518(56)	0.5332(71)	0.3922(101)	0.100(5.022)
C(2)	0.4137(57)	0.6519(70)	0.4322(99)	0.100(5.020)
C(3)	0.5650(142)	0.6729(167)	0.4291(212)	21.851(16.134)
C(4)	0.6552(56)	0.5743(70)	0.3850(101)	0.10(5.114)
C(5)	0.5934(68)	0.4560(86)	0.3453(118)	3.550(6.385)
C(6)	0.6833(107)	0.3570(125)	0.3008(171)	13.520(11.281)
C(7)	0.6214(76)	0.2389(91)	0.2616(127)	5.620(7.35)
C(8)	0.4697(56)	0.2182(71)	0.2648(101)	0.100(5.054)
C(9)	0.3798(74)	0.3164(92)	0.3084(129)	5.160(7.050)
C(10)	0.4415(69)	0.4350(84)	0.3485(118)	3.650(6.41)
C(11)	0.8524(56)	0.0245(71)	0.3839(101)	0.100(5.058)
C(12)	0.9184(58)	0.1423(70)	0.4277(101)	0.310(5.129)
C(13)	1.0709(120)	0.1604(140)	0.4270(183)	16.800(13.119)
C(14)	1.1580(67)	0.0598(81)	0.3821(116)	3.020(6.266)
C(15)	1.0923(91)	-0.0573(91)	0.3386(121)	4.600(6.812)
C(16)	1.1796(136)	-0.1581(160)	0.2933(212)	20.700(15.448)
C(17)	1.1134(97)	-0.2749(114)	0.2502(154)	11.550(10.260)
C(18)	0.9605(80)	-0.2928(98)	0.2508(134)	6.850(7.928)
C(19)	0.8736(94)	-0.1929(115)	0.2952(134)	10.560(9.614)
C(20)	0.9393(61)	-0.0753(75)	0.3392(155)	1.050(5.404)

Isotropic Thermal Factor = exp $(-B'\sin^2\theta)$ for MoK-α radiation.

TABLE 4.5

Bond Distances (Å) and Angles (°)

a) In the $SbCl_3$.

Sb(1) — Cl(1)	2.270(57)	Sb(2) — Cl(4)	2.377(50)
Sb(1) — Cl(2)	2.334(53)	Sb(2) — Cl(5)	2.288(49)
Sb(1) — Cl(3)	2.335(59)	Sb(2) — Cl(6)	2.422(64)
Sb(1) ... Cl(4)	3.488(50)	Sb(2) ... Cl(1^{II})	3.646(57)
Sb(1) ... Cl(5)	3.682(49)	Sb(2) ... Cl(2^{II})	3.387(53)
Sb(1) ... Cl(3^{IV})	3.770(27)	Sb(2) ... Cl(6^{V})	3.770(27)
		Sb(2) ... C(7)	3.399

Sb(1) ... Perpendicular distance to naphthalene plane: 3.344 Å

Sb(2) ... Perpendicular distance to naphthalene plane: 3.304 Å

Angles Around Sb(1)

	Cl(2)	Cl(3)	Cl(4)	Cl(5)	Cl(3^{IV})
Cl(1)	91.76(16)	96.10(17)	68.90(18)	124.49(17)	159.97(14)
Cl(2)		96.18(17)	160.60(15)	143.70(14)	71.03(18)
Cl(3)			87.74(18)	79.69(15)	76.31(18)
Cl(4)				55.69(18)	128.25(18)

Angles Around Sb(2)

	Cl(5)	Cl(6)	Cl(1^{II})	Cl(2^{II})	Cl(6^{V})
Cl(4)	91.91(14)	90.81(16)	142.16(14)	161.57(13)	74.38(17)
Cl(5)		96.42(16)	125.78(14)	69.87(17)	163.84(14)
Cl(6)			82.46(18)	88.64(17)	75.67(18)
Cl(1)				55.92(18)	67.86(17)

Symetry Code: I: 1-x,1-y,1-z II: x-1, y, z III: 1-x, -y, -z
IV: 2-x, -y, -z V:1-x,1-y, -z

b) <u>In the Free 1-Bromonaphthalene</u> (Typical σ_{c-c}= 0.28 Å and σ= 1.7 °).

Br(1)-C(1)	1.90	Br(1)-C(1)-C(2)	120.1	C(8)-C(9)-C(10)	119.8
C(1)-C(2)	1.40	Br(1)-C(1)-C(4)	179.9	C(9)-C(10)-C(1)	119.9
C(2)-C(3)	1.40	Br(1)-C(1)-C(10)	120.1	C(5)-C(10)-C(1)	119.9
C(3)-C(4)	1.41	C(2)-C(1)-C(10)	119.9	C(4)-C(5)-C(10)	120.3
C(4)-C(5)	1.39	C(1)-C(2)-C(3)	120.3		
C(5)-C(6)	1.40	C(2)-C(3)-C(4)	119.9		
C(6)-C(7)	1.39	C(3)-C(4)-C(5)	119.8		
C(7)-C(8)	1.40	C(4)-C(5)-C(6)	119.9		
C(8)-C(9)	1.40	C(5)-C(6)-C(7)	119.8		
C(9)-C(10)	1.40	C(6)-C(7)-C(8)	120.3		
C(5)-C(10)	1.40	C(7)-C(8)-C(9)	120.0		
C(1)-C(10)	1.40				

Br(2)-C(11)	1.90	Br(2)-C(11)-C(12)	120.00	C(17)-C(18)-C(19)	120.00
C(11)-C(12)	1.40	Br(2)-C(11)-C(20)	120.2	C(18)-C(19)-C(20)	119.9
C(12)-C(13)	1.40	Br(2)-C(11)-C(14)	179.9	C(19)-C(20)-C(11)	119.9
C(13)-C(14)	1.40	C(11)-C(12)-C(13)	120.3		
C(14)-C(15)	1.39	C(12)-C(13)-C(14)	119.7		
C(15)-C(16)	1.41	C(13)-C(14)-C(15)	120.0		
C(16)-C(17)	1.40	C(14)-C(15)-C(16)	119.9		
C(17)-C(18)	1.40	C(14)-C(15)-C(20)	120.2		
C(18)-C(19)	1.40	C(15)-C(16)-C(19)	119.6		
C(19)-C(20)	1.40	C(16)-C(19)-C(18)	120.5		
C(11)-C(20)	1.39				

(continued in page 95)

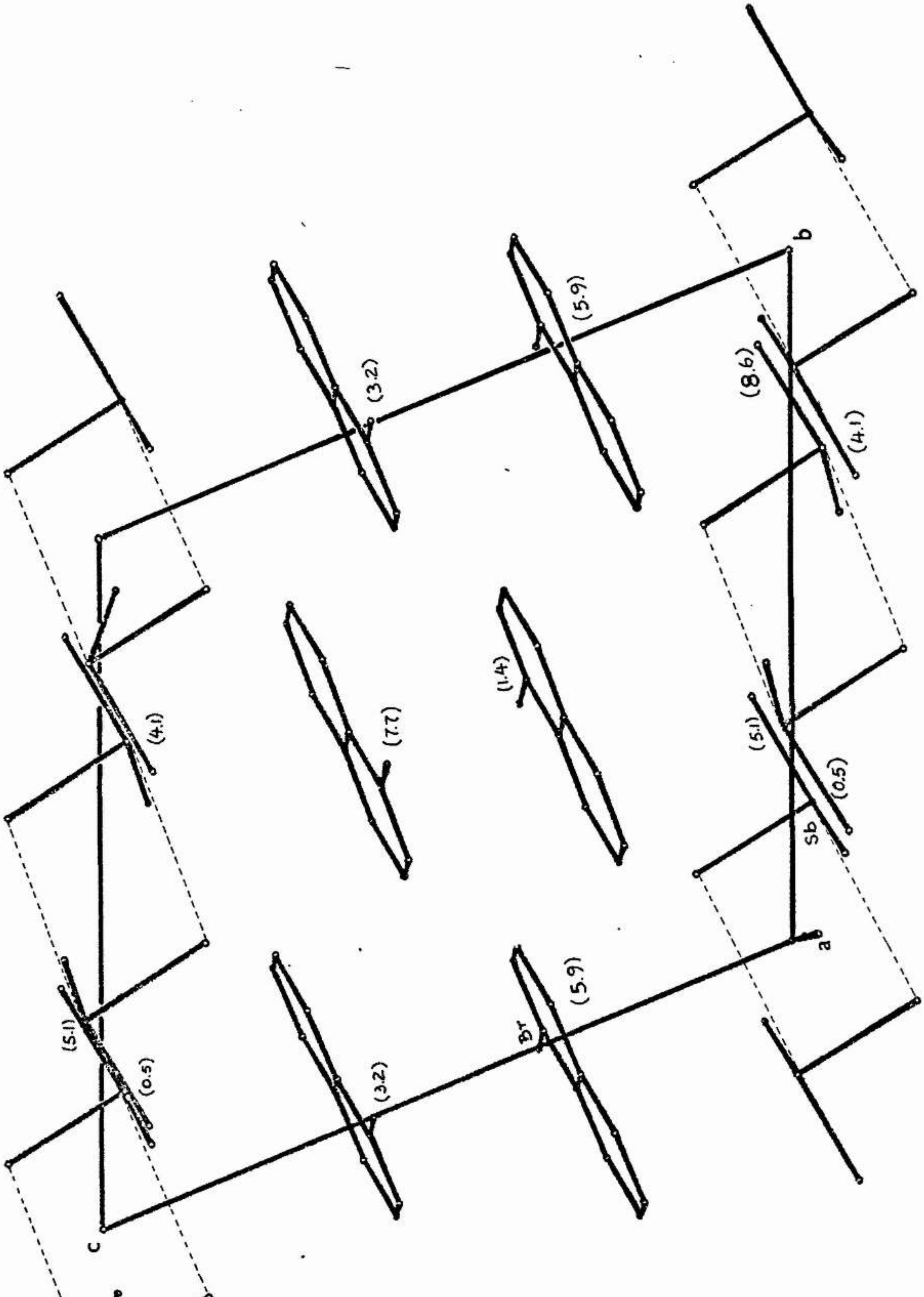


Fig. 4.2 A view of the structure from a point close to the **a**-axis. Molec. height in Å indicated approximately. Plotted using Comp. Prog. PAMOLE.

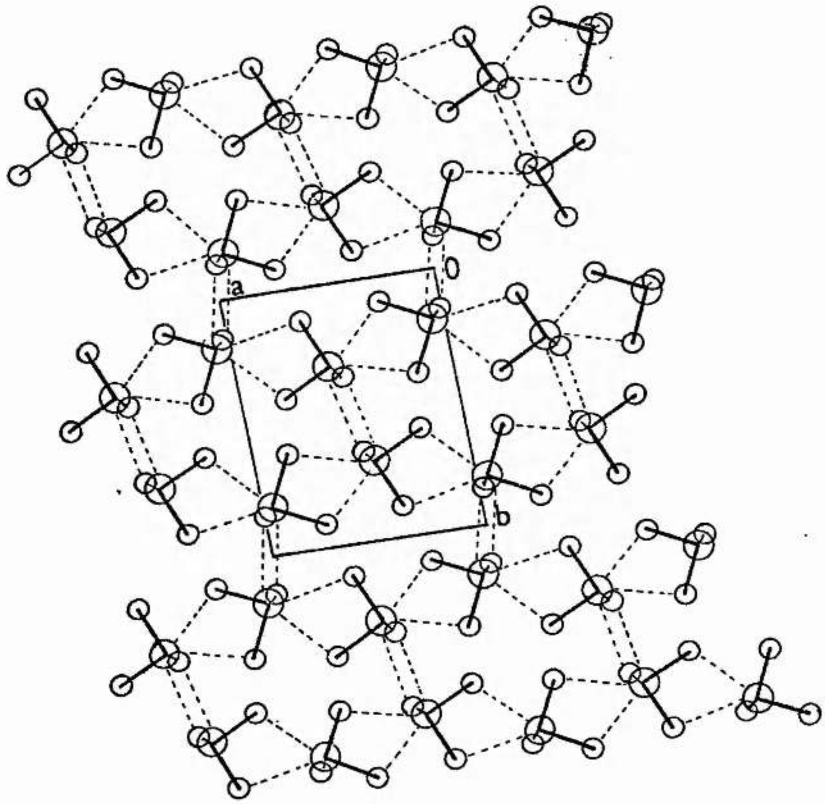


Fig.4.2a

A projection of one double-layer of $SbCl_3$ molecules along [001].Dotted lines were added to show intermolecular interactions between $SbCl_3$ molecules. Plotted using Computer Program STEREO.

c) Equation of Selected Planes and Out of Plane Distances (Å) (*)

i) First Bromonaphthalene: $0.103X - 0.392Y + 0.914Z - 2.729 = 0$

Sb_2: 3.304 Cl_4: 3.131 Cl_5: 3.449 Å

ii) Second Bromonaphthalene: $0.072X - 0.421Y + 0.904Z - 5.268 = 0$

Sb_1: 3.343 Cl_1: 3.611 Cl_2: 3.475 Å

iii) Sb(1), Cl(1), Cl(2), Cl(4), Cl(5), Cl(3^{IV}): $0.046X + 0.411Y - 0.911Z = 1.624$

($\overline{0.093}$, +0.091, − 0.221, +0.088, −0.001, +0.208)

iv) Sb(2), Cl(4), Cl(5), Cl(1^{II}), Cl(2^{II}), Cl(6^{V}): $-0.008X + 0.420Y - 0.907Z = 1.258$

(+0.116 +0.058 −0.063, +0.173, −0.044, −0.174)

The plane refer to these orthogonal Å coordinates.

4.6 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

1-Bromonaphthalene forms a 1:1 complex with antimony trichloride, the crystal structure of which is built up of double layers of $SbCl_3$ molecules alternating with double layers of 1-Bromonaphthalene tilted about 25° to [010] (see Fig 4.2). By halogen bridging pairs of $SbCl_3$ molecules form dimers which are themselves part of an infinite chain of molecules by further halogen bridging and these chains in turn are cross linked to others to produce the double sheet. (Fig 4.2a). Finally the structure contains plane-to-plane molecular stacks of 1-$C_{10}H_7Br$ molecules in a similar arrangement to that found in the crystal structure of naphthalene. The layers of antimony trichloride and organo component are parallel to the ab plane and alternate in the

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(*) The transformation matrix from triclinic xyz(Å) to orthogonal XYZ(Å) is given by:

$$\begin{bmatrix} 1 & \cos\gamma & \cos\beta \\ 0 & \sin\gamma & -\cos\alpha \sin\gamma \\ 0 & 0 & \sin\beta \sin\alpha^* \end{bmatrix}$$

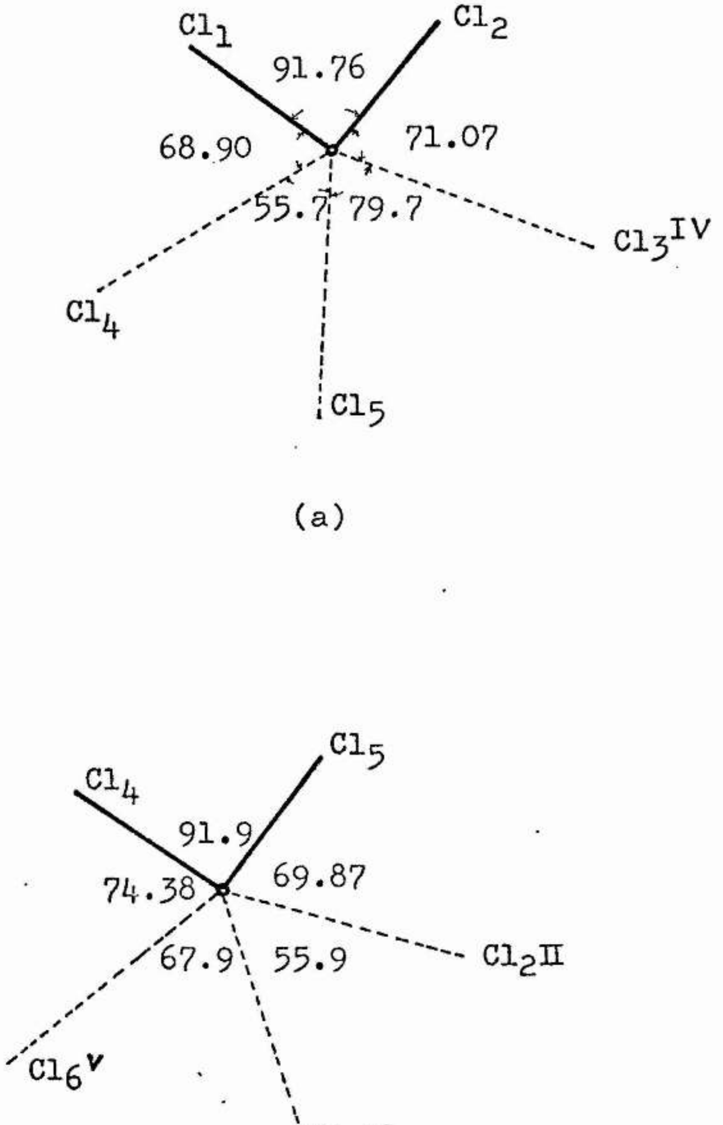

Fig.4.5 A view of the equatorial arrangement around the Sb atoms. view down Cl_3- Sb_1 and Cl_6- Sb_2 respectively.

c direction. Fig (4.2).

Bond distances and angles in the $SbCl_3$ and $1-C_{10}H_7Br$ molecules are quoted in Table 4.5a,b. There are two pairs of non-equivalent molecules. Both the non-equivalent antimony atoms are bonded to three chlorine atoms, (average 2.31 and 2.37 Å) and are close to a further three chlorine atoms - two from a non-equivalent molecule (3.49, 3.68 and 3.39, 3.65 Å) and one from a symmetrically related molecule (3.77 and 3.77 Å) - and are situated near a bromo-naphthalene molecule (3.34, 3.30 Å).

The usual criterion used to decide if a neighbouring atom is coordinated or not is the shortness of the interaction distance relative to the usually expected sum of the van der Waals radii. Generally Sb...Br, Sb...Cl, and Sb...C contacts are 4.05, 3.95 and 3.90 respectively (Pauling, 1960; Bondi A., 1964). In the present structure all the above mentioned distances are appreciably shorter the sum of the van der Waals radii so that the coordination number of the two atoms becomes seven. Geometrically this corresponds to a distorted pentagonal bipyramidal arrangement around the Sb atoms. The Sb(1), Cl(1), Cl(2), Cl(4), Cl(5), $Cl(3^{IV})$ and Sb(2), Cl(4), Cl(5), $Cl(1^{II})$, $Cl(2^{II})$, $Cl(6^{V})$ are approximately in the equatorial plane (see Table 4.5c and Fig. 4.5a,b) with average out of plane distances 0.12 and 0.10 Å.

The crystal structure of $SbCl_3$, has been described in terms of an eight fold coordination (Lipka, 1979) i.e. a 3:2:3 coordination (see diagram 1.6.1 p 17). The change of coordination number to 1:5:1 in the present case could be due to the interaction with a relatively large organic molecule which blocks further approach. According to the proposed geometry it would seem that the lone electron-pair is stereochemically inactive.

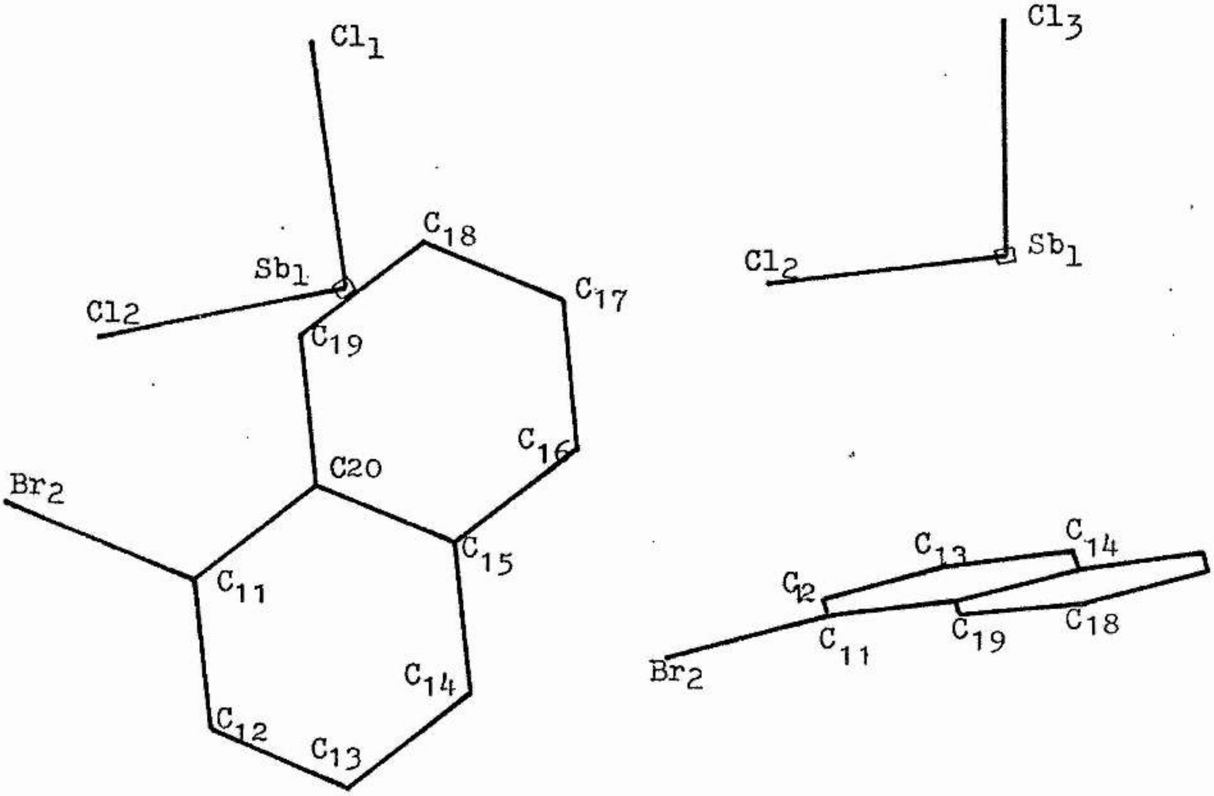

Fig.4.3.1
A view of $SbCl_3$·1-Bromonaphthalene down Cl_3-Sb_1 and at right angle . Plotted using Comp.Prog. STEREO.

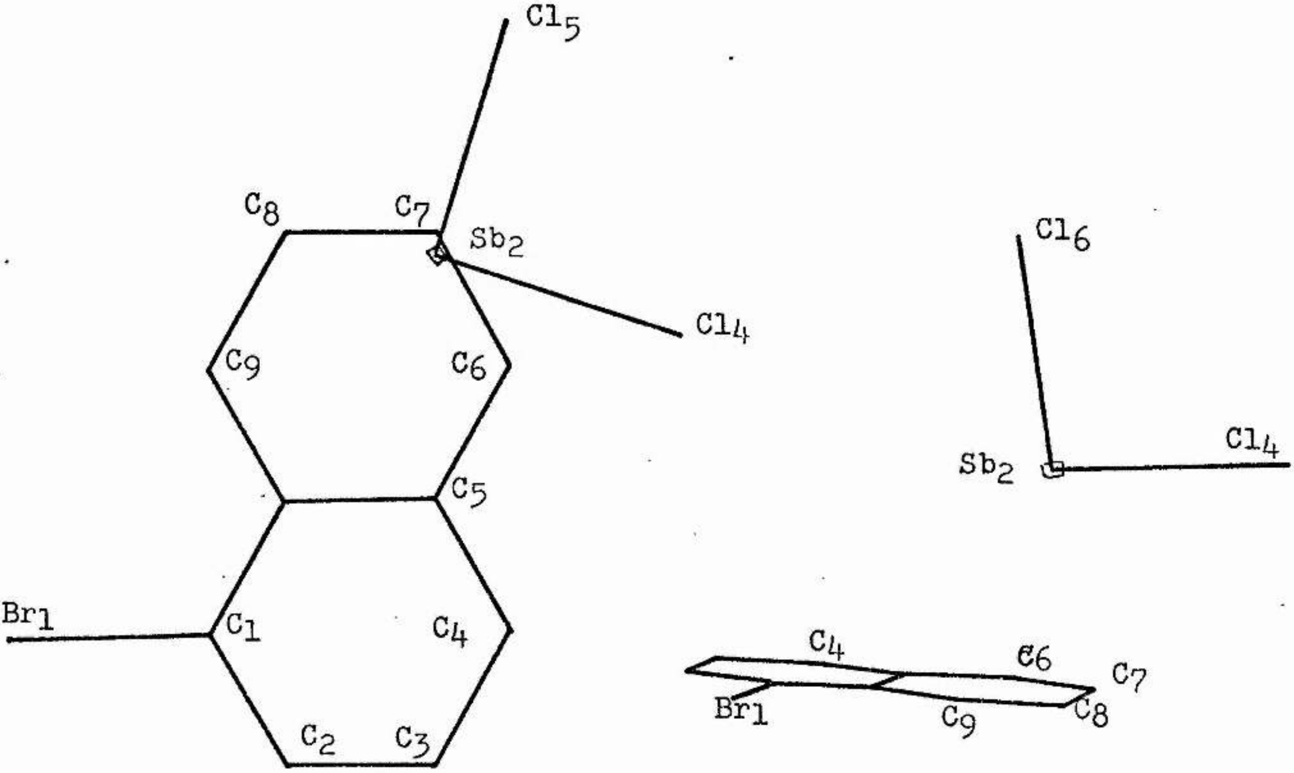

Fig.4.3.2

A view of $SbCl_3$·1-Bromonaphthalene down Cl_6-Sb_2 and at right angle. Plotted using Comp. Prog. STEREO.

In each $SbCl_3$ molecule, one of the Sb-Cl bonds is significantly shorter (2.270 and 2.288 Å respectively) than those found (2.34 and 2.37 Å) in the $SbCl_3$ molecule alone (Lipka, 1979), and a long Sb-Cl bond (2.422 Å) is also observed in the second molecule. These phenomena seem to be related in some way to the donor-acceptor nature of the interaction of $SbCl_3$ and 1-bromonaphthalene.

In both molecules of $SbCl_3$, two bonds lie in a plane nearly parallel to that of the organic molecule, which the third bond is approximately perpendicular to that plane (see Fig 4.2,4.3,4.4); more exactly, the Cl(3)-Sb(1) bond directs towards the mid-point of the C(8)-C(9) bond, (see Fig **4.3.**1), while the Cl(6)-Sb(2) bond points almost exactly to C(7) (Fig 4.**3.**2). The perpendicular distances from the two independent antimony atoms to the plane of the corresponding bromonaphthalene molecule are 3.34 and 3.30 Å respectively. A similar situation is found in the $2SbCl_3$. naphthalene (Hulme and Szymanski, 1969), but in this compound two $SbCl_3$ molecules related by a centre of symmetry are situated on opposite sides of the plane of the aromatic molecule, giving an alternating distribution of organic and inorganic layers. In addition to this, in $2SbCl_3$.naphthalene the distances between Sb atoms and the plane of the organic component (3.20 Å) is of the same order of magnitude as that found in the present work. Therefore, in the $SbCl_3$. 1-$C_{10}H_7Br$ compound, it seems there may also be electron donation from the aromatic π-system to the Sb atom. The Sb-Cl bonds apposite to the interaction with the π-systems are not of the same length. For the longer Sb-aromatic ring contact, the Sb(1)-Cl(3) distance is essentially the same as the other Sb-Cl bonds. On the other hand, the shorter Sb-aromatic ring contact is opposite a much longer Sb(2)-Cl(6) bond. Such an extension of an Sb-halogen bond has been already observed in other compounds. For example, (2.37 Å) in $2SbCl_3$.naphthalene (Hulme and Szymanski, 1969); (2.37 Å) in $2SbCl_3$-p-xylene (Hulme and Mullen, 1976); (2.44 Å) in $2SbCl_3$.1,4-dithiane (Kiel and Engler, 1974); (2.51 Å) in $SbCl_3$.aniline (Hulme and Scruton, 1968) and (2.39 Å) in $2SbCl_3$. Phenanthrene (Demaldé, et.al. 1972). This lengthening of the Sb-Cl bonds give some support to the view that antimony in the $SbCl_3$ molecule may act as an acceptor towards π-donors.

The large values of some carbon atom temperature factors (especially $C_{3(13)}$, $C_{6(16)}$) suggests some departure from ideality, but could also be due to residual errors (e.g. absorption ($\mu \sim 61$), and extinction effects) uncorrected in the experimental data.

There is no significant shortening of C-C bond in the region to which the Sb atom is pointing in contrast with the situation found in the $2SbCl_3$.naphthalene complex. Instead slight alterations of some other C-C bonds as well as some angles were observed (see Table 4.5b).

5.0 STUDY OF (2:1) $SbCl_3$.1-CHLORONAPHTHALENE COMPLEX

5.1 PHASE DIAGRAM FOR $SbCl_3$-1-$C_{10}H_7Cl$ SYSTEM

Determination of the phase diagram for this system was carried out according to the method described in Chapter 2. During the experiment a considerable amount of supercooling occurred in spite of continuous agitation.

The results in Table 5.1 permit the construction of a phase diagram as shown in Fig (5.1) and suggest (2:1) $SbCl_3$.1-$C_{10}H_7Cl$ compound formation with melting point ca.42°C. This is in good agreement with earlier results mentioned in the literature (Menschutkin, 1912).

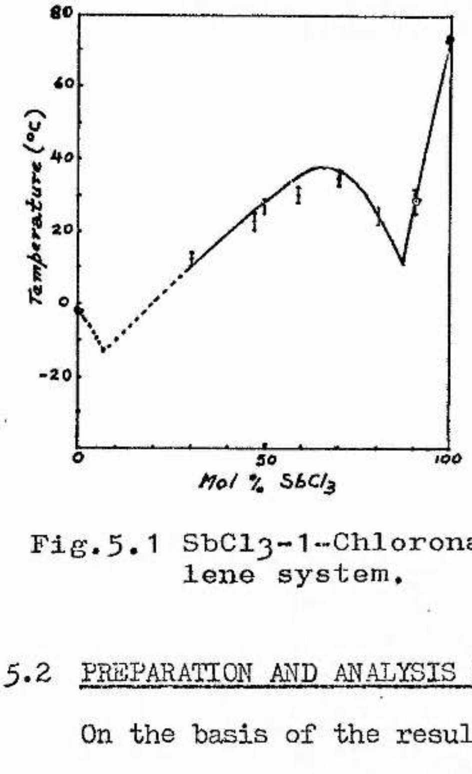

Fig.5.1 $SbCl_3$-1-Chloronaphthalene system.

TABLE 5.1

% Mol $SbCl_3$	T°C
0	-2±0.5
30	16±1.0
45	23±1.0
50	28±1.0
60	32±2.0
70	35±2.0
80	27±1.0
90	30±1.5
100	73±1.0

5.2 PREPARATION AND ANALYSIS OF THE CRYSTALS

On the basis of the results summarised in Fig (5.1), $2SbCl_3$.1-$C_{10}H_7Cl$ was prepared following a procedure described below.

Antimony trichloride was dissolved in 10-15% excess of 1-chloronaphthalene at about 45°C under anhydrous conditions away from the atmosphere. When the solution was allowed to cool to room temperature, yellowish crystals started to grow. A variety of crystals were obtained after several hours.

Analyses for Sb(III) and 1-chloronaphthalene were carried out by titration vs. 0.025 M KIO_3 and by NMR respectively as described in Chapter 2. Results which are shown in Table 5.2, confirm the mole ratio obtained from the phase diagram.

TABLE 5.2

RESULTS OF ANALYSIS FOR Sb(III) AND $1\text{-}C_{10}H_7Cl$

Sample (g)	Vol 0.025M KIO_3(ml)	% $SbCl_3$ (w/w)	NMR Ref(*) Wt(g)	NMR Integrated Height Reference	NMR Integrated Height Compound	% $1\text{-}C_{10}H_7Cl$ (w/w)	Mole Ratio $SbCl_3:C_{10}H_7Cl$
0.1117	7.11	72.73	0.08960	55.4	39.35	27.97	1.85:1.00
0.1102	7.33	76.00	0.18380	68.0	22.50	27.11	1.99:1.00
0.0819	7.27	73.59	0.08996	70.5	35.00	26.79	1.96:1.00

(*) NMR reference compound was CH_3I

5.3 PRELIMINARY INFORMATION AND UNIT CELL DETERMINATION

A crystal elongated in one direction[+] and which seemed reasonably single was chosen and sealed in a Lindemann tube (ϕ = 0.25 mm). The tube containing the crystal was taken out of the dry box for further observation through the polarizing microscope. The crystal showed straight extinction. The crystal is thus non-cubic and one of the crystallographic axes may be parallel to the direction of extinction.

The crystal was then mounted about an axis ("c_T") lying between the extinction directions. Oscillation and Weissenberg photographs were taken using CuKα nickel filtered X-radiation. These photographs showed no mirror symmetry and suggested that the crystal was probably triclinic,

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[+] Needle axis is [112] triclinic, equivalent to "c" in the monoclinic cell "C".

space group P1 or $P\bar{1}$.

From the oscillation photograph, zero and upper layer Weissenberg photographs, approximate cell parameters were calculated by direct measurement and by the angular-lag procedure as described in Chapter 2. Results obtained by these procedures are shown below (Table 5.3).

TABLE 5.3

LATTICE CONSTANTS FOR THE FIRST SETTING CELL (TRICLINIC) USING CuKα-RADIATION

DIRECT (Å), (°)	PARAMETER	RECIPROCAL (RLU)
11.458	a_T	0.1356
9.245	b_T	0.1964
9.241	c_T	0.1976
121.7	α_T	58.13
96.1	β_T	82.99
89.7	γ_T	86.54
	ζ_{CT}	0.1669
828. Å^3	V_T	0.00121

Flotation in a (1:1) mixture of CH_2Br-CH_2Br (1,2-dibromo-ethane) and CH_3I (iodomethane) gave an observed density, $D_o = 2.23$ Mg. m^{-3}. The calculated density was, $D_c = 2.48$ Mg. m^{-3} for Z = 1.80 (~2.0) units of $2SbCl_3.1-C_{10}H_7Cl$ (M=618.9).

5.4 DETERMINATION OF APPROXIMATE STRUCTURE

Intensity data were collected using nickel filtered CuKα radiation on a multiple film pack. Layers 0 to 2 about "c_T" axis were recorded.

Corrections for Lorentz and Polarization factors were applied in computing the structure amplitudes, $|Fhkl|$, but no corrections were made for absorption or extinction,($\mu_{Cu_{K\alpha}} = 339\ cm^{-1}$).

All the hkl reflections (191 in total) were used to compute a three-dimensional Patterson map in order to locate the heavy atoms. This showed the following highest vector peaks:

TABLE 5.4

PATTERSON COORDINATES (U,V,W) OF HIGHEST PEAKS FOR $SbCl_3.1\text{-}C_{10}H_7Cl$.

No.	Height	Fractional vector coordinate U	V	W	Interpreted Source of Vector
1	730	0.51	0.61	0.01	Sb_1-Sb_2
2	710	0.11	0.46	0.88	Sb_1-Sb_2'
3	440	0.00	0.00	0.50	
4	390	0.41	0.17	0.12	Sb_2'-Sb_2
5	360	0.15	0.12	0.27	
6	350	0.34	0.75	0.16	
7	350	0.40	0.92	0.08	Sb_1'-Sb_1
8	280	0.34	0.37	0.17	
9	270	0.24	0.57	0.15	
10	270	0.65	0.53	0.23	

where $x'=-x$, $y'=-y$ and $z'=-z$. Equivalent centrosymmetrically related peaks are not listed.

Interpretation of the vector map was carried out assuming the space group $P\bar{1}$. Considering two formula units of $2SbCl_3.1\text{-}C_{10}H_7Cl$ in the unit cell, there are 4 Antimony, 14 Chlorine and 20 Carbon atoms (leaving out the H atoms).

Out of the expected total of $38 \times 37 = 1406$ vector peaks in $P(U,V,W)$, the Sb-Sb vectors will be the greatest in height (apart from possible overlapping). Thus in the interpretation of the vector map peaks of smaller value can be ignored to leave an expected 12 Sb-Sb vectors in the unit cell. Less than this number is observed due to overlapping.

The space group $P\bar{1}$ requires two types of antimony atoms in the cell. Vectors between non-related Sb atoms will be augmented (doubled, vector Sb_1-Sb_2 overlaps Sb_2'-Sb_1') relative to those between related Sb atoms. Thus with Sb_1 at (x_1, y_1, z_1) and Sb_2 at (x_2, y_2, z_2) generating Sb_1' at $(-x_1, -y_1, -z_1)$ and Sb_2' at $(-x_2, -y_2, -z_2)$ the largest peaks, P, will be peak 1 (Tab 5.4), Sb_1-Sb_2 at (x_1-x_2) etc. and peak 2 Sb_1-Sb_2' at (x_1+x_2), etc. The coordinates of the two asymmetric Sb atoms may be evaluated as half the sum and half the difference of the vector coordinates for peak 1 and 2, $x_1 = \frac{P_2+P_1}{2}$, $x_2 = \frac{P_2-P_1}{2}$ i.e. Sb_1 at (0.310, 0.535, 0.445) and Sb_2 at $(\overline{0.200}, \overline{0.075}, 0.435)$ so that Sb_2' is at (0.200,0.075,0.565). A lower vector due to Sb_1'-Sb_1 at $(-0.62, -0.07, -0.89) \equiv (0.38, 0.93, 0.11)$ is then equated to peak 7 and that due to Sb_2'-Sb_2 at (0.40 0.15 0.13) is peak 4.

To locate the remaining atoms an electron-density synthesis was computed using all the observed structure amplitudes with signs calculated from the Sb atoms as located. This showed some peaks corresponding to the chlorine atoms Cl_3 at (0.369, 0.700, 0.355), Cl_1 at (0.444, 0.629, 0.703), Cl_2 at $(0.846, 0.290, 0.387) \equiv (0.154\ 0.710\ 0.613)$ and Cl_6 at (0.128 0.323 0.581). A second 3D electron density synthesis with structure factors given by two antimony atoms and four chlorine atoms showed the fifth chlorine atom Cl_4 at $(0.954\ 1.048\ 0.694) \equiv (0.046\ 0.952\ 0.306)$. From a third 3D electron density synthesis the remaining chlorine atoms were located.

They were Cl_5 at (0.330, 0.087, 0.368) and Cl_N at (0.687, 0.752, 0.039).

At this stage it was decided to refine the position of antimony and chlorine atoms using a Stanley Shift parameter method. After several cycles the overall R_1 factor was 0.175.

A difference synthesis calculated using all hkl reflections with signs calculated for two antimony and seven chlorine atoms in the asymmetric unit did not show outstanding peaks corresponding to the carbon atoms. Therefore it was thought that packing consideration might suggest the possible position of the 1-$C_{10}H_7Cl$ molecule. With this in view it was decided to calculate the best position of the 1-$C_{10}H_7Cl$ rigid molecule to fit in the cell space available and then to use it in further refinements. Thus a FORTRAN IV (HONEYWELL/TSS) computer program was written to perform such a calculation (see appendix A).

The strategy for this consists in taking the known Cl_N coordinates and rotating the rigid molecule about this point (angles θ , ϕ , ψ about three orthogonal axes X, Y, Z respectively). Atoms belonging to the 4 $SbCl_3$ molecules (4 Sb and 12 Cl) are kept in fixed positions so that distances from these atoms to the rigid molecule can be calculated after each rotation step. Provided all these distances exceed a minimal value (the distance limit) there is space for the rigid molecule to fit into the structure. Such acceptable positions are expressed by the magnitudes of the rotation angles θ, ϕ, ψ. A typical example of computer output is given in Table 5.5. From the acceptable rotations of the rigid molecule, triclinic fractional coordinates for each carbon atom were then calculated. Each set of coordinates were compared with the difference map and false unacceptable coordinates were taken to be those in markedly negative regions. In this way only two of the possible positions of the rigid molecule remained acceptable

(3 and 9 in Table 5.5).

TABLE 5.5

POSSIBLE ROTATIONS OF THE RIGID MOLECULE COMPUTED

FOR A DISTANCE-LIMIT = 3.30Å

No.	θ	ϕ	ψ
1	0.0	0.0	240.0
2	145.0	190.0	70.0
3	150.0	35.0	250.0
4	180.0	180.0	60.0
5	190.0	355.0	210.0
6	310.0	170.0	75.0
7	315.0	150.0	80.0
8	340.0	345.0	280.0
9	345.0	170.0	75.0
10	350.0	80.0	280.0

The Stanley Shift Parameter procedure was used to refine the rigid molecule starting from the deduced positions. Only set 9 was capable of refinement to the angles (328.2, 157.90, 69.1) with CL_N shifted from (0.687, 0.752, 0.039) to (0.7404, 0.7476, 0.0464) and corresponded to an R_1 factor = 0.165 for 191 reflections.

5.5 ALTERNATIVE CELLS

At this stage because it was realised that the temperature factor of one Sb atom went to a near -zero value and attempts to further improve the R_1 factor were not successful it was decided to calculate cell distances and angles in the hope that they might suggest a different cell of higher symmetry. The following results were found (Table 5.6).

TABLE 5.6

SOME CELL DISTANCES AND ANGLES IN CRYSTALS

OF $2SbCl_3.1\text{-}C_{10}H_7Cl$.

Direction (1)	Distance (1) Å	Direction (2)	Distance (2) Å	Interangle (°)
[112]	18.297	[012]	15.732	141.6
[012]	15.732	[0$\bar{1}$0]	9.245	91.0~90.0
[112]	18.297	[0$\bar{1}$0]	9.245	89.0~90.0

These suggest a possible monoclinic cell confirmed by subsequent oscillation and Weissenberg photographs (oscillating about the extinction direction - the longer axis of the crystal, named "c"). Other monoclinic cells are also possible (see Table 5.7 and Fig 5.2).

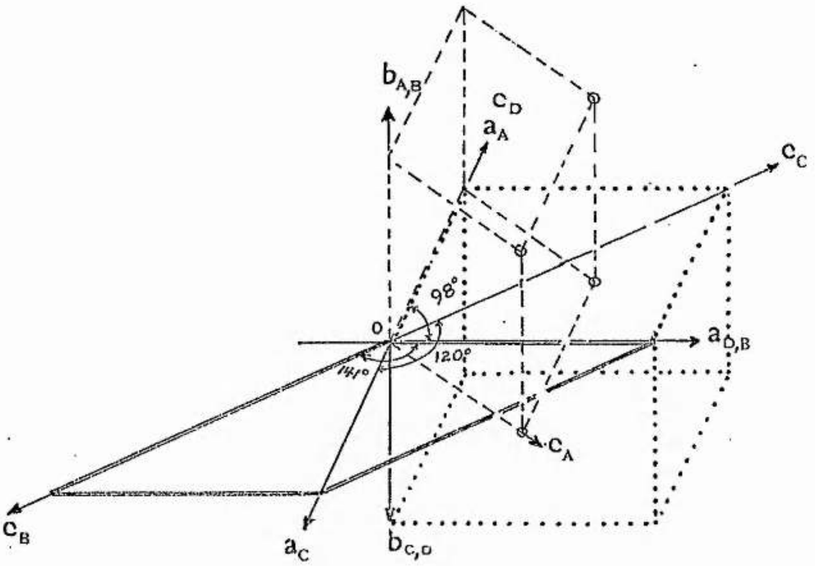

Fig 5.2

Relation between the different cells.

------ Cell A – Triclinic
═══ Cell B fc Monoclinic
——— Cell C bc Monoclinic
········ Cell D fc Monoclinic.

The cell with $\beta = 98.625^{\circ}$ was confirmed by Delaunay Reduction (Inter. Tables For X-Ray Crystallography, Vol 1 p.530) and was chosen for resolving the structure as β is close to 90°. However since alignment of the crystal about one of the axis of this cell was not physically convenient for data collection, it was necessary to use the cell with $\beta = 120.263^{\circ}$ for this purpose, and to oscillate about "c".

TABLE 5.7

RELATIONSHIP BETWEEN THE DIFFERENT CELLS

Cell Parameter Å & (°)	A First Setting Triclinic $P\bar{1}$ CuKα, photog.	B β=141.50 Second Setting Monoclinic Cc/ or $C_{2/c}$. MoKα, photog.	C β=120.3° Third Setting Monoclinic I_2 or I_c; Diffractometer, MoKα	D β=98.6° Monoclinic Cc Transformed from C
a	11.458	15.853	11.6735(10)	16.059(6)
b	9.245	9.370	9.5247(10)	9.525(1)
c	9.241	18.228	18.3833(11)	11.674(1)
α	121.7	90.0	90.00°	90.000
β	96.1	141.5	120.263°(20)	98.63(5)
γ	89.7	90.0	90.00	90.000
V	829.	1687.	1765.34Å^3	1765.34Å^3
a*	0.1356rlu	0.07195	0.07049	0.04476
b*	0.1964	0.07585	0.07462	0.07462
c*	0.1976	0.06258	0.04476	0.06158
α^*	58.13°	90.00°	90.00°	90.00°
β^*	82.99°	38.54°	59.737°	81.375°
γ^*	86.54°	90.00	90.00°	90.00°
ζ_c	0.1669	0.03899	0.03866	

TABLE 5.7 (continued)

MATRICES FOR INDEX AND CELL TRANSFORMATION:

$$\mathrm{I} \quad [\overrightarrow{AB}] = \begin{bmatrix} 0 & 1 & 2 \\ 0 & 1 & 0 \\ \bar{1} & \bar{1} & \bar{2} \end{bmatrix} \qquad [\overrightarrow{AC}] = \begin{bmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 1 & 1 & 2 \end{bmatrix} \qquad [\overrightarrow{AD}] = \begin{bmatrix} 0 & 1 & 2 \\ 0 & \bar{1} & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$[\overrightarrow{CD}] = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix} \qquad [\overrightarrow{DA}] = \begin{bmatrix} 0 & 0 & 1 \\ 0 & \bar{1} & 0 \\ \frac{1}{2} & \overline{\frac{1}{2}} & 0 \end{bmatrix} \qquad [\overrightarrow{CB}] = \begin{bmatrix} 1 & 0 & 1 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{bmatrix}$$

The recognition of monoclinic symmetry raised the possibility of significant systematically absent reflections. In cell D it was found that

$h + k$ = odd was absent in hkl, therefore C

and l = odd was absent in h0l, therefore c,

correspond to space groups Cc or $C_{2/c}$. The equivalent space group in cell "C" would be I_2 or I_c.

More accurate cell dimensions were then calculated using an automatic Stoe STADl-2, two-circle diffractometer (MoK_α radiation), equipped with scintillation counter and controlled by a PDP 8/A computer. This involved two main steps: (i) The precise adjustment of the crystal, which was carried out firstly by optical means (-Telescopic and microscopic), and secondly by using the x-ray counter. The adjustment by this last procedure uses zero layer reflections with small 2θ values corresponding to reflection by lattice planes coinciding approximately with one of the arcs of the goniometer head. Then the peak of the particular reflection (at W_1) was sought using a large counter aperture by rotating the W-circle. At position W_1 a narrow vertical slit was placed centrally in front of the counter to determine the extent of miss-set by measuring the μ

angle of the counter arm, μ_1, needed to remaximise the peak. Additional values, W_2, μ_2, of W and μ were found for the related reflection ca. 180 + W_1 and $-\mu_1$.

From μ_1 and μ_2 an arc correction was calculated, and the whole process repeated until the average absolute value of μ is zero.

The process was then repeated with a new reflection in the same 2θ range appropriate to the other arc and at $W \approx (W_1 + 90)$.

(ii) The precise determination of lattice constants depends on the accurate measurement of W and μ for selected reflections. First W_o is defined from the best values above as $(W_1 - \theta_1)$ or $(W_2 - 90 - \theta_2)$.

For rotation about c, known h00 and 0k0 reflections were selected, initially with low 2θ values, and approximate W values as estimated from a zero layer Weissenberg photography. The inclination angle was set to zero, approximate cell parameters and the indices chosen were input to the computer which calculated the $2\theta_c$ and W_c values. W was then manually rotated around W_c and the 2θ circle also was manually rotated around $2\theta_c$ to maximise intensity with the narrow slit in position.

In this way a number of further h00 and 0k0 reflections were identified and their best 2θ, W values determined and used to compute new and improved cell dimensions, as well as an improved W_o value [as $W_0 = W_{h00} - \frac{1}{2}(2\theta_{h00})$].

Accurate $2\theta_{h00}$ permits the computation of a number of a^* values = $\frac{\sin\theta_{h00}}{h} \frac{2}{\lambda}$, from which $\bar{a}^*$ was calculated. $\bar{b}^*$ was found in a similar way. c was determined from the 00l reflections, optimising for maximum intensity the values 2θ, W and $\mu 1$. $c = l\lambda/2 \sin\mu_1$. Then W_0 was found for 00l (as for h00 and 0k0) or from $W_0 = W_{00l} - \theta_{00l} = W_0(c^*)$ Also $\zeta_1 = W_0(c^*) - W_0(a^*)$ and $\zeta_2 = W_0(c^*) - W_0(b^*)$. As $\alpha^* = \gamma^* = 90°$ the projection of c $(c^{*\prime})$

on the a* b* plane should lie along $\bar{a}^*$. Therefore $\zeta_1 = 0^\circ$ and $\zeta_2 = 90^\circ$. $c^{*\prime}$ was calculated as for a* and b* . and c* from the expression:

$$c^* = \sqrt{\frac{1}{c^2} + c^{*\prime 2}}$$

and β^* from:

$$\cos \beta^* = \underline{c}^{*\prime} \cos \zeta_1 / c^* = c^{*\prime} / c^*$$

5.6 MEASUREMENT OF INTENSITIES

Intensity data were collected using carbon monochromatised Mok$_\alpha$ radiation. The θ-2θ , step-scan technique, 0.01°/step counting for 0.500 sec/step, was employed. The measurement was carried out with constant W-range. Individual backgrounds were obtained from stationary counter measurements for one-half the total through-one-spot scan time (100 sec) at each end of the scan. Filters were used where they were necessary in order to attenuate intensities with factors of $F_1=2.032$, $F_2=4.443$, $F_3=17.069$.

As a general check on the electronic and crystal stability, the intensities of standard reflections were measured periodically during the data collection. Typical results for the 200 reflection are

hkl	Bgd(1)	Counts	Bgd(2)
200	297	155247	356
200	299	155665	366
200	295	155891	366

A total of 1307 reflections were recorded in this manner from l=0 to l=22.

The intensity data were corrected$^{(1)}$ for Lorentz-polarization effects, allowing for use of monochromatised radiation$^{(2)}$ (eq. 2.3.16 2.3.18) but not for absorption or extinction ($\mu_{\mathrm{MoK}\alpha} = 38.26\ \mathrm{cm}^{-1}$). 80 equivalent reflections were averaged. Standard deviations were estimated from the average intensity and background values by using equation 3.15 (Ch.3)$^{(3)}$. Of the 1227 independent reflections 1048 had $|Fo|^2 > 3\,\sigma(I)$. These were considered observed and were used in the refinement.

5.7 REFINEMENT OF THE STRUCTURE.

Assuming that the present structure has a C2/c space group in the D cell ($\beta = 98.63^\circ$); the indices as they were collected in the monoclinic cell "C" and the atomic coordinates obtained for Sb and Cl atoms in the triclinic cell were transformed to relate to the monoclinic cell "D", according to the following transformation matrices:

a) For indices $C \rightarrow D$: $\begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ \bar{1} & 0 & 0 \end{bmatrix}$

b) For coordinates $(A \rightarrow D)$:

$$\begin{bmatrix} 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & \frac{1}{2} \\ 1 & 0 & 0 \end{bmatrix} \quad \text{or} \quad \begin{aligned} x_M &= \tfrac{1}{2}z_T \\ y_M &= \tfrac{1}{2}z_T - y_T \\ z_M &= x_T \end{aligned}$$

The old and the new coordinates are listed in Table 5.8.

In cell D, $D_o = 2.230\ \mathrm{M_g.m^{-3}}$ and $D_c = 2.328\ \mathrm{Mg.m^{-3}}$ for $Z = 3.83\ (\sim 4.0)$, units of $2\ \mathrm{SbCl_3.1\text{-}C_{10}H_7Cl}$ (M = 618.8).

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(1) Using a computer program "LIDRED" written by DAVID LILES.

(2) Lp for monochromatised beam $= \dfrac{\sin 2\theta(\sin^2\theta - \sin^2\mu)^{\frac{1}{2}}}{\sin\theta}\left[\dfrac{2}{\cos^2 2\theta' + \cos^2 2\theta_{mon}(1-2\sin^2\mu)^2}\right]$ where $\theta' = \tan^{-1}\left[\dfrac{(\sin^2\theta - \sin^2\mu)^{\frac{1}{2}}}{\cos\theta}\right]$ and θ_{mon} is the Bragg angle for the monochromator.

(3) $\sigma(I) = \sqrt{N_c} + \dfrac{t_c}{2t_b}\left(\sqrt{B_1} + \sqrt{B_2}\right)$, N_c is the total count at the peak in a scan of time t_c ; B_1 and B_2 are the backgrounds, each obtained in a time t_b.

TABLE 5.8

TRANSFORMATION OF TRICLINIC COORDINATES INTO MONOCLINIC ($\beta = 98.63^\circ$)

$x_M = \frac{1}{2} z_T \quad y_M = \frac{1}{2} z_T - y_T \quad z_M = x_T$

ATOM	TRICLINIC COORDINATES			MONOCLINIC Cc COORDINATES		
	x_T	y_T	z_T	x_M	y_M	z_M
* Sb_1	0.306	0.538	0.464	0.232	$\overline{0.306}$	0.306
Sb_2	0.193	0.079	0.539	0.270	0.191	0.193
* Cl_1	0.444	0.616	0.727	0.364	$\overline{0.252}$	0.444
Cl_4	0.046	0.919	0.317	0.159	$\overline{0.760}$	0.046
* Cl_2	0.172	0.702	0.644	0.322	$\overline{0.380}$	0.172
Cl_5	0.338	0.104	0.415	0.208	0.104	0.338
* Cl_3	0.380	0.734	0.413	0.207	$\overline{0.527}$	0.380
Cl_6	0.124	0.322	0.562	0.281	$\overline{0.041}$	0.124

As an atom in C2/c (see Fig. 5.3) at xyz (I) generates one at $\frac{1}{2}-x\ \frac{1}{2}+y\ \frac{1}{2}-z$ (IV) the structure is now adequately described in C2/c by reference to the asterisked coordinates in Tab. 5.8 (cf. Tab. 5.9, LH set).

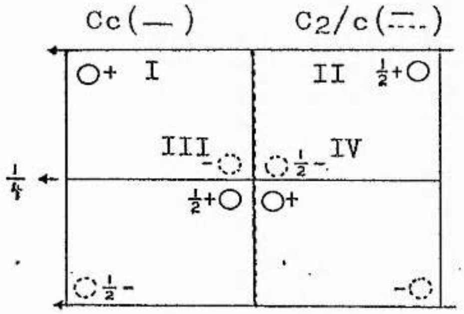

Fig. 5.3. Relationship between Cc and C2/c space groups.

Sb+3Cl coordinates were then refined isotropically by full-matrix least squares procedure(*). Two cycles gave an R = 0.310 ($R^G = 0.358$, where $R^G = \left[\sum(W\,\Delta F^2)/\sum(WF_o^2)\right]^{\frac{1}{2}}$ with W = unity and defined by $W = K/(\sigma^2(F) + |g| \times F^2)$) for all the observed reflections.

A difference synthesis showed the chlorine attached to the naphthalene molecule to be in a special position at (0.000, 0.6200, 0.2500). The inclusion of this atom resulted in R = 0.304 and acceptable bond-distances and angles.

Anisotropic refinement of antimony and three chlorine atoms performed for two additional cycles lowered R to 0.224 (R^G = 0.266)(* *). At this stage there were 5 reflections showing a large difference between F_o and F_c. These were omitted in further calculations. The inclusion of six fixed carbon atoms constituting a ring attached to CL_N resulted in R = 0.161.

Since there are only four molecules of $C_{10}H_7Cl$ in the cell, in order to "generate 8 molecules" to simulate a centric structure ($C_{2/c}$), the organic component of 1-Chloronaphthalene was assumed to be disordered about the Cl_N, which is in a special position on the 2 fold axis. In this way a naphthalene molecule (with site occupational factor of 0.5) was included. The disordered components were related by the two-fold axis.

Two more cycles of refinement, maintaining the organic molecule geometrically constrained gave R = 0.147 (R^G = 0.155) for all reflections. At this point the bond distances and angles were all reasonable but attempts to further reduce the R factor were not successful.

At this stage, since the difference synthesis and packing considerations did not show any other possible alternative position for the organic molecule, it was decided to refine the structure in the noncentric (Cc) space group. The coordinates of antimony and chlorine atoms were transformed into the new space group, as they are

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(*) In solving this structure, computer program SHELX from University of Cambridge was used.

(* *) A Hamilton test (Hamilton, 1965) for the hypothesis that the atoms vibrate iso-tropically (R=1.344) gave $R_{20,977,0.005}$ = 1.021, from which we conclude that there is an anisotropic motion.

shown in Table 5.9. (Also see Fig. 5.3 for relationship between Cc and $C_{2/c}$).

TABLE 5.9

COORDINATES OF Sb AND Cl IN THE CENTRIC ($C_{2/c}$) AND

NON-CENTRIC (Cc) SPACE GROUPS. FIG. (5.3)

xyz (I) $\longrightarrow$ $x\ \bar{y}\ \frac{1}{2}+z$ (II) and $\frac{1}{2}-x\ \frac{1}{2}-y\ 1-z$(III)

ATOM	OLD CENTRIC ($C_{2/c}$)			NEW NON-CENTRIC (Cc)		
	x	y	z	x	y	z^*
Sb_1	0.2330	$\overline{0.3060}$	0.3057	0.2330	0.3060	0.8057
Sb_2				0.2670	0.8060	0.6943
Cl_1	0.3529	$\overline{0.2668}$	0.4394	0.3529	0.2668	0.9394
Cl_4				0.1471	0.7668	0.5606
Cl_2	0.3080	$\overline{0.3992}$	0.1596	0.3080	0.3992	0.6596
Cl_5				0.1920	0.8992	0.8404
Cl_3	0.2081	$\overline{0.5316}$	0.3707	0.2081	0.5316	0.8707
Cl_6				0.2919	1.0316	0.6293
Cl_N	0.000	$\overline{0.6195}$	$\frac{1}{4}$	0.000	0.6195	0.2500

* Subsequently all z values were reduced by $\frac{1}{2}$ cf. Tab. 5.10.

Two cycles of isotropic refinement of two Sb and seven chlorine atoms resulted in $R = 0.270$ ($R^G = 0.293$); when anisotropic refinement was applied to two Sb atoms R became 0.190 ($R^G = 0.216$) and with six anisotropic chlorine atoms R was 0.161 ($R^G = 0.168$)(2)(3).

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(2) From a Hamilton test we concluded that the Sb and Cl atoms are involved in the anisotropic motion (R_{35}, 960, 0.005 = 1.031 against Ratio = 1.740).

(3) Because Cl_5 was giving an ill-defined anisotropic motion it was decided to refine isotropically.

The inclusion of the carbon atoms of a rigid naphthalene molecule gave a R = 0.144. However it was observed that e.s.d. of some temperature factors of some carbon atoms were large and that their positions shifted a little. At this stage 8 more reflections were omitted from further calculations because of large differences between Fo and Fc. Five cycles of refinement refinement resulted in R = 0.127 (RG = 0.128) for 1035 independent reflections. Freeing the carbon atoms from fixed geometry but with constrained bond-distances for 4 cycles of full-matrix least squares refinement resulted in R = 0.125 (RG = 0.126) for 1035 reflections. At this point shifts were smaller than the corresponding e.s.d. A Hamilton test for the structure in $C_{2/c}$ compared with that in Cc (Ratio: 0.155/0.126 = 1.2241) gave an $R_{36,932,0.005}$ = 1.032; from which we conclude that we can confidently reject the structure in the centric space group. The observed structure factors are shown in Appendix C.

Table 5.10 lists the final positional and thermal parameters along with their standard deviations. Standard deviations were obtained from the inverse matrix of the final least-squares refinement cycle.

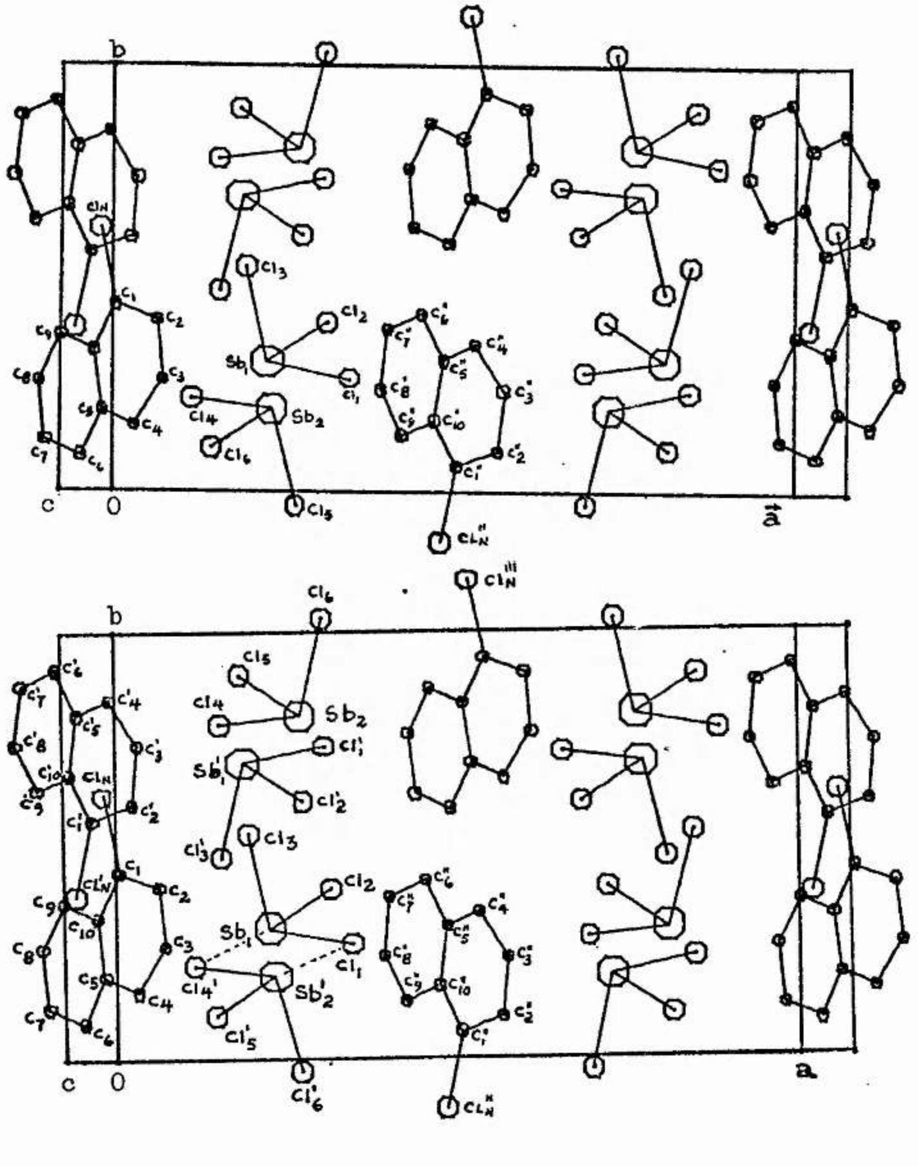

FIG.5.4

PLANE H AXIS   THETA =-0.8 0.8 PHI = 93.00 SBCL3. CL-NAPHTHALENE

TABLE 5.10

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS WITH e.s.d's BELOW OF EACH PARAMETER

(FOR ATOM NUMBERING SEE FIG 5.4)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb_1	0.2330 0	0.3064 8	0.3057 0	0.1620 66	0.0727 53	0.0217 31	-0.0050	0.0216 25	-0.0270 45
Cl_1	0.3534 24	0.2663 30	0.4361 25	0.1152 287	0.1000 184	0.0734 140	0.0435 137	0.0153 171	-0.0054 185
Cl_2	0.3042 20	0.3977 32	0.1614 17	0.2100 267	0.1065 167	0.0327 73	0.0157 89	0.0690 121	-0.0252 158
Cl_3	0.2091 21	0.5272 32	0.3739 24	0.0979 252	0.1022 210	0.0773 132	-0.0262 127	0.0070 157	0.0150 171
Sb_2	0.2666 5	0.8053 7	0.1941 5	0.0972 36	0.0668 43	0.0902 43	0.0245 35	0.0704 33	0.0312 38
Cl_4	0.1478 19	0.7823 43	0.0526 22	0.1449 180	0.1739 355	0.0481 112	0.0327 168	0.0508 117	0.0669 214
Cl_5	0.1950 17	0.8965 30	0.3366 22	0.0797 74					
Cl_6	0.2955 19	1.0316 33	0.1274 25	0.1709 227	0.0591 228	0.0684 165	0.0199 141	0.0967 161	0.0342 168
ClN	0.0000 33	0.6182 18	0.2350 45	0.2254 342	0.0805 141	0.1919 319	0.0383 245	-0.0124 243	-0.0934 271
$C_{(1)}$	0.0192 37	0.4381 24	0.2019 41	0.0663 160					
$C_{(2)}$	0.0686 40	0.4028 35	0.1171 47	0.0654 202					
$C_{(3)}$	0.0745 56	0.2626 40	0.0839 60	0.0841 287					
$C_{(4)}$	0.0406 39	0.1561 31	0.1456 39	0.0623 185					
$C_{(5)}$	0.0034 47	0.1913 21	0.2429 44	0.0573 111					

TABLE 5.10 cont.

$C_{(6)}$	-0.0205	0.0847	0.3138	0.0783
	45	23	46	222
$C_{(7)}$	-0.0617	0.1199	0.4072	0.0847
	53	37	52	284
$C_{(8)}$	-0.0682	0.2604	0.4389	0.0751
	53	41	47	246
$C_{(9)}$	-0.0437	0.3667	0.3684	0.1071
	60	30	57	357
$C_{(10)}$	-0.0053	0.3313	0.2724	0.0775
	52	20	150	214

ANISOTROPIC THERMAL FACTOR =

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\,l^2c^{*2} + 2U_{12}\,ha^*kb^* + 2U_{13}ha^*lc^* + 2U_{23}kb^*lc^*\right].$$

$B = 8\pi^2U$, where isotropic thermal factor is $\exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right]$

TABLE 5.11

BOND DISTANCES (Å) AND ANGLES (°) (SEE FIG. 5.5)

a) IN THE $SbCl_3$

$Sb_1 - Cl_1$	2.307 (38)	$Sb_2 - Cl_4$	2.339(27)
$Sb_1 - Cl_2$	2.341 (16)	$Sb_2 - Cl_5$	2.335 (26)
$Sb_1 - Cl_3$	2.301 (28)	$Sb_2 - Cl_6$	2.356 (31)
$Sb_1 \ldots Cl_4^{I}$	3.475	$Sb_2 \ldots Cl_1^{V}$	3.569
$Sb_1 \ldots Cl_6^{IV}$	3.584	$Sb_2 \ldots Cl_3$	3.586
$Sb_1 \ldots Cl_5^{IV}$	3.958	$Sb_2 \ldots Cl_2$	3.956

Sb_1 ... Perpendicular distance to naphthalene plane: 3.273 Å.

Sb_2 ... Perpendicular distance to naphthalene plane: 3.374 Å.

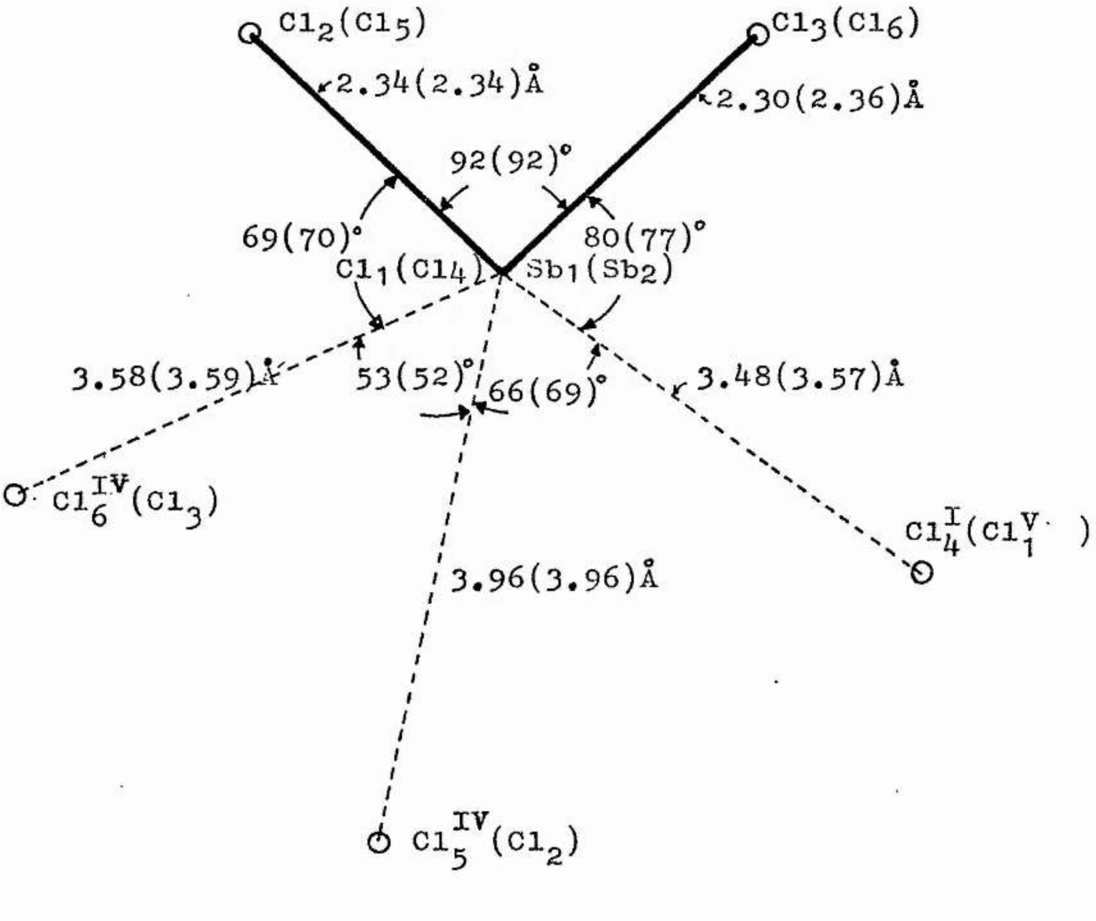

Fig. 5.5.Composite view Cl_1-Sb_1 and Cl_4-Sb_2. The bond-distances-angles of second $SbCl_3$ molecule are shown in parenthesis.

ANGLES AROUND Sb_1

	Cl_2	Cl_3	Cl_4^{I}	Cl_6^{IV}	Cl_5^{IV}
Cl_1	94.87 (1.00)	95.15 (1.20)	78.91	88.97	84.42
Cl_2		91.96 (1.10)	169.36	69.17	121.93
Cl_3			80.12	160.99	146.06
Cl_4^{I}				118.89	66.45
Cl_6^{II}					52.77

ANGLES AROUND Sb_2

	Cl_5	Cl_6	Cl_1^{V}	Cl_3	Cl_2
Cl_4	95.86 (1.00)	91.85 (1.20)	76.50	95.15	87.71
Cl_5		91.78 (1.00)	166.00	70.50	122.71
Cl_6			76.95	161.49	145.38
Cl_1^{III}				121.35	69.30
Cl_3					52.26

SYMMETRY CODE:

I	(x, 1-y , 0.5 + z)	IV	x, y-1, z
II	(x + 0.5, y - 0.5, z + 0.5)	V	x, 1-y, z-0.5
III	(0.5 + x, 0,5 + y, z)		

b) IN THE 1-CHLORONAPHTHALENE

CL_N-C_1	1.795(18)	$CLN-C_1-C_2$	121.0(1.2)	$C_8-C_9-C_{10}$	119.5(0.9)
C_1-C_2	1.399(12)	$CLN-C_1-C_4$	179.5(1.0)	$C_9-C_{10}-C_1$	119.4(0.8)
C_2-C_3	1.398(13)	$CLN-C_1C_{10}$	119.7(1.1)	$C_5-C_{10}-C_1$	120.2(0.9)
C_3-C_4	1.400(12)	$C_2-C_1-C_{10}$	118.7(1.3)	$C_4-C_5-C_{10}$	120.1(0.8)
C_4-C_6	1.400(10)	$C_1-C_2-C_3$	119.6(1.2)		
C_5-C_6	1.399(8)	$C_2-C_3-C_4$	120.1(1.1)		
C_6-C_7	1.399(10)	$C_3-C_4-C_5$	119.3(1.1)		
C_7-C_8	1.396(9)	$C_4-C_5-C_6$	119.6(0.9)		
C_8-C_9	1.398(9)	$C_5-C_6-C_7$	119.4(0.9)		
C_9-C_{10}	1.399(8)	$C_6-C_7-C_8$	119.9(1.0)		
$C_{10}-C_5$	1.390(10)	$C_7-C_8-C_9$	120.(0.9)		

c) EQUATION OF SELECTED PLANES REFERRED TO ORTHOGONAL COORDINATES$^{(1)}$ AND OUT-OF-PLANE DISTANCES (Å).

i) Chloronaphthalene: $0.807X + 0.017Y + 0.590Z - 1.445 = 0$

ii) $Sb_1\ Cl_2\ Cl_3\ Cl_4{}^{I}\ Cl_5{}^{IV}\ Cl_6{}^{IV}$: $0.820X - 0.065Y + 0.569Z - 4.487 = 0$

iii) $Sb_2\ Cl_5\ Cl_6\ Cl_1{}^{V}\ \ Cl_2\ Cl_3$: $0.825X + 0.069Y + 0.562Z - 5.016 = 0$

DISTANCES OUT-OF-PLANE (Å)

ATOM	DIST (Å)	ATOM	DIST (Å)	ATOM	DIST (Å)
CL_N	0.079	Sb_1	0.041	Sb_2	-0.020
C_1	0.037	Cl_2	-0.098	Cl_5	0.148
C_2	-0.140	Cl_3	0.143	Cl_6	-0.215
C_3	-0.015	$Cl_4{}^{I}$	-0.161	$Cl_1{}^{V}$	0.177
C_4	0.108	$Cl_5{}^{IV}$	0.128	Cl_2	-0.086
C_5	0.060	$Cl_6{}^{IV}$	-0.037	Cl_3	0.018
C_6	0.003				
C_7	0.028				
C_8	-0.081				
C_9	-0.035				
C_{10}	-0.009				

(1)The transformation matrix from monoclinic x,y,z(Å)to orthogonal X,Y,Z (Å) coordinates is:

$$\begin{bmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{bmatrix}$$

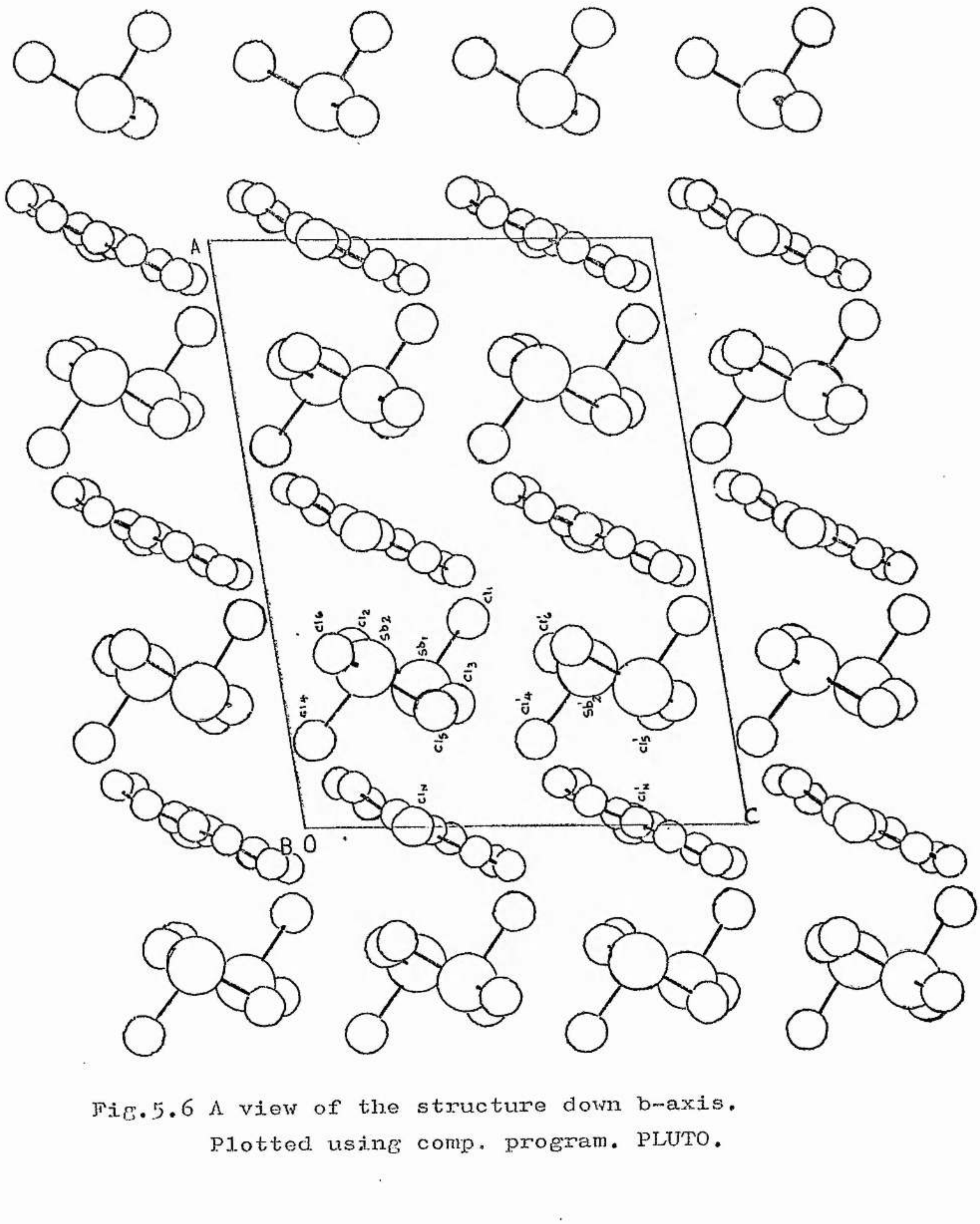

Fig.5.6 A view of the structure down b-axis.
Plotted using comp. program. PLUTO.

5.8 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The formation of the compound $2SbCl_3 \cdot 1\text{-}C_{10}H_7Cl$ has been confirmed. The crystal structure is built up of double layers of $SbCl_3$ molecules alternating with a single layer of 1-chloronaphthalene molecules which are tilted 25° to [001] (see Fig 5.6). Pairs of $SbCl_3$ molecules form dimers by halogen bridging, at the same time they are part of an infinite chain of molecules by further halogen bridging and these chains in turn are cross linked to others to produce the double sheet already observed in (1:1) $SbCl_3 \cdot 1\text{-}C_{10}H_7Br$. The layers of antimony trichloride and chloronaphthalene are parallel to the bc plane and alternate in the "a" direction.

Bond distances and angles in the $SbCl_3$ and $1\text{-}C_{10}H_7Cl$ molecules are listed in Table 5.11 a,b,c. There are two sets of non-equivalent $SbCl_3$ molecules. Each set contains four molecules related by symmetry and both sets simulate a pseudo centric structure. Each non-equivalent antimony atom is bonded to three chlorine atoms (average 2.32 and 2,34 Å respectively), and are close to three further chlorine atoms - from non-equivalent molecules (3.48, 3.58, 3.96 Å, 3.57, 3.58 and 3.95 Å) - and are situated near to a chloronaphthalene molecule (3.27 and 3.37 Å). Sb_1 is closer to the first ring carrying Cl_7(*) and Sb_2 to the second one from the opposite side of the aromatic molecule (Fig. 5.7) in a similar arrangement to that found in the naphthalene compound, $2SbCl_3 . C_{10}H_8$ (Hulme and Szymanski, 1969).

The two distances of interaction, Sb...Cl, are appreciably shorter than the corresponding Van der Waals radii, and one is approximately equal to it, so that the coordination number of the two antimony atoms becomes seven instead of eight found in the crystal structure of $SbCl_3$ alone (Lipka, 1979). It seems that the interaction with the large

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(*) Cl_N and Cl_7 are used interchangeably to denote the chlorine atached to the naphthyl group.

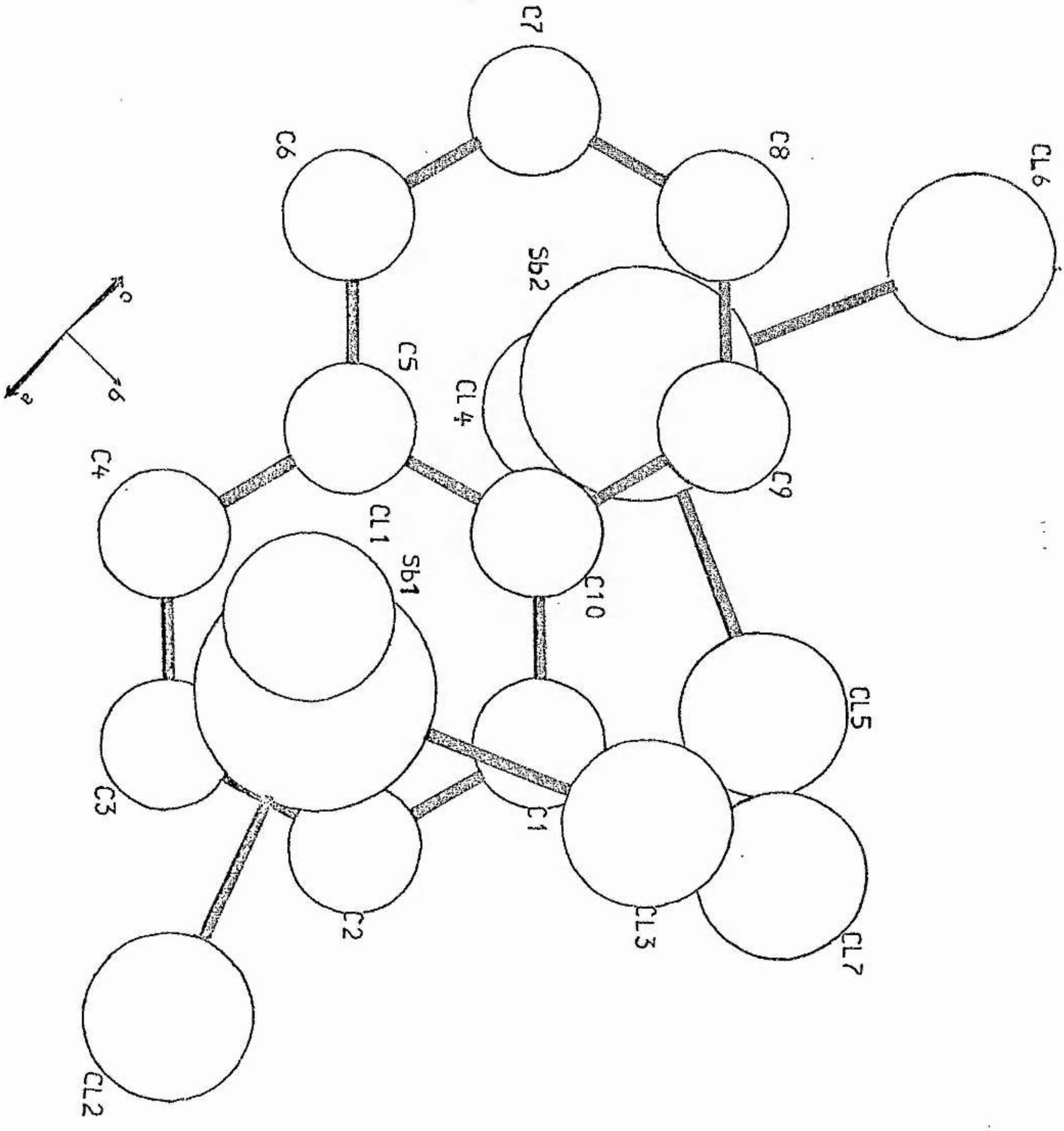


Fig 5.7.The projection of the antimony trichloride molecule onto the 1-chloronaphthalene plane. Plotted using Comp. Prog. PLUTO.

π-system of $1\text{-}C_{10}H_7Cl$ blocks further interaction. The geometry around the Sb atoms is similar to that found in the $SbCl_3\cdot 1\text{-}C_{10}H_7Br$ complex, that is a distorted pentagonal bipyramidal arrangement, where Sb_1, Cl_2, Cl_3, Cl_4^{I}, Cl_5^{IV}, Cl_6^{IV} and Sb_2, Cl_5, Cl_6, Cl_3, Cl_2, Cl_1^{V} are approximately located in the equatorial plane (Table 5.11c, Fig. 5.5). The out-of-plane distances for each atom are listed in Table 5.11c. According to the proposed geometry, it would seem that the lone electron-pair on each Sb atom is stereochemically inactive.

In both molecules of $SbCl_3$, two bonds lie in a plane approximately parallel to that of chloronaphthalene with the third nearly perpendicular and away from that plane (see Fig 5.8). Thus Cl_1-Sb_1 is directed towards C_2, while Cl_4-Sb_2 points towards the C_8-C_9 bond.(Fig.5.7). The distances from the two independent antimony atoms to the plane of the corresponding chloronaphthalene molecule are 3.27 and 3.37 Å respectively, which are shorter than the van der Waals radii. A similar situation is found in the $2SbCl_3$·naphthalene (Hulme and Szymanski, 1969), where the two $SbCl_3$ molecules related by a centre of symmetry (located in the naphthalene molecule plane) are situated on opposite sides of the plane of the aromatic molecule, giving an alternating distribution of organic and inorganic layers. The distance between Sb atoms and the plane of the organic component of the compound under investigation has an average of 3.32Å. The fact that this distance is of the same order of magnitude (3.20 Å) as that of the $2SbCl_3\cdot C_{10}H_8$ complex seems to suggest that within the $2SbCl_3\cdot 1\text{-}C_{10}H_7Cl$ compound there is also electron donation from the aromatic π-system to the Sb atoms. There is no significant alteration in the Sb-Cl bonds opposite to the interaction with the π-system as observed in $SbCl_3\cdot 1\text{-}C_{10}H_7Br$ and other systems. However this seems to indicate that the electron-donor-acceptor interaction between the π-system and the antimony atom is weaker in $2SbCl_3\cdot 1\text{-}C_{10}H_7Cl$, compared with that of

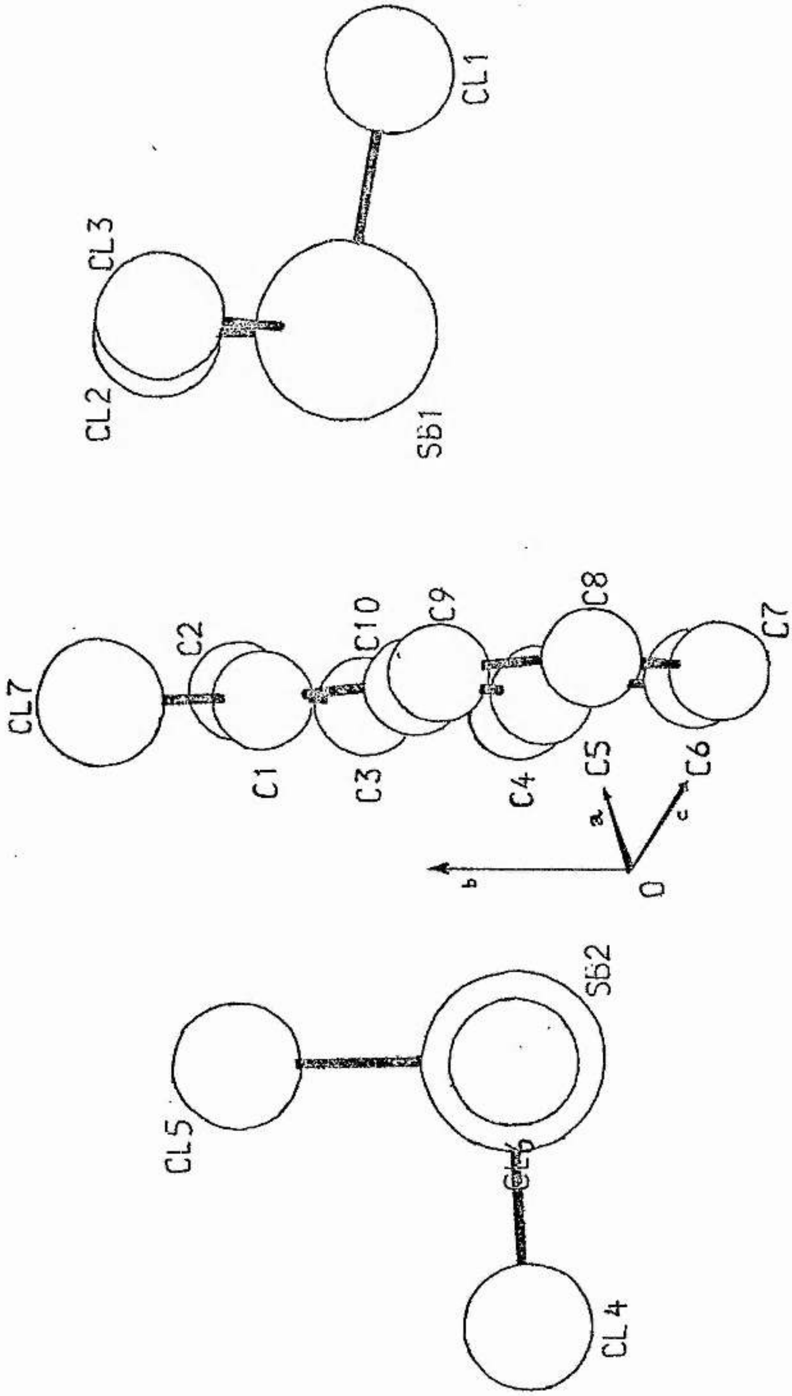


Fig. 5.8 A view of the structure down Cl(6)-Sb(2).
Plotted using Comp. Prog. PLUTO.

$SbCl_3 \cdot 1\text{-}C_{10}H_7Br$ system. A possible explanation for this variation in the interaction for different systems could be found in the type of substituent in the naphthalene molecule. More detailed discussion of this point will be given later in the general conclusion.

There is no significant variation in the bond distances and angles of the chloronaphthalene which could suggest any interaction between the Sb atom and any particular atom of the $1\text{-}C_{10}H_7Cl$. This is in contrast to that found in the $2SbCl_3 \cdot C_{10}H_8$ complex, where there are remarkable alterations in the bond distances and angles adjacent to the possible sites of interaction between Sb and carbon atoms of the naphthalene molecule. This might suggest that the interaction in the present compound is with the delocalized π-system rather than with any particular atom, or that interaction is much weaker in the present case.

6.0 STUDY OF THE (1:1) $SbCl_3$·1-IODONAPHTHALENE COMPLEX.

6.1 PREPARATION OF 1-IODONAPHTHALENE

1-iodonaphthalene was prepared following a standard procedure described in the literature (Birchenbach and Goubeau, 1932).

The method of preparation consisted in the iodination of naphthalene in the presence of silver perchlorate. An alternative method (Varma et.al. 1933) via nitration, reduction and diazotation was tried but gave much less pure product.

0.22 mol of naphthalene was dissolved in half its weight of ether to which solution 0.1 mol $AgClO_4$, 0.2 mol iodine and 0.1 mol magnesium oxide were added. The mixture was stirred and refluxed at 50°C until all the iodine had been used as evidenced by the disappearance of the dark colour.

The solution was filtered, poured into water and residual iodine was extracted from the organic layer with sodium thiosulphate. The organic layer and several ethereal extracts of the aqueous layer were combined. The ether and any excess of naphthalene were distilled off under reduced pressure at 150°C, leaving the 1-iodonaphthalene to distil as an oily liquid at 200°C. The 1-iodonaphthalene was purified by redistillation.

The mass spectrum of the final product showed two main peaks. The first at m/e = 127 which was interpreted as overlapped peaks due to $[I]^{\cdot}$ and $[C_{10}H_7]^{\cdot}$ and a second one at m/e = 254 due to $[C_{10}H_7I]^{\cdot}$. The purity of the product was checked by a Gas Cromatography method, using a 20% EGSS-Y $5' \times \frac{1}{4}''$ column at 200°C with N_2 as carrier at 22 psi. Two spectra were obtained. One for naphthalene alone and the other for the 1-iodonaphthalene sample. From the comparison of the two spectra no naphthalene peak was noticed in the 1-iodonaphthalene spectrum although there was a small additional peak probably due to 2-iodonaphthalene (see Table 6.1). It is debateable whether or not this very small % impurity could be the cause of the disorder subsequently observed.

TABLE 6.1

PREPARATION OF 1-IODONAPHTHALENE

Amount of I_2 used (g)	Amount of Naphthalene used (g)	Amount of $AgClO_4$ used (g)	Amount of MgO used (g)	Vol. of $1-C_{10}H_7I$ obtained	Yield(I) %	Purity % $1-C_{10}H_7I$	Purity % others
28.16	50.8	20.75	4.03	15.0ml	51.4	99.8	0.2

(I) cf. the theoretical yield of 80% mentioned in the literature (Birchenbach and Goubeau, 1932).

6.2 THE PHASE DIAGRAM FOR THE $SbCl_3 \cdot 1-C_{10}H_7I$ SYSTEM.

A phase diagram was constructed, following similar procedures to those for the previous systems (Ch. 4 and 5), in order to establish compound formation and the appropriate stoichiometry. Results shown in Table 6.2 and Fig. 6.1 indicate that antimony trichloride forms a (1:1) compound with 1-iodonaphthalene.

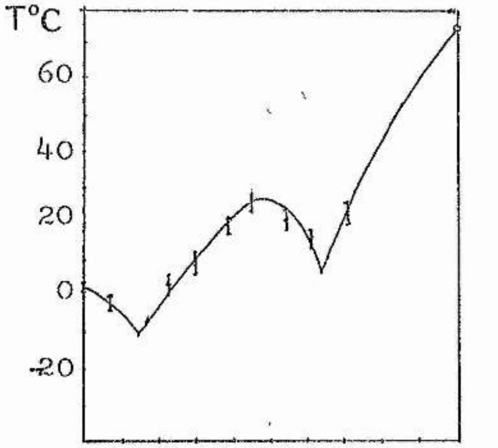


Fig.6.1 $SbCl_3$-1-Iodonaphthalene system.

TABLE 6.2

% Mol $SbCl_3$	T°C
5.0	-7.5±1.0
22.4	6.0±1.5
27.3	10.0±1.5
37.2	20.0±2.0
44.7	25.0±1.0
52.7	21.0±1.0
61.2	17.0±0.5
68.8	25.0±2

6.3 PREPARATION AND ANALYSIS OF THE (1:1) $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ COMPLEX

Crystals of antimony trichloride were dissolved in 10-15% excess of 1-iodonaphthalene at about 40°C. On cooling, the system gave a variety of yellow crystals.

Analysis for the components in the crystals was carried out in the usual way, i.e. for Sb(III) by titration vs. 0.025M KlO_3 and for 1-iodonaphthalene by the NMR method described in Chapter 2. Results of these analysis are shown in Table 6.3.

TABLE 6.3

ANALYSIS FOR Sb(III) AND $1\text{-}C_{10}H_7I$

Sample wt. (g)	Vol. 0.025M KlO_3 (ml)	% $SbCl_3$ (w/w)(3)	NMR Ref.(2) wt. (g)	NMR Integrated Height Ref.	Compd.	% $1\text{-}C_{10}H_7I$ (w/w)	Mole Ratio $SbCl_3$:$1\text{-}C_{10}H_7I$
0.2800	12.50	51.0	0.1240	40	66	56.0	1.01 : 1.00
0.2800	11.75	48.0	0.1240	41	68	56.4	0.95 : 1.00
0.2800	12.10	49.4	0.1240	40	65	55.2	0.99 : 1.00

(2) NMR Reference compound was CH_3I.

(3) Although the ratios suggest (1:1) both $SbCl_3$ and 1-Iodonaphthalene percentages are high (Theory: 47.3 : 52.7%).

6.4 PRELIMINARY INFORMATION AND UNIT CELL DETERMINATION

A square prismatic crystal which seemed single was chosen and sealed off in a Lindemann tube (diam. = 0.25 mm). Examination through the polarizing microscope showed straight extinction, from which it may be inferred that the crystal must be non-cubic and that one of the crystallographic axes may coincide with the direction of extinction.

The crystal was mounted on the goniometer head of the x-ray diffraction apparatus with the prismatic axis "c" parallel to the oscillation direction.

Oscillation and Weissenberg photographs were taken using Zirconium filtered Mo-Kα X-radiation, with the crystal oscillating about "c". These photographs did not show any mirror symmetry, from which it was deduced that the crystal belonged to the triclinic system, space group P1 or P$\bar{1}$. On the oscillation photograph odd layers showed horizontal streaks with specific reflections embedded. The odd level Weissenberg photographs showed continuous streaks parallel to a^* which suggested the presence of disorder.

Nevertheless cell parameters (Table 6.4) were evaluated from the measurements of the oscillation and even-layer Weissenberg photographs, the angles α and β, involving computation using a least square angular lag program (Ch. 2).

TABLE 6.4

a) Measured Cell Parameters For Crystals of $SbCl_3 \cdot 1\text{-}C_{10}H_7I$

(using MoK_α, Zr filtered Radiation).

$\pm n$	Y (mm)	$\tan\phi = Y/2R^{(*)}$	$\phi(°)$	$\sin\phi_n$	$\zeta_c = \sin\phi_{n/n}$	Mean ζ_c
6	17.0	0.29671	16.5259	0.28445	0.04741	
5	14.0	0.24435	13.7309	0.23736	0.04747	
4	11.05	0.19286	10.9159	0.18937·	0.04734	
3	8.20	0.14312	8.1449	0.14168	0.04723	
2	5.50	0.09599	5.4832	0.09555	0.04778	
1	2.70	0.04712	2.6978	0.04707	0.04707	0.04738±0.0003

(*) 2R = 57.296 mm

$\pm n$	s' (mm)	$\theta° = s'/2$	$2\sin\theta_n$	ξ_a	ξ_a (mean)
11	38.60	19.300	0.66103	0.06009	
9	31.42	15.710	0.54154	0.06017	
6	20.83	10.415	0.36155	0.06026	
5	17.27	8.635	0.30028	0.06010	
4	13.85	6.925	0.24114	·0.06028	
3	10.35	5.175	0.18039	0.06013	
2	6.88	3.440	0.12001	0.06000	0.06015±0.00012

$\pm n$	s' (mm)	$\theta° = s'/2$	$2\sin\theta_n$	ξ_b	ξ_b (mean)
6	36.56	18.280	0.62732	0.10455	
5	30.28	15.140	0.52236	0.10447	
4	24.17 .	12.085	0.41873	0.10468	
3	18.02	9.010	0.31321	0.10440	
2	12.00	6.000	0.20906	0.10453	
1	6.00	3.000	0.10467	0.10467	0.10455±0.00012

(1) Y is the respective inter-layer separation in the oscillation photograph.
s' is defined in fig. 2.3.4 p.55.

Measurement of γ^*

DIST. (D) BETWEEN h_1k_10 & h_2k_20 (mm)	D x $\sqrt{5}$ ($^\circ$)	Mean γ^* ($^\circ$)
29.90	66.858	
29.85	66.747	
29.95	66.970	66.86 ± 0.10

Measurement of α and β (Ang. Lag Method):

Reflections		Angle ($^\circ$)	
$h_1k_1l_1$	$h_2k_2l_2$	Ψ_o	Ψ_c
$1\,\bar{2}\,2$	$3\,\bar{1}\,2$	63.84	63.84
$1\,\bar{3}\,2$	$3\,\bar{1}\,2$	74.01	74.09
$\bar{3}\,0\,2$	$\bar{1}\,\bar{2}\,2$	66.30	66.36
$\bar{3}\,0\,2$	$0\,\bar{2}\,2$	83.07	83.13
$\bar{3}\,1\,2$	$\bar{1}\,\bar{2}\,2$	105.43	105.42
$\bar{2}\,1\,2$	$\bar{2}\,\bar{1}\,2$	97.83	97.99
$\bar{3}\,1\,2$	$\bar{3}\,\bar{1}\,2$	69.32	69.31
$\bar{3}\,\bar{1}\,2$	$2\,\bar{3}\,2$	75.91	75.78
$3\,\bar{1}\,4$	$0\,1\,4$	66.41	66.46
$3\,\bar{2}\,4$	$1\,0\,4$	62.39	62.42
$1\,\bar{2}\,4$	$1\,0\,4$	94.47	94.33
$\bar{3}\,0\,4$	$\bar{1}\,\bar{2}\,4$	85.42	85.30
$\bar{3}\,1\,4$	$\bar{3}\,\bar{1}\,4$	79.94	79.94
$\bar{3}\,1\,4$	$\bar{3}\,\bar{2}\,4$	99.28	99.25

Hence: $\langle\alpha\rangle = 104.70^\circ$

$\langle\beta\rangle = 102.19^\circ$

b) Measured and Calculated Cell Parameters for Crystals of $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ (using MoK$_\alpha$ Zr-filtered radiation).

DIRECT IN Å AND (°)		CELL PARAMETER	RECIPROCAL IN RLU.
FULL CELL	HALF CELL		
13.15(4)	13.15	a	0.06015 (12)
7.65(3)	7.65	b	0.10455 (12)
15.01(9)	7.51	c	0.05163
104.7(1)	104.7	α	69.74
102.2 (1)	102.2	β	71.45
108.5 (1)	108.5	γ	66.86 (10)
1312.4	656.2	V	0.000762
		ζ_c	0.04738 (30)

The Delaunay reduction procedure (Int. Tables for X-ray Crystallography, p.626 Vol.I), did not simplify the cell to one of higher symmetry.

Flotation in a mixture of (2:1:1) Bromoform + Iodoethane + 1,2-dibromoethane gave D_o = 2.29 Mgm^{-3} for the observed density of the complex. Hence Z= 3.75 (~ 4.0) for $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ (M = 482.0), leading to D_c = 2.44 Mgm^{-3}.

Intensity data corresponding to even layers 0 to 6 about "c" were collected from a particular crystal (about 0.1 x 0.1 x 0.2 mm) using zirconium filtered MoK$_\alpha$ radiation and a multiple film pack in a Weissenberg camera. The intensities of the reflections were evaluated visually and were corrected for Lorentz and polarisation effects but not for absorption or extinction (μ_{MoK_α} = 44.96 cm^{-1}). This gave a set of 680 structure amplitudes.

6.5 DETERMINATION OF THE APPROXIMATE STRUCTURE.(*)

A three-dimensional Patterson map was computed using all the hkl reflections in order to locate the heavy atoms in a pseudo cell half the size of the real cell. This showed the following highest vector peaks (Table 6.5a):

TABLE 6.5a

PATTERSON COORDINATES (U, V, W) OF THE STRONGEST PEAKS IN THE FULL CELL AND HALF CELL.

No.	U	V	full (2) cell W	half cell W'	Relative Height
1	0.000	0.000	0.000	0.000	3601
2	0.000	0.000	0.177	0.354	1104
3	0.580	0.709	0.248	0.496	922
4	0.420	0.194	0.189	0.378	860
5	0.635	0.139	0.061	0.122	850
6	0.635	0.230	0.110	0.220	782
7	0.780	0.050	0.138	0.276	775
8	0.000	0.000	0.323	0.646	1104
9	0.420	0.291	0.252	0.504	922
10	0.580	0.806	0.311	0.622	860
11	0.365	0.861	0.439	0.878	850
12	0.365	0.770	0.390	0.780	782
13	0.220	0.950	0.362	0.724	775
14	0.00	0.00	0.500	1.00	3605

(*) Comp. Prog. "PATT3D", "PARIBLES" written by R. Hulme and and SHELX-78 written by G. Sheldrick were used in solving this structure.

(2) Equivalent centrosymmetrically related peaks are not listed.

Considering four formula units of $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ in the unit cell, there are 4 iodine, 4 antimony, 12 chlorine and 40 carbon atoms (ignoring hydrogen) or two formula units of $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ in the half cell, with 2 iodine, 2 antimony, 6 chlorine and 20 carbon atoms.

Of the expected total of 60 x 59 = 3540 vector peaks in P(U,V,W), the 56 I-I, I-Sb, Sb-Sb vectors will be the greatest in height (except when overlapping occurs). This number would fall to 28 vector peaks in the half cell, although a smaller number of peaks were observed, probably due to overlapping.

Attempts to interpret the vector map in the full cell did not give a reasonable result either in space group P1 or $P\bar{1}$. Therefore an interpretation was sought in the pseudo cell (half cell) initially assuming $P\bar{1}$ and later a non-centric P1 structure. Attempts to evaluate a trial position for the iodine or antimony atoms using the strongest vector peaks gave no satisfactory results in terms either of the R factor (which remained above 0.55 for 680 reflections) or of structural features. However a reasonable R factor (~ 0.35) resulted when vector peak No.13 (at 0.22 0.95 0.72) was assumed to be an I_1-I_2 vector, so defining the coordinates of these two iodine atoms. As the structure is assumed to be non-centric, one iodine (1) may be fixed randomly (at 0.250 0.9700 0.7600) so that iodine (2) must be placed at (0.030, 0.020, 0.036).

A difference synthesis, computed using all the observed structure amplitudes with signs calculated from the two iodine atoms as located, showed positions corresponding to the two antimony atoms and two attached chlorine atoms (one on each antimony). They were Sb(1) at (0.6050, 0.8100, 0.6320), Sb(2) at (0.680, 0.270, 0.270) Cl(2) at (0.770, 0.990, 0.500) and Cl(6) at (0.507, 0.012, 0.234). Small adjustment was also made to the iodine positions.

From further difference syntheses, calculated using all the observed amplitudes with signs given by the already located atoms it was possible to find the remaining chlorine atoms. A final difference synthesis computed with signs calculated from two iodine, two antimony and six chlorine atoms suggested a possible position for the naphthalene groups. At this stage R factor was 0.250 for 680 reflections and the structure corresponded to reasonable bond-distances and angles.

6.6 REFINEMENT OF THE STRUCTURE.

Two Iodine, two antimony and six chlorine atoms were first refined isotropically by a full-matrix least squares procedure. Two cycles gave an R=0.230 for all the observed reflections.

It was noticed that the differences between F observed and F calculated of two particular reflections were very large and therefore they were omitted in further calculations. Two more cycles of isotropic refinement lowered R to 0.210.

At this stage the naphthyl groups were introduced as idealized units associated with the iodine atoms. Their positions were allowed to refine isotropically while they were geometrically constrained to give ideal molecules of $1\text{-}C_{10}H_7I$. Several cycles of least squares refinement gave an R factor of 0.196 for 678 reflections.

At this point it was observed that some of the bond-distances in the $SbCl_3$ molecules had increased. Several attempts were made to find a structure with a geometry nearer to that of the "ideal" $SbCl_3$ molecule (Lipka, A., 1979). However refinement of such structures was unsuccessful both in terms of R factor and geometry. Since the structure is known to be disordered it was decided to stop refinement here. The observed structure amplitudes and calculated structure factors are shown in Appendix D.

The final positional and thermal parameters with their respective standard deviations (obtained from the inverse matrix of the final cycle of least squares refinement) are listed in Table 6.6. Bond distances and angles are in Table 6.7.

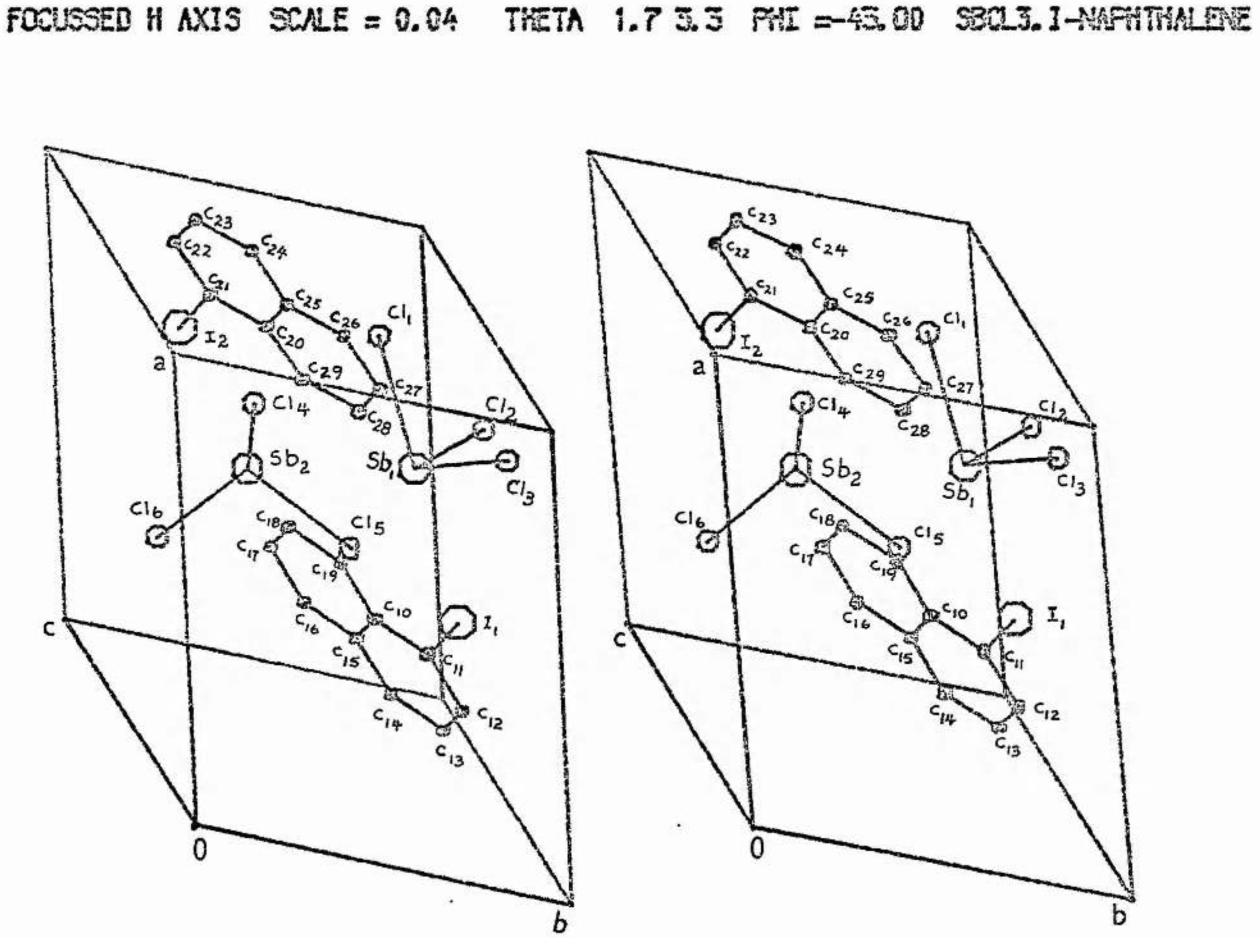


Fig. 6.2

Plotted using Comp.Prog. STEREO

TABLE 6.6

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS REFERRED TO THE HALF CELL. esd's IN PARENTHESIS

(For atom numbering see Fig 6.2)

ATOM	x	y	z	U *
I_1	0.2584( )	0.9715( )	0.7648( )	0.0010(47)
I_2	1.0419(13)	0.0262(25)	0.0321(40)	0.0010(40)
Sb_1	0.6194(16)	0.8335(28)	0.6319(42)	0.0067(40)
Cl_1	0.7501(60)	0.8680(115)	0.9936(180)	0.0432(242)
Cl_2	0.7688(58)	0.9924(94)	0.5335(140)	0.0295(179)
Cl_3	0.5965(41)	1.1435(71)	0.8353(110)	0.0010(119)
Sb_2	0.6813(16)	0.2714(27)	0.2741(42)	0.0034(39)
Cl_4	0.6909(93)	0.4237(160)	0.6269(180)	0.1155(350)
Cl_5	0.5846(49)	0.5122(83)	0.1992(139)	0.0209(150)
Cl_6	0.5066(48)	0.0130(80)	0.2399(130)	0.0031(140)
C_{11}	0.2784	0.8074	0.5053	0.0010(500)
C_{12}	0.2410	0.8357	0.3302	0.4400(1500)
C_{13}	0.2540	0.7288	0.1612	0.0010(568)
C_{14}	0.3044	0.5937	0.1673	0.0757(850)
C_{15}	0.3418	0.5655	0.3424	0.1986(1500)
C_{16}	0.3921	0.4304	0.3485	0.1504(1100)
C_{17}	0.4295	0.4022	0.5236	0.0075(648)
C_{18}	0.4165	0.5090	0.6926	0.1958(1500)
C_{19}	0.3661	0.6441	0.6865	0.0410(800)
C_{10}	0.3287	0.6723	0.5114	0.5903(1500)
C_{21}	1.0281	0.1984	0.2953	0.0063(583)
C_{22}	1.0603	0.1643	0.4689	0.0031(700)
C_{23}	1.0512	0.2772	0.6390	0.0549(700)
C_{24}	1.0100	0.4241	0.6355	0.0042(500)
C_{25}	0.9778	0.4582	0.4619	0.0010(500)
C_{26}	0.9366	0.6052	0.4584	0.0456(800)
C_{27}	0.9045	0.6393	0.2848	0.0010(8))
C_{28}	0.9135	0.5264	0.1147	0.1439(300)
C_{29}	0.9548	0.3794	0.11 2	0.0280(651)
C_{30}	0.9869	0.3453	0.2918	0.0010(497)

(*) $B=8\pi^2U$, where isotropic thermal factor is $\exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right]$

TABLE 6.7

BOND DISTANCES (Å) AND ANGLES (°)

a) IN THE $SbCl_3$.

$Sb_1 - Cl_1$	2.78 (9)	$Sb_2 - Cl_4$	2.57 (9)
$Sb_1 - Cl_2$	2.33 (8)	$Sb_2 - Cl_5$	2.65 (6)
$Sb_1 - Cl_3$	2.62 (5)	$Sb_2 - Cl_6$	2.42 (6)
$\langle Sb - Cl \rangle$	2.58	$\langle Sb - Cl \rangle$	2.57
$Sb_1 \cdots Cl_5$	3.40 (8)	$Sb_2 \cdots Cl_2^{II}$	3.52 (8)
$Sb_1 \cdots Cl_4$	3.54 (8)	$Sb_2 \cdots Cl_3^{III}$	3.01 (7)
$Sb_1 \cdots Cl^{I}_6$	3.77 (7)	$Sb_2 \cdots Cl_1^{III}$	3.75 (7)

$Sb_1 \cdots$ plane of aromatic molecule (1) = 3.01

$Sb_2 \cdots$ plane of aromatic molecule (2) = 3.18

ANGLES AROUND Sb_1

	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6^{I}
Cl_1	96.9(2.8)	83.1(2.4)	66.3(2.5)	125.9(2.1)	156.6(1.8)
Cl_2		98.3(2.0)	95.3(2.5)	75.0(2.2)	71.9(2.4)
Cl_3			147.5(2.5)	150.5(2.0)	78.7(1.7)
Cl_4				61.6(2.0)	133.8(3.0)
Cl_5					72.2(1.5)

ANGLES AROUND Sb_2

	Cl_5	Cl_6	Cl_2^{II}	Cl_3^{III}	Cl_1^{III}
Cl_4	86.6(2.8)	84.5(3.0)	71.3(2.8)	158.3(2.5)	136.5(3.0)
Cl_5		94.7(1.9)	156.4(2.4)	75.0(2.1)	137.4(2.8)
Cl_6			75.7(2.0)	85.8(2.2)	85.7(1.9)
Cl_2				124.7(1.6)	64.1(2.2)

b) IN THE 1-IODONAPHTHALENE MOLECULES

Constrained values used are I-C:2.15 and C-C:1.40, all angles 120°.

c) $I_1 \ldots\ldots I^{II}_2$: 3.88 I_1 - C plane (2) = 3.71

I_2 - C plane (1) = 3.99

EQUATION OF SELECTED PLANES REFERRED TO ORTHOGONAL COORDINATES.$^{(3)}$:

i) 1-Iodonaphthalene (1):

$0.692X + 0.691Y + 0.210Z - 4.510 = 0$

Out of plane distances Sb_1:3.01 Cl_1:3.81 Cl_2:5.04 Cl_3:3.55

I(1) and C atoms all zero

ii) 1-Iodonaphthalene (2):

$0.748X + 0.627Y + 0.217Z - 10.275 = 0$

Out of plane distances Sb_2:3.18 Cl_4:3.20 Cl_5:3.38 Cl_6:5.57

I(2) and C atoms all zero.

SYMMETRY CODE:

I) x y+1 z

II) x y-1 z

III) x y-1 z-1

---

(3) The transformation matrix from triclinic x y z (Å) to orthogonal X Y Z (Å) coordinates is:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 1 & \cos & \cos & \\ 0 & \sin & -\cos & \sin \\ 0 & 0 & \sin & \sin \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

FOCUSSED H AXIS SCALE = 0.02 THETA 257.2 258.8 PHI = 90.50 SBCL3. I-NAPHTHALENE

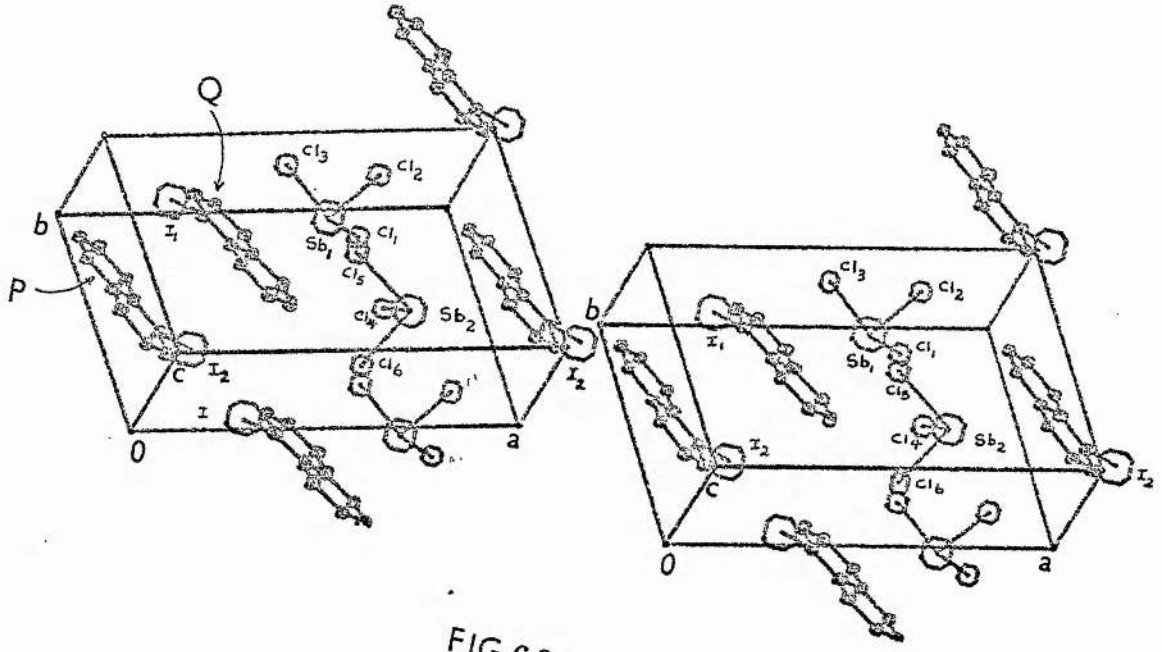


FIG.6.3

6.7 DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The formation of a (1:1) $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ compound has been established. The x-ray diffraction pattern of its crystal suggests a disordered structure. Thus the oscillation photographs showed continuous lines together with sharp reflections in the odd layers. Also, continuous streaks parallel to the a^*-axis in the odd layers of the Weissenberg photographs about 'c' were observed. This seems to suggest that there is an ordered cell assembled with another in a disordered full cell ($a = 13.15$, $b = 7.65$, $c = 15.01$ $\alpha = 104.7$, $\beta = 102.2$, $\gamma = 108.5$). The disordered structure relates to the a^* direction. This is probably one of the reasons for the difficulties found in solving the structure in the full cell. The present structure was solved by reference to a half-cell with dimensions $a = 13.153$, $b = 7.646$, $c = 7.506$, $\alpha = 104.7$, $\beta = 102.2$ and $\gamma = 108.5$. The approximate nature of the structure of the complex limits any description to a consideration of general features.

The crystal structure is built up of double layers of $SbCl_3$ molecules alternating with double layers of 1-iodonaphthalene tilted about 25° to [010] (see Fig 6.3). The two $SbCl_3$ molecules are linked to one another by Sb...Cl bridging ($Sb_1 \ldots Cl_5$:3.40Å, $Sb_2 \ldots Cl_3$:3.01Å, et. see Fig 6.4) so that an infinite chain of molecules are observed. These chains in turn are more loosely cross linked to others to produce the molecular sheet.

The structure suggests plane-to-plane molecular stacking of $1\text{-}C_{10}H_7I$ molecules (The separation between molecules P and Q (Fig 6.3) is about 3.20Å), in an arrangement similar to that found in the crystal structure of 1-Bromonaphthalene·$SbCl_3$ complex. The layers of antimony trichloride and 1-iodonaphthalene molecules are

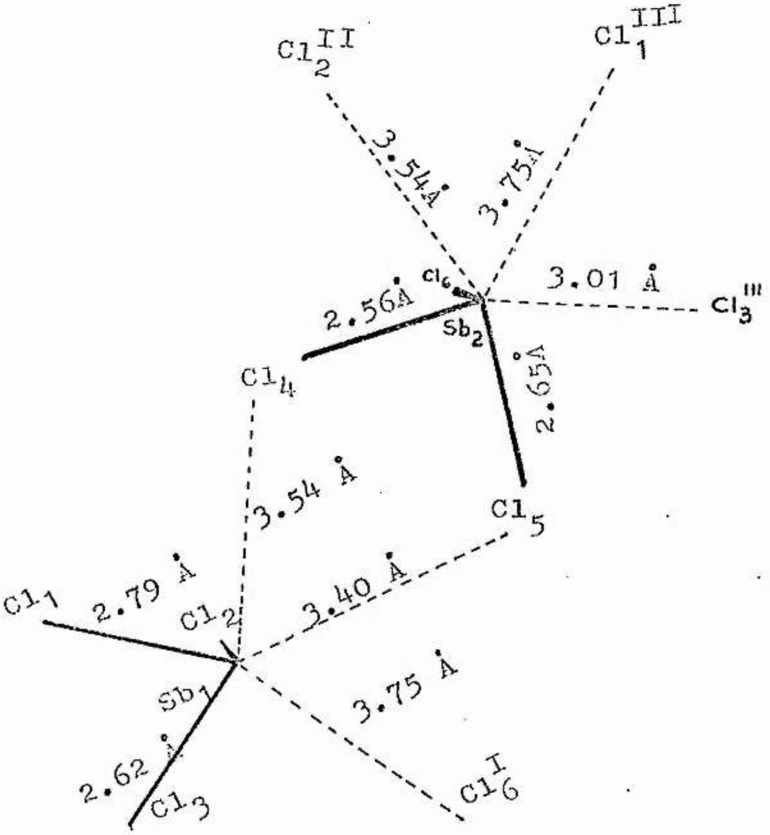


Fig. 6.4 Sb-Cl Bonding and Sb...Cl interactions in the $SbCl_3$ molecules.

approximately parallel to the bc plane and alternate in the a direction.

Bond distances and angles in the $SbCl_3$ and $1\text{-}C_{10}H_7I$ molecules are listed in Table 6.7. There are two non-equivalent molecules. Both the non-equivalent antimony atoms are bonded to three chlorine atoms, and are close to a further three chlorine atoms - Sb_1 is close(*) to Cl_4 (3.54Å), Cl_5 (3.40Å) and Cl^{I}_{6} (3.77Å); Sb_2 to Cl^{II}_{2} (3.54Å), Cl^{III}_{3}(3.01Å) and Cl^{III}_{1} (3.75Å). Furthermore the Sb atoms are situated near to an iodonaphthalene molecule (3.01 and 3.18 Å respectively). These distances are appreciably shorter than the sum of the corresponding van der Waals radii (4.05 Å, Bondi, A., 1964), so that the coordination number of the two Sb atoms becomes seven. The geometrical environment in both Sb atoms thus corresponds to a distorted pentagonal bipyramid. This geometrical arrangement around the Sb atoms clearly differs from that in the crystal structuee of $SbCl_3$ alone (Lipka A., 1979), but is similar to those found in the $SbCl_3\cdot 1\text{-}C_{10}H_7Br$ and $2SbCl_3\cdot 1\text{-}C_{10}H_7Cl$ compounds.

In each $SbCl_3$ molecule, two of the Sb-Cl bonds are significantly longer (2.79 , 2.62 , 2.65 and 2.56 Å) than those found in $SbCl_3$ alone (mean Sb-Cl = 2.35 Å, Lipka, A., 1979). Such an extension of an Sb-halogen has been already observed in other compounds. Thus (2.44 Å) in $2SbCl_3\cdot 1,4$-dithiane (Kiel and Engler, 1974), (2.51 Å) in $SbCl_3$·aniline (Hulme and Scruton, 1968). But these elongations occurred in the presence of interactions with strong electron donors atoms (such as S and N) which were located trans- to the longer Sb-Cl bond. Elongation in case of the disordered 1,4-Butanediyldiammonium Manganese Tetrachloride (Tichy R., Benes J.

(*) Superscripts defined at end of Table 6.7.

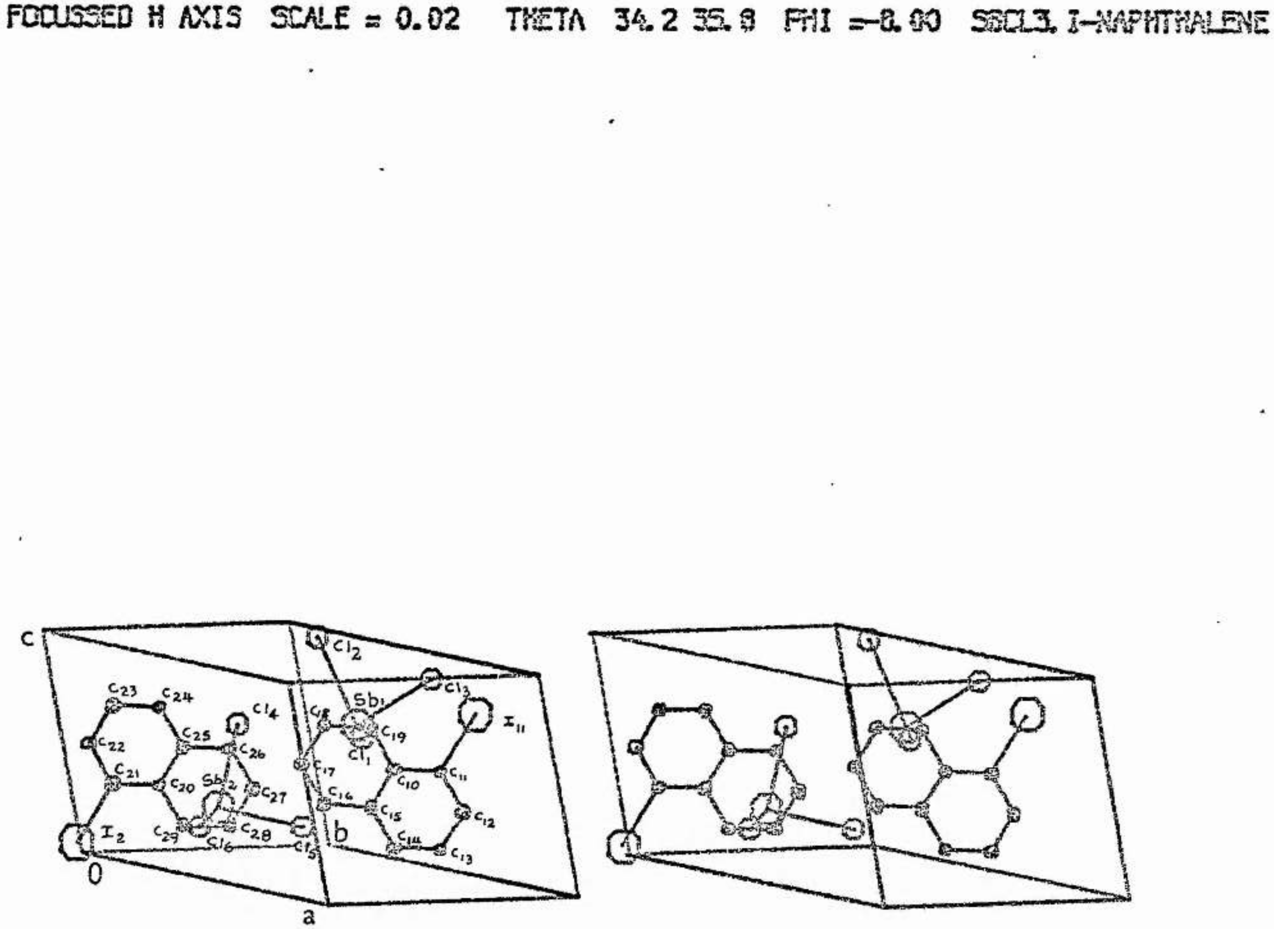


FIG.6.5. Projection of the $SbCl_3$ molecules onto the 1-Iodonaphthalene plane. Plotted using Comp. Prog. STEREO.

et.al., 1980) has been observed, and a similar explanation may well apply here, although there is no necessary relationship between elongation and disorder (e.g. complexes involving Histidine and Aspartic acid, Bhat T., and Vijayan, 1978).

One of the structural features observed in most of the complexes of $SbCl_3$ with aromatic molecules is that of two Sb-Cl bonds in each $SbCl_3$ molecule lying in a plane approximately parallel to that of the organic molecule with the third Sb-Cl bond approximately perpendicular and away from that plane. This does not seem to be the case in the $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ compound. Although one $SbCl_3(2)$ (Fig. 6.2), approximates to the mentioned feature (out of plane distances from the $1\text{-}C_{10}H_7I(2)$ molecule are Sb(2):3.18Å, Cl(4):3.21Å, Cl(5):3.38Å and Cl(6):5.57Å), the other $SbCl_3(1)$ shows a greater deviation with out-of-plane distances from the $1\text{-}C_{10}H_7I(1)$ of Sb(1):3.01Å, Cl(3):3.55Å, Cl(1):3.81Å, and Cl(2):5.04Å. Each $SbCl_3$ molecule is located nearest to the ring of the iodonaphthalene molecule which does not carry an attached iodine atom (see Fig. 6.5). The perpendicular distances from the two independent antimony atoms to the plane of the corresponding organic molecule are: 3.01 and 3.18Å respectively. Both these distances are of the same order of magnitude as those found in other similar structures. Thus 3.20Å was reported for $2SbCl_3 \cdot$naphthalene (Hulme and Szymanski, 1969), 3.09Å for $2SbCl_3 \cdot$p-xylene (Hulme and Mullen, 1976), 3.11 Å for $2SbCl_3 \cdot$phenanthrene (Demaldé, Nardelli, et.al., 1972), 3.17 Å for $2SbCl_3 \cdot$diphenyl (Lipka and Mootz, 1978a) and 3.09 Å for $2SbCl_3 \cdot$diphenylamine (Lipka A., 1978), which seems to suggest an interaction between Sb atom and the π-system of the aromatic molecule. More precisely this interaction is localized in an area between C_{18} - C_{19} in the 1-iodonaphthalene (1) i.e. C_7 and C_8 (Fig 6.6) and around C_{27} in the 1-iodonaphthalene (2). (i.e. C_6 in Fig 6.6)which both correspond to the same area of the 1-bromonaphthalene molecule.

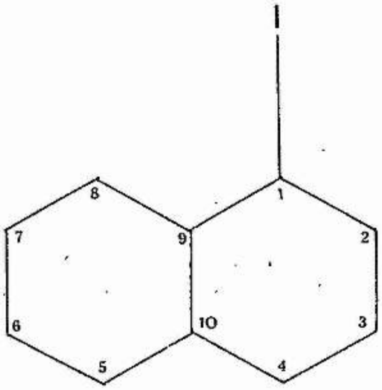


Fig. 6.6

Standard numbering of an 1-iodonaphthalene molecule

7.0 GENERAL DISCUSSION AND CONCLUSIONS

The purpose of the investigations stated early in this thesis was the structural study of the crystalline molecular complexes formed by antimony trichloride with 1-halonaphthalenes, to compare them with the $2SbCl_3$ naphthalene complex whose structure is known, and to understand some of the factors involved in complex formation when a substituent of graded size and electronegativity is atached to the naphthalene molecule.

By the application of three main methods, such as the construction of phase-diagrams, chemical and physico-chemical analysis, and x-ray diffraction structural studies, formation of (1:1) $SbCl_3 \cdot$1-bromonaphthalene and (2:1) $SbCl_3 \cdot$1-chloronaphthalene complexes have been confirmed, and in a similar manner the formation of the (1:1) $SbCl_3 \cdot$1-iodonaphthalene complex was established.

The results may be discussed from two aspects. The first is the orientation and interaction of one of the components of the complex with respect to its neighbouring molecules. The second is related to the changes in the internal geometry of both components.

It seems relevant to mention at this point the disorder observed in the $SbCl_3 \cdot 1\text{-}C_{10}H_7I$ complex which produced diffuse streaks parallel to a* in the odd layers of Weissenberg photographs (taken oscillating about "c"). Probably this is related to the disorder in the position of some of the heavy atoms. However this does not invalidate a discussion of the structural features of the complexes at a general level.

A common feature observed in the crystal structure of these compounds is that the structure consists of layers of $SbCl_3$ alternating with layers of 1-halonaphthalene molecules. Depending on the mole ratio of the components, the alternating layers in the structure are distributed as ...2$SbCl_3$...1(1-halonaphthalene)... 2$SbCl_3$... for a (2:1) $SbCl_3$·1-halonaphthalene complex, and ...2$SbCl_3$...2(1-halonaphthalene)...2$SbCl_3$··for a (1:1) $SbCl_3$·1-halonaphthalene complex. Furthermore pairs of $SbCl_3$ molecules form dimers by halogen bridging so that an infinite chain of molecules are formed by further-halogen bridging. These chains in turn are loosely cross linked to others to produce the molecular sheet.

The (1:1) $SbCl_3$·1-halonaphthalene complexes also show plane-to-plane molecular stacking, (the approximate distance between is in the order of 3.25Å), in an arrangement similar to that found in the crystal structure of naphthalene alone (Cruikshank D.W.J and Sparks, R.H., 1960).

In each compound, the antimony atoms are bonded to three chlorine atoms and are close to a further three chlorine atoms. (From a non-equivalent molecule and/or from a symmetrically related one), and are situated near an aromatic π-system with a perpendicular mean (Sb... plane π-system) distance of 3.25Å, so that the coordination number of the antimony atom becomes seven. Geometrically this corresponds to a distorted pentagonal bipyramid arrangement around the Sb atoms. Five chlorine atoms (two of which are bonding chlorine atoms) are approximately located in the equatorial plane. The third bonding chlorine atom and the interaction with the π-system are in axial positions. Greater distortion of this geometrical feature is observed around of one of the Sb atoms in the (1:1) $SbCl_3$·1-iodonaphthalene complex. This could be due to the disorder mentioned above. According to the observed geometry it seems that the lone electron-pair in the $SbCl_3$ is stereochemically inactive. Similar geometrical features are also found in the 2$SbCl_3$·$C_{10}H_8$ complex (Hulme and

Szymanski, 1969), if one takes account the long Sb...Cl interactions. A summary of bond-distances-angles and the Sb...Cl interaction distances less than the sum of the van der Waals radii around the Sb atoms for several compounds, are shown in Table 7.1

According to the results shown in Table 7.1, the bond-distance-angles in the $SbCl_3$ forming a complex are slightly different than those found in $SbCl_3$ alone (Lipka, 1979). These variations seem to be related in some way to the donor-acceptor nature of the interaction between the $SbCl_3$ and 1-halonaphthalenes.

The perpendicular distances from the Sb atom to the plane of the aromatic molecule, are very similar for the three molecular complexes under investigation (mean 3.25Å) and are shorter than the corresponding sum of the van der Waals radii (4.05Å, Pauling L., 1960 and Bondi, A., 1964). Similar distances were found in several other complexes of $SbCl_3$ with aromatic molecules by different authors. A comparative list of perpendicular Sb...plane of aromatic molecule distances are shown in Table 7.2.

These distances seem to indicate an interaction of electron donor-acceptor type between the $SbCl_3$ molecule and the delocalized π-system of the aromatic molecule, in which electron donation occurs from the π-system to the Sb atom. These interactions between $SbCl_3$ and 1-halonaphthalene molecules are localized in areas as shown in Table 7.3. For atom numbering in the 1-halonaphthalene see Fig. 7.1.

TABLE 7.1

COMPOUND	SB--CL DISTANCE IN Å	SB...CL DISTAN. IN Å (*)	ANGLES(°) CL--SB--CL	REFERENCE
SBCL3	2.34 2.37 2.37	3.46 3.74 3.60	90.58 95.70 95.70	LIPKA A.(1979)
2SBCL3.C10H8	2.35 2.35 2.37	3.58 3.83 3.66	91.59 94.41 94.70	HULME & SZYMANSKI,1969
2SBCL3.1-C10H7CL	2.30 2.31 2.34	3.48 3.96 3.58	91.96 94.90 95.15	THIS THESIS
	2.34 2.34 2.36	3.57 3.96 3.59	91.85 91.80 95.86	" "
SBCL3.1-C10H7BR	2.27 2.33 2.33	3.49 3.77 3.68	91.76 96.10 96.18	" "
	2.29 2.37 2.42	3.39 3.77 3.65	90.81 91.91 96.42	" "
SBCL3.1-C10H7I	2.33 2.62 2.79	3.40 3.75 3.54	83.10 96.90 98.30	" "
	2.42 2.56 2.65	3.01 3.75 3.54	84.50 86.60 94.70	" "

(*) THE CORRESPONDING SUM OF THE VAN DER WAALS RADII FOR SB...CL IS~3.95 Å,(PAULING L.,1960)

TABLES 7.2

COMPOUND	SB...PLANE OF AROMATIC RING(*) IN Å	REFERENCE
4SBCL3.DIBENZYL	3.40 3.40	HURSTHOUSE,1965
2SBCL3.DIPHENYL	3.26 3.08	LIPKA & MOOTZ,1978
2SBCL3.DIPHENYLAMINE	3.09 3.08	LIPKA & MOOTZ,1978
2SBCL3.NAPHTHALENE	<3.20>	HULME & SZYMANSKI,1969
2SBCL3.PHENANTHRENE	3.27 2.94	DEMALDE,ET.AL.,1972
4SBCL3.STILBENE	<3.40>	HURSTHOUSE,1965
2SBCL3.P-XYLENE	3.09	HULME & MULLEN,1976
2SBCL3.1-C10H7CL	3.27 3.37	THIS THESIS
SBCL3.1-C10H7BR	3.34 3.30	" "
SBCL3.1-C10H7I	3.01 3.18	" "

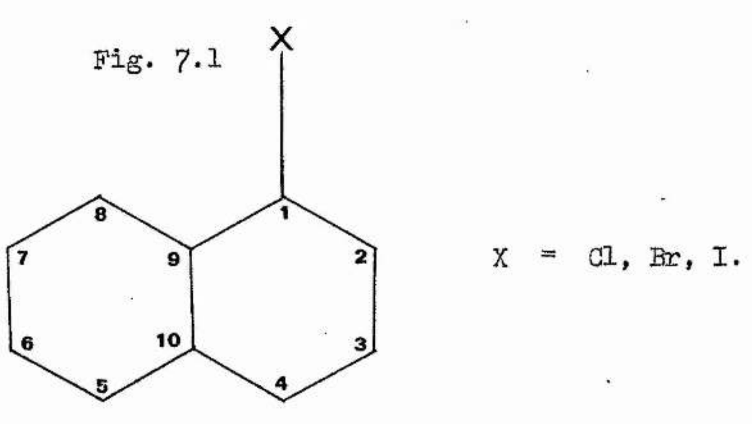
(*) SUM OF VAN DER WAALS RADII IS EQUAL TO 4.05 A.PAULING L.,1960,BONDI,1964.
< > MEANS MEAN DISTANCE

TABLE 7.3

Compound	Areas of Interaction localized in the Halonaphthalene molecule (1)
$SbCl_3 \cdot 1-C_{10}H_7Br$	i) Near to C(6) ii) Near to mid point of C(7)-C(8)
$2SbCl_3 \cdot 1-C_{10}H_7Cl$	i) Near to C(2) ii) Near to mid point of C(7)-C(8)
$SbCl_3 \cdot 1-C_{10}H_7I$	i) Near to C(6) ii) Near to a point between C(7)-C(8)

(1) For atom numbering: Fig. 7.1.

Fig. 7.1



Standard numbering of a 1-halonaphthalene molecule.

An explanation on the areas of interaction may be attempted by using results of theoretical studies on the electron density in the organic molecules (Higasi, et.al., 1965, p.264).

According to Coulson and Longuet-Higgins, (Coulson, C.A., and Longuct-Higgins, 1947), an electrophilic reaction will occur at carbon atom having the maximum value of π-electron density and the maximum absolute value of self-polarizability. Thus a molecular diagram for 1-chloronaphthalene (see Fig. 7.2a) will show that position 2, 4, 5, 7 and 9 are the possible sites of interaction by an acceptor molecule. From these, site 2 is the most preferred because higher electron density. This interaction will probably induce changes in the electron density population so that further interaction occurs near to C(7). In this way the formation of $2SbCl_3 \cdot 1\text{-}C_{10}H_7Cl$ may be explained.

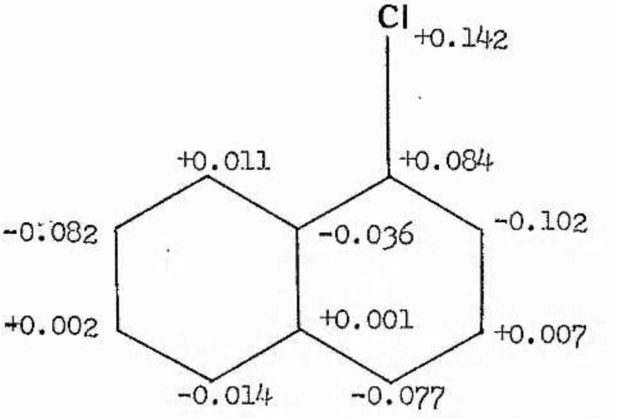


Fig. 7.2a Electron density distribution in the 1-Chloronaphthalene molecule (Ketelaar, 1958, p.302).

In the case of substituents with smaller electronegativity than chlorine, such as bromine and iodine, the molecular diagrams will have some differences in the charge distribution and polarizability. It seems that in these complexes C(2) is not the most preferred site of interaction but between C(5) — C(6) and C(7)-C(8), where the population of π-electrons is higher with a similar distribution to that in 1-naphthylamine (Baba H.m and Suzuki, S., 1961). See Fig 7.2b. Although this is not an accurate comparation, it gives an idea on the electron density distribution in the naphthalene molecule having a non-electron withdrawing substituent.

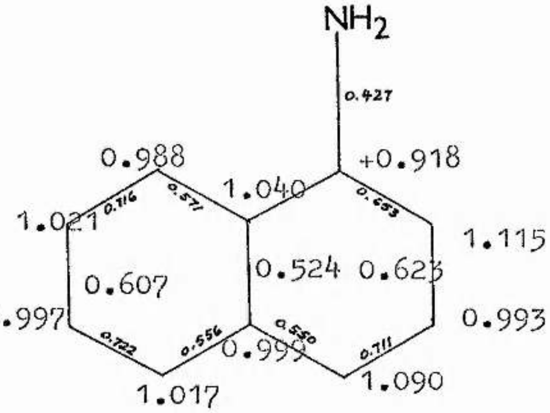


Fig.7.2b Electron density distribution and bond orders in the 1-naphthylamine.

There is no significant change of C–C bonds in the region with which the Sb atom is interacting, except for C_2 of the 1-chloronaphthalene molecule in the $2SbCl_3$.1-chloronaphthalene complex which is ~0.14 Å out of the aromatic plane and away from the Sb atom.But alterations of some other C–C bonds as well as some angles are observed in the $SbCl_3$.1-bromonaphthalene and $2SbCl_3$.1-chloronaphthalene complexes which could be due to some residual errors,such as absorption (e.g. in the $SbCl_3.1\text{-}C_{10}H_7Br$ it is considerably high: $\mu = 61.0$) and extinction,uncorrected in the experimental data.

Calculation of the electron density distribution in the naphthalene molecule carried out by using Computer Program GAUSSIAN-80, with the 3-21G basis set of Binkley J.S.,et. al.,(1980),gave the results shown in the following diagram(Ball J.,1980):

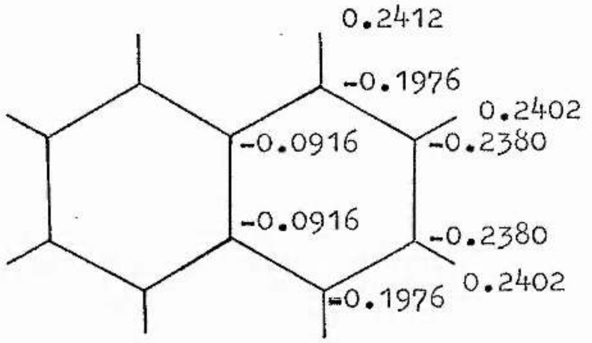


Fig. 7.3
Electron density distribution in the naphthalene molecule.

From Fig. 7.3, one may explain the areas of interaction in the $2SbCl_3$·naphthalene complex. According to it, C(2), C(3), C(6), C(7) are the most preferred sites. Thus in the crystal structure of this complex, the interactions are localized near C(2) and C(6) and they are related by a centre of symmetry. The introduction of an electronegative substituent changes this electronic distribution as that shown in Fig. 7.2.

No special structural reason was found to explain the difference between the structural features in the $SbCl_3$·1-$C_{10}H_7I$ complex and the structure of the other $SbCl_3$·1-halonaphthalene compounds. This seems to support the idea of disorder in the position of some heavy atoms as mentioned above. If it is real it could suggest that the 1-$C_{10}H_7I$ and some chlorine atoms are disordered in a direction and are responsible for the continuous streaking parallel to a* observed in the odd-layer of Weissenberg photographs.

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LIST OF COMPUTER PROGRAMMES USED IN THE PRESENT THESIS:

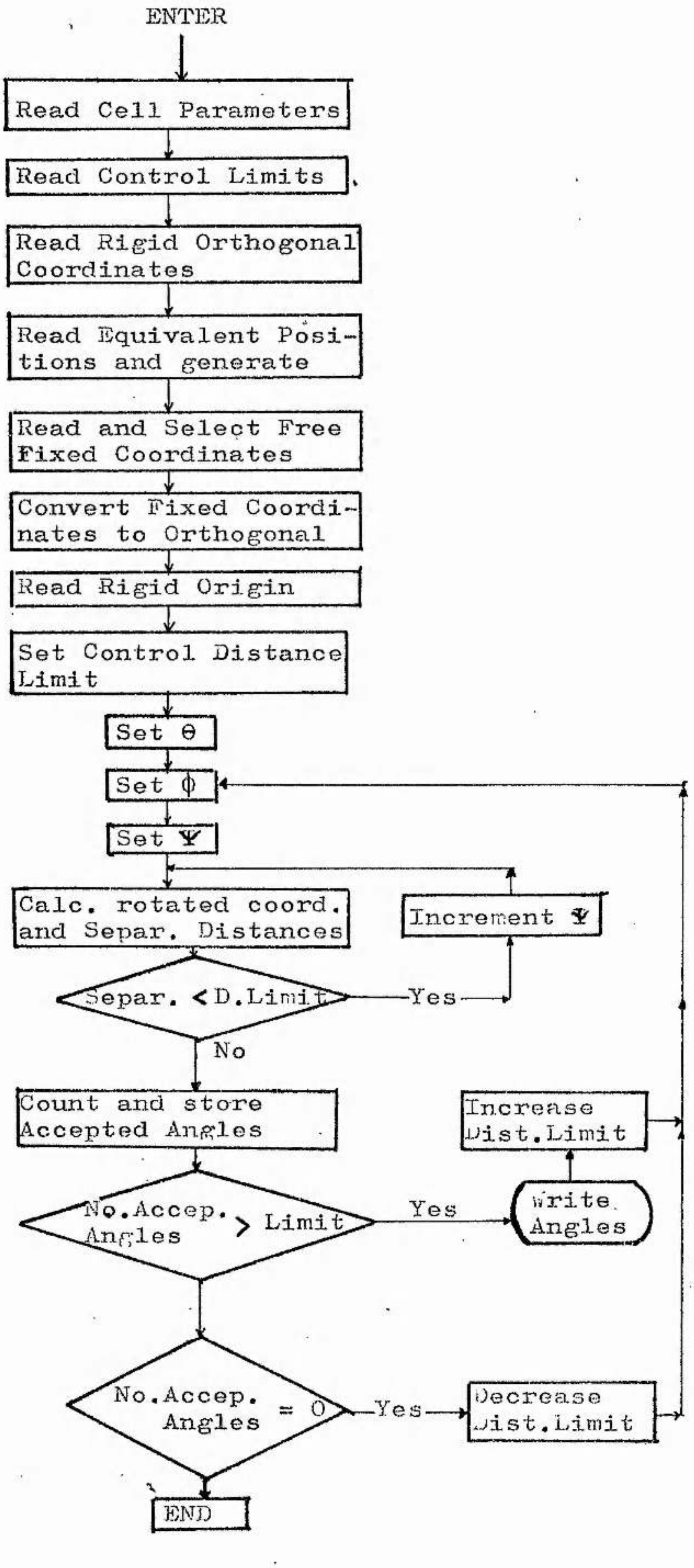
1.- Angular Lag,(1970) by Hulme R.,University of St. Andrews.
2.- Data reduction,"3DDP",Hulme R., " " " "
3.- Data reduction,"LIDRED",Liles D., " " " "
4.- Packing,"BFIT", Arroyo J., " " " "
5.- Patterson map,"PAT3D",Hulme R., " " " "
6.- Electron density map ,Hulme R., " " " "
7.- Stanley shift-parameter,Hulme R., " " " "
8.- Least Squares refinnement,Hulme R., " " "
9.- Multiple calculations,"SHELX",Sheldrick G.,University of Cambridge.
10.- Mean Plane,"YOPLAN",Hulme R., University of St Andrews.
11.- Bond distances-angles,"BONDANG",Hulme R., Univ. of St. Andrews.
12.- Molecule plots,"PAMOLE",Adamson P.,Univ. of St. Andrews.
13.- " " "STEREO",Hulme R., " " "
14.- " " "PLUTO",Clegg B.,University of Newcastle.

APPENDIX A

COMPUTING PROGRAM TO CALCULATE THE BEST FIT OF A RIGID MOLECULE IN A TRICLINIC CELL WHEN SOME ATOMIC POSITIONS ARE KNOWN.

FORTRAN IV FOR HONEYWELL/TSS.

FLOW DIAGRAM TO CALCULATE THE BEST FIT OF A RIGID MOLECULE IN A TRICLINIC CELL



```
c  Calculation of the best fit of a rigid molecule in a
c  triclinic cell. Some atoms in fixed position.
c  axis  a vertical,b down,c across
       dimension at(100),x(100),y(100),z(100)
       dimension xo(100),yo(100),zo(100)
       dimension xk(100),yk(100),zk(100)
       dimension xj(100),yj(100),zj(100)
       dimension xi(100),yi(100),zi(100),ist(36)
       dimension xl(4),yl(4),zl(4),xs(2),ys(2),zs(2)
        dimension att(20),xv(20),yv(20),zv(20)
C  Read cell dimensions,distance limit and delta
        read(5,1) a,b,c,alph,bet,gam,ral,nv,dlim,del
    1   format(3f7.3,4f7.2,i4,2f10.7)
c  Read initial distance-limit control and variation of
c  rotation angles
        read(5,5) tt,nph,nth,nps
    5   format(f7.2,3i3)
        ico=1
        rad=1./57.296
        al=alph*rad
        be=bet*rad
        ga=gam*rad
        ra=ral*rad
        ca=cos(al)
        cb=cos(be)
        cg=cos(ga)
        cra=cos(ra)
        sa=sin(al)
        sb=sin(be)
        sg=sin(ga)
        sra=sin(ra)
        bsg=b*sg
        abcg=a+b*cg
        it=0
        il=0
c  read coordinates cln and carbons in orthog. space(in A)
        do 55 jj=1,nv
   55   read(5,11) att(jj),xv(jj),yv(jj),zv(jj)
   11   format(a3,3f7.4)
        write(6,4)
    4   format(/,'  input coordinates ',/)
c  Read shifts to generate equivalent positions
        read(5,3)(xl(j),yl(j),zl(j),j=1,4)
    3   format(12f5.2)
        i=0
c  Read fractional triclinic coordinates of fixed atoms
    9   read(5,7) at(1),xs(1),ys(1),zs(1)
        if(xs(1).gt.9.0) go to 30
    7   format(a3,3f7.4)
        write(6,22) at(1),xs(1),ys(1),zs(1)
   22   format(2x,a3,3f7.4)
        xs(2)=1.-xs(1)
        ys(2)=1.-ys(1)
        zs(2)=1.-zs(1)
   15   do 25 k=1,2
        if(zs(k)*zs(k).gt.0.292) go to 25
```

```
570         do 20 j=1,4
580         i=i+1
590         x(i)=xs(k)+xl(j)*sign(1.0,(0.5-xs(k)))
600         y(i)=ys(k)+yl(j)*sign(1.0,(0.5-ys(k)))
610      20 z(i)=zs(k)
620      25 continue
630         if(zs(2).lt.0.0) go to 9
640         zs(1)=zs(1)-1.
650         zs(2)=zs(2)-1.
660         go to 15
670      30 nf=i+1
680         m=i
690         read(5,7) at(nf),x(nf),y(nf),z(nf)
700         write(6,22) at(nf),x(nf),y(nf),z(nf)
710         write(6,333) m
720   333   format(/,2x,' number of fixed atoms =',i4,/)
730         do 31 j=1,nf
740         x(j)=x(j)*a
750         y(j)=y(j)*b
760      31 z(j)=z(j)*c
770c  convert coord. of fixed atoms into orthog. coord.
780         do 201 l=1,nf
790         xo(l)=x(l)+y(l)*cg+z(l)*cb
800         yo(l)=y(l)*sg-z(l)*sb*cra
810     201 zo(l)=z(l)*sb*sra
820c  rotate rigid molecule
830         write(6,16)
840     16  format(/,2x,' rotation about axes ',/)
850         write(6,18)
860     18  format(2x,'   A     B     C  ',/)
870     399 continue
880         dslim=dlim*dlim
890         t=1.+tt
900         tt=tt*tt
910         inst=0
920         write(6,398) dlim,del,ico,tt,t,inst
930   398   format(/,1x,' dlimt = ',f9.7,1x,' delt = ',f8.6,' cycles=',
940              & i8,'ico=',i6,' tt=',f9.5,'  t=',f9.5,'  inst=',i8,/)
950          moo=0
960c  rotate about A an angle theta
970         do 440 k=moo,350,nth
980         ak=k
990         ph=ak*rad
1000         cph=cos(ph)
1010         sph=sin(ph)
1020         do 310 l=1,nv
1030         xk(l)=xv(l)
1040         yk(l)=yv(l)*cph-zv(l)*sph
1050     310 zk(l)=yv(l)*sph+zv(l)*cph
1060c  rotate about B an angle phi
1070         do 400 j=moo,350,nph
1080         aj=j
1090         th=aj*rad
1100         cth=cos(th)
1110         sth=sin(th)
```

```
      do 320 l=1,nv
      xj(l)=xk(l)*cth+zk(l)*sth
      yj(l)=yk(l)
  320 zj(l)=zk(l)*cth-xk(l)*sth
      nst=0
c rotate about C an angle psi
      do 500 i=moo,350,nps
      ai=i
      ps=ai*rad
      cps=cos(ps)
      sps=sin(ps)
      do 330 l=1,nv
      xi(l)=xj(l)*cps-yj(l)*sps+xo(nf)
      yi(l)=yj(l)*cps+xj(l)*sps+yo(nf)
  330 zi(l)=zj(l)+zo(nf)
      do 340 kk=1,nv
      do 510 ii=2,m
      pa=xi(kk)-xo(ii)
      pb=yi(kk)-yo(ii)
      pc=zi(kk)-zo(ii)
      ico=ico+1
      d=pa*pa+pb*pb+pc*pc
      if(d.lt.dslim) go to 500
  510 continue
      sxx=abcg-xi(kk)
      syy=bsg-yi(kk)
      szz=-zi(kk)
      do 360 ll=kk,nv
      qx=sxx-xi(ll)
      qy=syy-yi(ll)
      qz=szz-zi(ll)
      d=qx*qx+qy*qy+qz*qz
      if(d.lt.dslim) go to 500
  360 continue
  340 continue
      nst=nst+1
      ist(nst)=i
  500 continue
      if(nst.gt.0) write(6,10) k,j,(ist(i),i=1,nst)
   10 format(1x,2i4,2x,36i3)
      inst=inst+nst
      if(inst.gt.t) go to 700
      if(inst.eq.0.and.j.gt.10) go to 750
  400 continue
  440 continue
      write(6,12) ico
   12 format(1x,' all job finished ',' rounds =',i8,/)
      go to 999
  700 if(it.gt.0) del=0.5*del
      il=1
      dlim=dlim+del
      go to 399
  750 if(il.gt.0) del=0.5*del
      it=1
      dlim=dlim-del
      go to 399
  999 stop
      end
```

APPENDIX B

OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS(x5) FOR (1:1) $SbCl_3$.1-BROMONAPHTHALENE COMPLEX.

Scale=5 F(000)= 816

h	k	l	F$_o$	F$_c$	h	k	l	F$_o$	F$_c$	h	k	l	F$_o$	F$_c$
8	-2	0	542.4	509.8	3	2	0	388.5	-353.2	4	-6	-1	377.5	310.9
8	-1	0	501.7	457.0	3	1	0	809.9	920.8	4	-5	-1	329.1	-239.5
7	-5	0	594.8	-593.2	4	7	0	460.2	-554.1	4	-4	-1	400.7	284.8
7	-4	0	484.6	-362.9	4	4	0	422.5	-401.0	4	-1	-1	663.9	636.3
7	-1	0	425.0	-258.6	4	2	0	697.4	-578.0	4	0	-1	627.3	527.5
6	-8	0	507.3	460.1	4	1	0	738.7	-686.0	4	1	-1	661.1	-715.2
6	-7	0	524.1	572.3	4	0	0	384.6	-314.5	4	2	-1	278.0	216.2
6	-4	0	363.1	178.1	5	4	0	516.1	585.8	4	3	-1	314.1	226.1
5	-4	0	737.8	-656.3	5	2	0	785.4	-743.7	4	7	-1	409.7	-375.3
5	-2	0	836.5	738.0	5	1	0	413.3	-229.8	4	9	-1	503.6	535.4
4	-8	0	482.1	-393.7	6	7	0	502.9	-524.3	3	-9	-1	350.0	-336.5
4	-7	0	445.8	454.4	6	3	0	410.5	296.2	3	-7	-1	398.0	-327.5
4	-6	0	366.4	-270.3	6	2	0	450.5	405.4	3	-6	-1	332.5	377.1
4	-4	0	688.8	-497.1	6	1	0	540.8	-479.3	3	-4	-1	704.3	-762.7
4	-3	0	347.9	-228.0	6	0	0	387.6	177.9	3	-3	-1	653.4	-975.4
4	-2	0	690.9	-575.0	7	5	0	483.7	-535.2	3	-2	-1	497.5	358.7
4	-1	0	782.9	720.3	7	4	0	478.2	440.7	3	1	-1	314.9	179.4
3	-7	0	451.6	372.8	7	2	0	454.4	-306.3	3	2	-1	281.3	-243.3
3	-6	0	477.9	501.6	7	1	0	483.3	-479.1	3	3	-1	974.2	-1167.0
3	-5	0	444.7	444.5	10	-2	-1	466.9	477.3	3	4	-1	657.4	660.0
3	-4	0	738.7	-760.2	10	2	-1	428.7	497.6	3	5	-1	523.2	-397.2
3	-3	0	495.5	-339.4	9	-5	-1	458.1	-405.5	3	6	-1	562.6	-458.0
3	-2	0	333.8	270.6	9	-1	-1	432.4	-390.0	3	7	-1	317.8	-365.4
3	-1	0	914.8	919.7	8	-1	-1	447.7	423.9	2	-6	-1	815.6	928.2
2	-8	0	627.4	-628.4	8	0	-1	364.8	-373.2	2	-5	-1	398.6	-310.5
2	-6	0	638.5	565.3	8	1	-1	417.8	-358.3	2	-4	-1	658.0	601.4
2	-5	0	408.4	-374.5	7	-4	-1	450.4	-414.5	2	-2	-1	465.0	-359.4
2	-2	0	825.8	-824.1	7	-3	-1	329.5	296.0	2	-1	-1	558.1	610.8
2	-1	0	649.3	690.7	7	-2	-1	373.2	250.6	2	0	-1	853.4	1000.9
1	-9	0	663.2	-728.4	7	1	-1	301.8	224.5	2	1	-1	540.9	-669.4
1	-7	0	450.5	-406.1	7	2	-1	324.3	-251.7	2	3	-1	274.9	204.3
1	-6	0	315.3	274.8	7	3	-1	454.8	499.0	2	4	-1	496.7	438.3
1	-5	0	556.7	383.0	7	4	-1	423.9	415.0	2	5	-1	304.9	313.3
1	-3	0	988.4	-1291.9	6	-7	-1	501.5	563.5	2	6	-1	653.4	727.1
1	-2	0	378.8	279.5	6	-6	-1	391.9	-291.5	2	7	-1	372.7	-316.5
1	-1	0	438.9	332.8	6	-5	-1	325.8	-306.2	1	-10	-1	361.7	-349.5
0	10	0	510.7	530.1	6	-4	-1	591.7	-592.5	1	-8	-1	333.7	-193.6
0	6	0	854.0	875.5	6	-3	-1	405.3	-361.1	1	-5	-1	806.6	868.0
1	9	0	423.4	-470.9	6	-2	-1	504.0	-356.3	1	-3	-1	846.0	-934.6
1	6	0	319.2	-270.8	6	-1	-1	496.1	438.1	1	-2	-1	273.4	164.6
1	5	0	493.6	484.0	6	0	-1	512.3	-439.7	1	-1	-1	297.0	176.4
1	3	0	990.8	-1246.8	6	1	-1	496.5	-407.2	1	2	-1	322.8	-262.3
1	2	0	322.9	-270.8	6	2	-1	297.0	-131.2	1	3	-1	584.3	-555.0
1	1	0	451.1	412.9	6	3	-1	430.7	365.5	1	5	-1	568.7	465.3
2	8	0	452.1	-482.2	6	4	-1	554.9	-486.4	0	8	1	641.1	-747.7
2	7	0	357.4	-297.4	6	7	-1	474.2	-496.4	0	4	1	694.8	-752.8
2	6	0	477.0	471.1	5	-5	-1	453.9	308.0	0	2	1	826.9	-1002.2
2	5	0	383.7	355.3	5	-4	-1	530.7	-551.5	0	-4	1	891.8	-942.4
2	2	0	786.3	-953.1	5	-2	-1	763.0	793.7	0	-8	1	467.9	-516.0
2	1	0	582.8	-646.5	5	2	-1	695.2	-712.2	1	10	1	365.0	316.4
2	0	0	610.1	671.2	5	3	-1	293.2	199.6	1	6	1	303.2	-243.5
3	7	0	392.2	331.2	5	4	-1	546.4	587.4	1	4	1	238.3	194.5
3	6	0	425.7	-390.3	5	5	-1	515.9	461.9	1	3	1	490.4	-420.6
3	5	0	458.1	451.1	5	6	-1	368.3	-291.8	1	2	1	304.1	-221.4
3	4	0	740.4	714.6	4	-9	-1	398.2	-516.1	1	1	1	641.5	735.9
3	3	0	342.1	-210.5	4	-7	-1	478.7	529.4	1	-2	1	339.6	244.4

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	-3	1	287.6	128.8	5	-9	1	416.1	-338.7	2	-4	2	958.7	983.1
1	-5	1	990.7	1046.0	6	7	1	476.4	-480.6	2	-3	2	477.3	-401.7
1	-9	1	481.2	375.3	6	6	1	407.4	-313.2	2	-2	2	435.4	369.3
1	-11	1	490.6	623.3	6	5	1	390.3	410.7	8	0	-2	596.7	-623.1
2	8	1	500.0	-571.7	6	3	1	330.2	270.5	7	5	-2	517.4	-522.7
2	7	1	305.5	-323.7	6	1	1	560.3	-469.6	7	-3	-2	452.9	519.7
2	6	1	654.9	667.3	6	-1	1	477.3	388.7	7	-4	-2	465.7	-385.7
2	5	1	359.6	338.3	6	-3	1	509.8	-413.7	6	3	-2	450.0	417.0
2	2	1	847.3	-1026.2	6	-7	1	444.9	446.6	6	2	-2	539.1	524.3
2	1	1	521.9	-585.0	6	-9	1	434.9	-376.8	6	-1	-2	472.8	429.5
2	0	1	280.9	156.4	7	4	1	450.8	387.4	6	-2	-2	446.1	441.3
2	-1	1	660.7	689.4	7	3	1	553.5	594.6	6	-4	-2	387.9	354.5
2	-2	1	578.5	-541.7	7	2	1	397.4	-319.5	6	-5	-2	403.3	-376.1
2	-3	1	333.1	-276.5	7	-1	1	413.4	271.9	6	-7	-2	466.6	513.7
2	-4	1	250.9	-171.3	7	-3	1	634.2	566.8	5	5	-2	445.5	-440.9
2	-5	1	338.7	-226.9	7	-4	1	400.3	-320.8	5	4	-2	650.4	583.2
2	-6	1	275.7	179.8	7	-5	1	322.4	-281.3	5	2	-2	562.8	-553.9
2	-7	1	327.4	326.3	7	-6	1	371.9	328.9	5	0	-2	357.0	-257.2
2	-8	1	575.6	-577.8	7	-7	1	404.2	396.9	5	-1	-2	805.8	-724.9
3	7	1	317.4	-258.5	8	0	1	657.8	-577.0	5	-2	-2	724.4	724.2
3	4	1	698.1	805.0	8	-1	1	543.9	473.1	5	-3	-2	472.2	-318.1
3	3	1	677.4	-728.4	8	-4	1	478.3	-347.9	5	-4	-2	476.7	-481.2
3	2	1	493.1	-410.0	8	-6	1	469.4	-385.0	4	3	-2	398.6	329.8
3	1	1	453.3	407.2	9	3	1	412.8	450.2	4	1	-2	706.9	-679.0
3	-1	1	435.5	337.1	9	-3	1	438.5	452.2	4	0	-2	528.7	414.1
3	-2	1	240.6	176.6	10	-2	1	466.9	505.9	4	-1	-2	622.5	567.6
3	-3	1	954.4	-972.8	3	-1	-2	801.3	800.8	4	-7	-2	490.3	611.2
3	-4	1	611.9	-601.6	3	-2	-2	465.7	403.6	3	6	-2	528.4	-554.1
3	-6	1	671.8	571.5	3	-3	-2	521.5	-402.4	3	5	-2	290.5	403.8
4	7	1	542.6	-583.1	3	-4	-2	727.1	-756.5	3	4	-2	538.5	535.7
4	6	1	404.7	486.6	3	-5	-2	460.1	428.1	3	3	-2	390.0	-334.8
4	5	1	355.2	270.5	2	8	-2	666.2	-735.9	3	1	-2	708.0	699.7
4	4	1	435.6	460.6	2	7	-2	363.5	-340.5	2	-1	2	614.8	675.3
4	2	1	289.0	220.9	2	3	-2	437.8	335.6	2	0	2	707.2	821.3
4	1	1	650.9	-618.2	2	2	-2	718.1	-823.9	2	1	2	374.2	-370.0
4	0	1	938.5	973.1	2	1	-2	599.0	-630.9	2	2	2	342.4	-197.6
4	-1	1	714.6	725.8	2	-1	-2	463.6	456.3	2	6	2	765.4	858.7
4	-2	1	583.7	492.2	2	-2	-2	1115.2	-1297.0	3	-5	2	430.4	290.2
4	-3	1	403.6	-270.2	2	-4	-2	684.6	-607.5	3	-4	2	548.0	-522.2
4	-4	1	386.9	185.5	2	-5	-2	321.1	-357.3	3	-3	2	700.6	-593.2
4	-6	1	454.7	291.9	1	-1	-2	594.6	548.2	3	1	2	526.0	402.9
4	-7	1	356.2	357.3	1	-3	-2	698.8	-588.8	3	2	2	578.6	-585.9
4	-9	1	489.8	-548.7	1	-5	-2	953.1	1037.7	3	3	2	426.5	-440.5
4	-10	1	386.1	344.4	0	-6	2	419.7	356.0	3	4	2	606.8	638.7
5	4	1	426.0	406.3	0	-4	2	346.0	-266.9	4	-6	2	369.8	-266.4
5	3	1	371.9	-390.4	0	2	2	316.0	182.8	4	-3	2	472.2	-388.8
5	2	1	715.8	-737.6	0	4	2	357.6	-256.6	4	-2	2	354.9	-283.8
5	1	1	553.2	-522.8	0	6	2	473.7	550.6	4	-1	2	758.5	723.8
5	0	1	394.4	259.6	0	8	2	443.7	-413.2	4	1	2	448.2	-428.4
5	-1	1	248.6	-133.4	1	-7	2	867.5	-911.3	4	2	2	541.1	-461.1
5	-2	1	689.1	589.2	1	-3	2	911.5	-919.4	4	7	2	440.5	-573.3
5	-3	1	257.9	-153.6	1	1	2	412.8	-417.6	5	-4	2	746.4	-691.1
5	-4	1	731.5	-690.1	1	2	2	274.4	-160.5	5	-3	2	778.4	718.1
5	-5	1	763.2	-372.8	1	3	2	1061.2	-1358.4	5	-2	2	460.1	366.2
5	-6	1	386.3	279.7	2	-7	2	412.8	358.5	5	0	2	489.2	471.0
5	-7	1	375.7	-171.6	2	-6	2	580.3	535.1	5	-1	2	583.0	443.2

h	K	l	F_o	F_c	h	K	l	F_o	F_c	h	K	l	F_o	F_c
5	2	2	666.8	-635.6	0	2	3	376.8	382.6	2	-4	5	585.0	577.3
5	4	2	459.8	397.1	0	8	3	556.9	-630.9	2	-3	5	601.7	-533.9
5	5	2	521.5	550.5	1	-7	3	533.1	-533.5	2	-2	5	467.9	-306.7
6	-4	2	528.1	-482.1	1	-5	3	700.6	729.8	2	-1	5	530.1	503.3
6	-3	2	547.4	-404.3	1	-3	3	206.6	151.0	2	0	5	512.3	436.4
6	0	2	493.9	-431.6	1	1	3	405.2	430.0	2	4	5	668.4	-699.4
6	1	2	518.9	-488.6	1	2	3	256.5	-200.4	3	-8	5	486.9	-485.9
7	-5	2	687.6	-726.2	1	3	3	350.3	-324.1	3	-6	5	617.8	576.1
7	1	2	548.0	-411.6	1	4	3	307.1	101.4	3	-5	5	945.3	989.6
8	-2	2	739.5	732.0	1	5	3	561.2	677.7	3	-1	5	430.6	-365.8
8	2	-3	579.7	597.3	2	-8	3	766.2	-791.0	3	0	5	408.3	324.3
8	-4	-3	461.2	427.7	2	-7	3	388.1	307.3	3	1	5	680.0	764.7
7	5	-3	493.7	-621.3	2	-6	3	682.6	-643.1	3	2	5	678.0	-700.7
7	3	-3	406.3	99.7	2	-4	3	293.7	151.1	4	-8	5	459.2	-329.1
7	-1	-3	518.6	-474.3	2	-3	3	531.7	-505.2	4	-3	5	612.7	-640.9
7	-3	-3	394.8	303.5	2	-2	3	666.5	-666.6	4	-2	5	857.6	-810.6
7	-4	-3	454.5	-393.2	2	-1	3	552.3	614.5	4	-1	5	597.2	552.8
6	3	-3	447.6	451.4	2	0	3	284.1	-196.5	5	-6	5	654.4	619.3
6	-1	-3	458.8	444.6	2	1	3	254.6	-228.0	5	-4	5	562.9	-487.2
5	4	-3	595.5	592.9	2	2	3	774.5	-852.0	5	0	5	746.8	742.8
5	3	-3	596.3	661.5	2	4	3	514.8	-550.8	6	-3	5	450.9	-432.2
5	2	-3	396.4	-330.3	3	-9	3	423.7	326.6	6	-1	5	413.6	332.2
5	1	-3	343.8	257.6	3	-6	3	673.2	707.5	2	1	-5	520.3	-506.4
5	0	-3	436.6	-469.6	3	-5	3	556.4	558.5	2	-2	-5	429.4	-323.8
5	-2	-3	628.7	682.1	3	-4	3	366.6	-354.2	2	-3	-5	367.1	227.5
5	-3	-3	377.9	386.3	3	0	3	262.4	181.8	2	-4	-5	655.6	-669.6
5	-5	-3	415.7	366.1	3	1	3	695.5	735.8	1	5	-5	627.3	487.2
4	6	-3	429.3	-481.3	3	2	3	559.0	-532.4	1	4	-5	349.6	247.5
4	4	-3	318.1	-238.3	3	3	3	335.8	318.5	1	-1	-5	647.6	580.3
4	3	-3	428.5	417.0	3	4	3	441.9	566.9	1	-3	-5	802.8	-814.9
4	2	-3	631.7	-594.5	4	-9	3	482.1	-535.9	0	-6	5	736.7	710.8
4	1	-3	637.6	-678.2	4	-6	3	369.8	-286.6	0	-4	5	941.1	1158.4
4	0	-3	387.0	-429.8	4	-3	3	590.1	-525.1	0	0	5	575.4	730.2
4	-1	-3	398.5	314.7	4	-1	3	623.6	591.3	0	2	5	791.8	939.0
4	-2	-3	531.7	-377.3	4	1	3	389.7	-348.1	0	6	5	499.4	604.8
5	5	-3	365.8	345.0	4	8	3	532.0	-113.3	1	-7	5	877.9	-1027.6
3	6	-3	566.3	-639.5	5	-9	3	524.5	-167.5	1	-5	5	316.2	205.7
3	5	-3	325.6	273.3	5	-6	3	486.7	486.6	1	-4	5	280.7	-207.6
3	4	-3	426.7	407.0	5	-5	3	417.0	-306.7	1	0	5	272.4	191.9
3	3	-3	453.2	-435.9	5	-4	3	715.3	-649.9	1	1	5	521.2	427.6
3	1	-3	328.6	-274.1	5	-1	3	415.9	-295.5	1	3	5	845.4	-974.1
3	-1	-3	511.9	510.8	5	0	3	616.9	618.6	2	-9	5	450.0	-258.8
3	-2	-3	515.4	532.6	5	1	3	589.6	-533.0	2	-8	5	466.4	-444.2
3	-4	-3	513.5	-587.0	5	2	3	415.1	-536.3	2	-7	5	384.1	269.1
2	4	-3	802.9	946.9	5	3	3	530.4	-397.9	2	-5	5	344.5	283.0
2	3	-3	446.2	441.1	6	-6	3	467.4	365.5	6	3	-5	541.2	476.6
2	1	-3	550.5	-588.2	6	-5	3	391.3	323.4	6	2	-5	488.4	358.1
2	0	-3	647.2	609.4	6	-4	3	420.8	344.8	6	-2	-5	627.9	599.2
2	-1	-3	263.4	238.7	6	-3	3	448.4	-382.9	5	7	-5	524.8	-461.9
2	-6	-3	670.3	807.2	6	-2	3	522.1	552.6	5	6	-5	515.8	-590.0
1	-1	-3	498.2	-422.3	6	-1	3	389.1	308.3	5	4	-5	627.3	560.5
1	-3	-3	843.7	-1055.4	6	1	3	439.8	-341.5	5	0	-5	728.9	-766.0
1	-9	-3	470.1	-731.7	6	2	3	452.1	434.0	5	-2	-5	427.3	451.3
0	-6	3	351.9	319.6	7	-6	3	457.7	359.6	4	3	-5	671.4	680.1
0	-4	3	503.0	537.5	7	1	3	414.6	-471.8	4	2	-5	566.2	-537.0
0	-2	3	164.0	-462.0	7	2	3	424.0	-390.3	4	1	-5	584.7	-552.2

h	k	l	F_o	F_c
4	0	-5	356.1	-278.8
4	-2	-5	423.5	-219.8
3	8	-5	402.3	387.1
3	6	-5	711.3	-629.0
3	5	-5	942.3	1036.2
3	4	-5	297.7	245.9
3	0	-5	348.1	-283.8
3	-1	-5	826.1	863.3
3	-2	-5	681.8	644.4
3	-3	-5	419.9	191.3
2	8	-5	643.1	-648.5
2	7	-5	316.2	-329.1
2	6	-5	352.5	-288.1
2	5	-5	290.3	-261.3
2	4	-5	574.8	366.8
2	3	-5	603.7	531.0
2	2	-5	759.6	-728.6
7	0	-6	477.6	-330.5
6	4	-6	464.8	-342.8
6	1	-6	497.9	-385.9
6	0	-6	545.5	-421.5
5	6	-6	539.8	-524.6
5	5	-6	436.7	300.7
5	4	-6	461.7	533.6
5	1	-6	409.7	355.9
5	0	-6	647.9	-658.4
5	-1	-6	410.3	221.6
5	-2	-6	451.2	529.8
4	3	-6	635.4	604.8
4	2	-6	507.3	-383.3
4	1	-6	584.7	-602.0
4	-5	-6	499.6	-554.3
3	8	-6	489.4	428.2
3	7	-6	490.8	-492.6
3	6	-6	594.9	-495.3
3	5	-6	434.7	301.2
3	3	-6	734.8	-688.8
3	1	-6	849.1	-966.2
3	0	-6	404.9	-337.3
3	-1	-6	337.3	345.8
3	-2	-6	595.9	651.3
3	-3	-6	394.1	-309.1
2	5	-6	388.0	-264.4
2	4	-6	827.1	904.6
2	1	-6	382.3	-335.7
2	0	-6	780.4	859.2
2	-2	-6	642.2	625.9
2	-3	-6	374.8	335.7
2	-4	-6	451.9	-391.3
1	7	-6	1010.6	-959.6
1	5	-6	513.1	378.9
1	0	-6	339.4	-291.6
1	-1	-6	781.5	721.0
1	-3	-6	568.9	-674.0
0	-8	6	601.0	-522.7
0	0	6	411.0	-200.8
0	2	6	374.5	308.4
0	4	6	565.5	-636.9
1	-9	6	546.2	651.8
1	-5	6	820.0	1016.7
1	1	6	852.4	1135.6
2	-8	6	517.5	-500.7
2	-6	6	592.9	-590.6
2	-5	6	352.2	278.5
2	-3	6	572.9	-607.4
2	-2	6	633.8	-664.9
2	-1	6	312.6	251.5
2	0	6	312.0	188.5
2	3	6	521.5	-427.3
3	-8	6	464.8	-539.9
3	-7	6	471.2	-367.1
3	-6	6	596.6	572.5
3	-5	6	509.4	436.3
3	-1	6	640.8	-585.3
3	0	6	528.6	538.2
3	2	6	483.3	-537.4
4	-5	6	380.3	296.3
4	-4	6	457.3	336.8
4	-3	6	656.1	-644.3
4	-1	6	457.0	424.6
4	0	6	438.4	393.4
5	-6	6	541.5	590.5
5	-5	6	442.1	-418.9
5	-4	6	472.2	-395.3
5	-2	6	466.4	-425.2
5	0	6	686.8	597.5
7	-7	6	602.3	655.7

REFLECTIONS NOT USED IN REFINEMENT

h	k	l	Fo	Fc
6	-3	0	468.5	-355.0
6	-2	0	502.2	377.5
3	-9	0	475.6	91.7
0	4	0	291.3	-34.9
9	0	0	562.5	-44.3
5	1	-1	448.1	249.6
2	2	-1	198.7	92.8
2	-10	1	349.1	192.8
8	2	2	661.7	252.1
6	-7	-2	466.6	513.7
3	-6	2	793.0	678.0

h	k	l	Fo	Fc
1	3	-3	566.6	-593.8
0	4	3	299.6	-39.1
4	0	3	301.2	-152.4
2	0	-5	265.8	122.8
2	3	-6	520.9	555.6
2	2	-6	574.3	-122.9
3	-9	6	447.9	10.4

NON OBSERVED REFLECTIONS FOR SBCL3.1-BROMONAPHTHALENE

BS=Back Stop, OR=Out of the observable Range
NA=Not Available

h	k	l	Fo	Fc	h	k	l	Fo	Fc		h	k	l	Fo	Fc	
1	0	0	137.4	4.4	5	6	0	391.5	-157.1		1	-1	-1	129.6	176.4	
3	0	0	240.5	-9.3	6	6	0	416.7	84.9		1	-4	-1	209.5	-125.1	
5	0	0	316.2	120.6	5	-7	0	398.0	-206.1		1	-6	-1	255.2	217.6	
7	0	0	384.4	-39.2	2	-7	0	350.2	267.0		1	-7	-1	277.1	-41.8	
8	0	0	417.6	-257.5	0	7	0	342.3	36.1		0	-7	1	260.2	24.2	
5	-1	0	316.9	17.1	1	7	0	347.0	-270.5		0	-6	1	237.5	56.7	
8	1	0	420.4	-278.4	5	7	0	411.9	156.2		0	-5	1	213.7	12.6	
7	-2	0	387.6	242.3	5	-8	0	418.8	-100.2		0	-3	1	159.2	-48.1	
8	2	0	426.2	252.4	3	-8	0	386.7	145.5		0	-2	1	125.0	-1381.9	BS
8	-3	0	425.5	37.7	0	8	0	370.1	-185.4		0	-1	1	77.6	2.7	
7	-3	0	394.1	46.5	1	8	0	374.5	41.1		0	0	1	59.3	696.6	BS
5	-3	0	331.9	113.1	3	8	0	396.9	-136.7		0	1	1	114.4	29.7	
2	-3	0	244.2	-178.4	5	8	0	433.6	25.4		0	3	1	180.9	13.3	
0	3	0	217.1	-5.1	2	-9	0	402.9	-177.8		0	5	1	231.4	17.7	
2	3	0	251.1	127.3	0	9	0	397.6	58.5		0	6	1	254.4	67.9	
5	3	0	340.3	6.2	2	9	0	410.0	145.9		0	7	1	276.5	24.8	
7	3	0	402.6	93.7	7	0	-1	300.3	-7.1		1	-7	1	261.3	118.8	
8	-4	0	433.6	124.0	7	-1	-1	301.2	75.9		1	-6	1	239.2	184.3	
2	-4	0	270.5	-30.9	5	0	-1	246.7	-37.2		1	-4	1	192.0	-93.3	
1	-4	0	255.9	-90.7	5	-3	-1	262.8	70.6		1	-1	1	114.6	462.4	BS
1	4	0	260.3	59.9	4	5	-1	265.5	128.8		1	0	1	112.7	109.1	
2	4	0	277.7	-102.7	4	4	-1	250.6	39.5		1	7	1	280.1	250.5	
6	4	0	384.2	52.2	4	-2	-1	228.9	54.8		2	3	1	205.1	-8.6	
8	4	0	444.9	139.2	4	-3	-1	239.8	-186.5		2	4	1	226.0	-10.8	
6	-5	0	387.2	-105.7	3	0	-1	187.4	2.7		3	-7	1	277.2	-89.7	
5	-5	0	360.6	180.2	3	-1	-1	192.2	41.1		3	-5	1	240.6	-140.4	
4	-5	0	336.1	-137.6	3	-5	-1	252.9	-97.7		3	0	1	190.7	4.5	
0	5	0	283.9	-1.9	2	-3	-1	198.3	18.9		3	5	1	261.3	61.5	
4	5	0	347.0	207.2	1	7	-1	264.0	-366.8	OR	3	6	1	279.9	-222.2	
5	5	0	372.4	67.4	1	6	-1	241.9	-138.8		4	-5	1	258.6	-24.5	
6	5	0	399.6	355.5	1	-4	-1	209.5	-125.1		4	3	1	248.3	126.7	
6	-6	0	402.6	142.5	1	1	-1	114.4	-139.8		5	5	1	298.0	-186.4	
5	-6	0	378.4	221.6	1	0	-1	107.7	-69.2		6	-2	1	277.8	159.0	

h	k	l	Fo	Fc
6	0	1	276.5	-72.0
6	2	1	286.7	-34.1
6	4	1	306.2	-127.9
7	-2	1	303.6	175.4
7	0	1	302.8	9.7
7	1	1	306.0	32.8
8	3	-2	433.0	-52.4
8	2	-2	426.5	235.3
8	1	-2	422.9	-413.7
8	-1	-2	423.8	293.1
8	-2	-2	428.9	72.2
8	-3	-2	436.3	88.9
7	4	-2	410.2	313.6
7	3	-2	400.1	287.3
7	2	-2	392.9	-147.5
7	1	-2	389.1	71.9
7	0	-2	388.2	-20.3
7	-1	-2	390.9	-288.6
7	-2	-2	396.5	247.1
6	5	-2	392.6	-41.9
6	4	-2	378.7	22.1
6	1	-2	354.9	-342.9
6	0	-2	354.0	160.8
6	-3	-2	374.5	-328.8
6	-4	-2	387.9	354.5
5	6	-2	381.9	-302.9
5	3	-2	334.4	-217.8
5	1	-2	319.6	-280.8
5	-5	-2	378.1	-133.9
5	-6	-2	397.7	138.8
5	-7	-2	418.8	-231.8
4	6	-2	356.7	-53.3
4	5	-2	335.9	-14.5
4	4	-2	317.2	160.7
4	2	-2	289.3	227.4
4	-2	-2	300.3	-186.6
4	-3	-2	316.3	-27.5
4	-4	-2	334.7	87.6
4	-5	-2	355.5	-214.4
4	-6	-2	377.5	203.2
3	7	-2	358.8	176.3
3	2	-2	251.6	-117.0
3	0	-2	242.9	-39.4
3	-6	-2	360.6	160.3
3	-7	-2	385.5	89.5
2	6	-2	315.4	-7.4
2	5	-2	288.1	151.0
2	4	-2	260.8	-93.4
2	0	-2	198.1	-236.7 BS
2	-3	-2	266.4	88.7
2	-6	-2	348.1	349.5 OR
2	-7	-2	375.1	250.4
2	-8	-2	401.8	-662.5 OR
1	8	-2	359.7	251.9
1	7	-2	331.5	-140.2
1	6	-2	302.3	-161.3
1	4	-2	239.7	74.4
1	3	-2	204.9	47.7
1	2	-2	167.8	-180.1
1	1	-2	137.8	566.4 BS
1	0	-2	145.5	-96.7
1	-2	-2	217.1	209.7
1	-4	-2	282.7	-58.3
1	-6	-2	341.3	289.1
1	-7	-2	369.2	161.8
1	-8	-2	397.1	144.6
0	-8	2	355.2	-262.2
0	-7	2	326.7	79.7
0	-5	2	265.2	2.6
0	-3	2	191.3	-59.6
0	-2	2	142.6	-645.3 BS
0	-1	2	65.6	-33.6
0	0	2	109.0	1114.2 BS
0	1	2	167.5	-52.7
0	3	2	247.4	-86.4
0	5	2	311.3	-72.6
0	7	2	368.9	-23.1
1	-8	2	356.7	-290.6
1	-6	2	299.4	149.1
1	-5	2	269.4	249.7
1	-4	2	237.3	-113.1
1	-2	2	168.4	234.3 BS
1	-1	2	144.9	-309.9 BS
1	0	2	156.5	144.9
1	4	2	287.8	214.9
1	5	2	317.5	250.5
1	7	2	373.6	-327.7
1	8	2	401.2	-57.0
2	-8	2	363.5	-158.7
2	-5	2	283.3	-142.3
2	3	2	276.5	-74.5
2	4	2	303.2	57.6
2	5	2	330.3	422.4
2	7	2	383.4	-228.9
2	8	2	410.2	-138.5
3	-7	2	351.1	-212.6
3	-6	2	793.0	678.0
3	-2	2	251.9	26.4
3	-1	2	246.8	-92.5
3	0	2	251.0	11.9
3	5	2	348.1	22.7
3	6	2	372.7	-206.9
3	7	2	397.7	-208.1
4	-5	2	329.1	39.3
4	-4	2	312.1	-139.3
4	0	2	289.9	-247.9
4	3	2	329.4	90.7
4	4	2	348.7	-77.3
4	5	2	369.8	354.3
4	6	2	392.0	-86.6
5	-6	2	372.7	362.0
5	-5	2	356.4	256.7
5	1	2	333.2	89.5
5	3	2	358.8	337.6
5	6	2	414.6	-158.1
6	-5	2	384.9	183.1
6	-2	2	359.7	67.0
6	-1	2	358.5	291.9
6	2	2	376.3	-71.2
6	3	2	388.8	115.8
6	4	2	403.6	166.4
6	5	2	420.6	374.8
7	-4	2	404.8	-175.3
7	-3	2	397.7	130.2
7	-2	2	393.5	106.4
7	-1	2	392.3	-39.6
7	0	2	394.7	91.2
7	2	2	408.7	-295.7
7	3	2	419.7	371.8
7	4	2	433.0	423.1
8	-1	2	426.2	394.4
8	0	2	428.6	-185.5
8	1	2	433.3	-43.2
7	2	-3	400.1	-67.8
7	1	-3	397.2	-110.8
7	0	-3	397.7	-157.2
7	-2	-3	408.7	275.6
6	4	-3	383.0	-157.4
6	2	-3	365.3	59.9
6	1	-3	362.1	-281.2
6	0	-3	363.1	-252.6
6	2	-3	365.3	59.9
6	-3	-3	388.1	-75.9
6	-4	-3	402.5	2.9
5	-1	-3	333.7	47.8
5	-4	-3	375.5	-332.8
4	5	-3	336.6	-120.0
4	-3	-3	330.2	-42.5
4	-4	-3	350.3	-141.9
4	-5	-3	372.3	-345.2
4	-6	-3	395.3	-78.3
3	2	-3	252.5	71.4
3	0	-3	250.6	-34.0
3	-3	-3	304.4	-86.0
3	-5	-3	353.5	111.6
3	-6	-3	379.0	126.0
3	-6	-3	379.0	126.0
2	6	-3	313.0	97.2
2	5	-3	284.6	-30.6
2	2	-3	207.7	119.0
2	-2	-3	254.9	-14.4
2	-3	-3	283.3	98.5
2	-4	-3	311.4	172.7
2	-5	-3	339.3	-326.4
1	7	-3	329.1	-1198.1 OR
1	6	-3	298.8	-124.7
1	5	-3	266.9	93.1

h	k	l	Fo	Fc
1	2	-3	157.0	-120.9
1	1	-3	136.1	-161.9 BS
1	0	-3	160.0	-192.7 BS
1	-2	-3	235.6	114.0
1	-4	-3	301.2	-158.8
1	-5	-3	331.5	120.1
1	-6	-3	360.7	181.2
1	-7	-3	389.1	-408.3 OR
0	-7	3	324.0	64.8
0	-5	3	259.4	12.6
0	-3	3	179.3	17.1
0	-1	3	48.0	92.9 BS
0	0	3	136.9	1416.1 BS
0	1	3	189.2	56.6
0	3	3	266.9	47.8
0	5	3	330.4	69.3
0	6	3	360.2	431.3 NA
0	7	3	389.1	14.3
1	-6	3	296.4	74.4
1	-4	3	231.3	-181.6
1	-2	3	162.7	123.2
1	-1	3	150.6	692.1 BS
1	0	3	173.4	110.3
1	6	3	365.6	-274.0
1	7	3	394.0	209.2
2	-5	3	281.1	-33.0
2	3	3	294.5	-206.0
2	5	3	349.5	313.1
2	6	3	376.5	249.6
3	-3	3	267.2	17.8
3	-2	3	257.0	16.4
3	-1	3	255.1	35.0
3	5	3	367.2	372.6 OR
3	6	3	392.4	0.2
4	-5	3	331.8	131.4
4	-4	3	315.7	-10.1
4	-2	3	296.7	-120.0
4	2	3	327.5	27.3
4	3	3	346.0	-139.0
4	4	3	366.4	81.0
4	5	3	388.6	314.3
5	-3	3	338.8	-29.2
5	-2	3	333.7	144.3
5	4	3	392.9	333.0
6	3	3	405.2	-11.7
6	4	3	421.0	237.3
7	-2	3	404.1	-9.2
7	-1	3	404.1	-51.0
6	2	5	399.0	282.5
6	1	5	386.2	-256.2
6	0	5	376.7	7.9
6	-2	5	367.1	168.7
5	2	5	368.6	-308.5
5	1	5	354.0	192.6
5	-1	5	335.0	165.3
5	-2	5	332.0	-191.4

h	k	l	Fo	Fc
5	-3	5	333.5	183.2
5	-5	5	349.6	144.6
4	3	5	358.8	-275.3
4	2	5	339.1	-269.1
4	1	5	321.8	-114.9
4	0	5	307.8	-351.1
4	-4	5	305.5	-210.5
4	-5	5	318.3	234.2
4	-6	5	335.0	-190.4
3	4	5	357.9	229.8
3	3	5	334.1	160.9
3	-2	5	254.8	-136.8
3	-3	5	258.7	41.3
3	-4	5	270.6	-207.5
3	-7	5	331.7	23.7
2	3	5	312.6	-224.4
2	2	5	285.8	-4.7
2	1	5	259.3	70.2
2	-6	5	286.7	-63.2
1	4	5	326.0	147.2
1	2	5	265.8	-247.0
1	-1	5	166.6	-756.1 BS
1	-2	5	152.6	-87.1
1	-3	5	171.6	-295.1 PS
1	-6	5	271.2	30.3
0	5	5	348.7	-27.2
0	4	5	319.2	32.8
0	3	5	288.5	-23.9
0	1	5	218.4	-22.6
0	-1	5	119.2	-34.0
0	-2	5	58.7	-590.0 BS
0	-3	5	138.9	-24.4
0	-5	5	230.4	27.8
0	-7	5	298.0	-17.0
0	-8	5	328.4	-81.8
1	-4	-5	319.8	-93.3
1	-2	-5	257.5	164.1
1	0	-5	184.5	-127.9
1	1	-5	145.4	-546.0 BS
1	2	-5	131.1	68.9
1	3	-5	162.4	-66.6
1	6	-5	271.8	-51.8
1	7	-5	303.1	-748.9 OR
2	-5	-5	355.2	-335.1
2	-1	-5	243.2	-64.5
3	-4	-5	342.1	-346.9 OR
3	1	-5	243.2	-168.3
3	2	-5	241.7	108.6
3	3	-5	250.3	47.7
4	-4	-5	360.9	-336.5
4	-3	-5	339.7	259.7
4	-1	-5	303.4	151.0
4	4	-5	301.3	-81.9
4	5	-5	317.4	-204.4
4	6	-5	336.4	-340.7 OR
5	-3	-5	365.0	-23.7

h	k	l	Fo	Fc
5	-1	-5	335.5	-35.7
5	1	-5	320.9	-51.7
5	2	-5	320.9	6.1
5	3	-5	325.7	80.6
5	5	-5	348.7	1.0
6	-1	-5	367.7	315.4
6	0	-5	360.3	114.9
6	1	-5	356.4	-322.0
6	3	-6	433.0	397.3
6	2	-6	429.6	-280.8
6	-1	-6	448.2	292.3
6	-2	-6	462.7	-258.8
5	3	-6	390.1	255.2
5	2	-6	386.3	242.1
5	-3	-6	448.9	105.0
4	6	-6	397.5	2.9
4	5	-6	375.2	-303.6
4	4	-6	357.3	111.1
4	0	-6	355.6	217.1
4	-1	-6	373.2	-46.1
4	-2	-6	394.8	195.4
4	-3	-6	419.5	187.2
3	4	-6	313.0	183.2
3	2	-6	290.0	120.8
3	-4	-6	424.5	-182.6
2	7	-6	369.4	-176.8
2	6	-6	335.0	92.0
2	-1	-6	306.2	-19.9
1	6	-6	314.0	-95.8
1	4	-6	225.8	115.4
1	3	-6	177.1	-295.3 NA
1	2	-6	154.1	-31.0
1	1	-6	191.3	-450.0 BS
1	-2	-6	325.8	-2.9
1	-4	-6	400.2	-240.6
0	-7	6	346.8	31.7
0	-6	6	306.6	15.4
0	-5	6	261.6	113.5
0	-4	6	208.9	572.4 PS
0	-3	6	139.6	78.5
0	-2	6	81.5	-1257.2 BS
0	-1	6	172.7	69.3
1	-7	6	352.2	-275.1
1	-6	6	314.7	65.4
1	-4	6	233.9	-184.0
1	-3	6	197.7	303.1 PS
1	-2	6	188.9	-61.0
1	-1	6	216.7	155.2
1	0	6	257.2	231.9
1	2	6	336.3	-161.4
1	3	6	372.8	-136.5
2	-7	6	368.4	95.9
2	-4	6	277.5	91.8
2	1	6	326.5	22.9
2	2	6	358.6	89.3
3	-4	6	322.8	-7.8

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
3	-3	6	312.0	-180.1	4	-6	6	398.8	248.5	5	-3	6	403.6	-352.8
3	-2	6	311.0	-32.0	4	-2	6	359.3	99.5	5	-1	6	409.7	-121.1
3	1	6	361.3	347.7										

FOURTH LAYER

This layer was omitted in refinement due to poor
Fo & Fc agreement.

h	k	l	Fo	Fc
8	0	-4	500.8	-620.7
7	3	-4	466.8	538.4
7	1	-4	388.0	277.2
6	3	-4	395.5	437.8
6	1	-4	353.8	-324.1
6	0	-4	355.9	-370.1
5	6	-4	431.4	-527.0
5	4	-4	622.4	655.6
5	0	-4	518.5	-576.9
5	-1	-4	403.4	-388.8
5	-2	-4	528.6	633.6
4	4	-4	527.9	540.2
4	3	-4	487.7	556.6
4	2	-4	490.2	481.3
4	1	-4	562.3	-641.9
4	0	-4	460.7	476.5
4	-2	-4	381.7	436.4
4	-4	-4	414.6	410.7
4	-6	-4	395.2	351.1
3	7	-4	418.2	-458.9
3	6	-4	584.5	-676.7
3	4	-4	322.0	287.6
3	3	-4	527.7	-551.4
3	1	-4	625.7	-633.3
3	0	-4	248.0	-256.9
3	-2	-4	474.6	554.8
3	-4	-4	404.6	-555.5
2	8	-4	470.8	-569.3
2	6	-4	850.3	-169.3
2	4	-4	653.1	735.6
2	3	-4	559.3	588.6
2	2	-4	436.4	-475.3
2	1	-4	429.9	-456.6
2	0	-4	263.0	242.8
2	-4	-4	344.9	-403.5
2	-6	-4	367.5	409.2
1	5	-4	781.3	1017.3
1	3	-4	479.2	359.7
1	-1	-4	671.6	965.7

h	k	l	Fo	Fc
1	-3	-4	301.9	-144.0
1	-5	-4	449.7	538.0
1	-7	-4	479.7	604.3
0	4	4	431.5	-578.5
0	8	4	459.6	-538.6
1	-8	4	385.6	-250.3
1	-6	4	580.6	102.1
1	-4	4	583.6	-148.7
1	1	4	483.0	665.6
1	3	4	357.1	-424.6
2	-9	4	578.4	-266.6
2	-7	4	350.5	267.7
2	-3	4	688.7	-646.0
2	-2	4	513.2	-228.6
2	-1	4	447.4	504.4
2	0	4	496.3	604.8
2	6	4	464.5	539.9
3	-6	4	505.2	709.1
3	-3	4	283.4	-611.3
3	-1	4	742.5	-891.3
3	0	4	311.2	256.1
3	2	4	500.8	-604.1
3	4	4	377.9	409.0
4	-8	4	431.7	165.9
4	-4	4	305.6	456.7
4	-3	4	396.6	-528.7
4	-2	4	567.2	249.1
4	-1	4	613.5	647.1
4	0	4	341.9	306.5
5	-3	4	661.5	325.5
5	-2	4	387.5	-131.9
5	-1	4	360.4	295.7
5	0	4	580.3	598.3
5	2	4	392.7	-516.4
6	-5	4	360.8	381.6
6	0	4	466.8	-524.6
6	1	4	413.7	-248.4
6	2	4	476.9	-141.5

THE FOLLOWING REFLECTIONS WERE NOT USED IN COMPUTING
LEAST SQUARES REFINEMENT OF THE FOURTH LAYER:

0	-9	4	399.7	-17.7	3	-5	4	553.6	90.4
0	-7	4	530.9	22.4	3	-2	4	557.9	-58.4
0	-3	4	254.4	-56.5	5	-5	4	430.3	-20.9

NON-OBSERVED REFLECTIONS

FOURTH LAYER

h	k	l	Fo	Fc	h	k	l	Fo	Fc		h	k	l	Fo	Fc
7	4	-4	550.7	264.7	2	-1	-4	317.1	204.7		1	-2	4	209.3	148.6
7	2	-4	532.6	51.2	2	-2	-4	354.6	-224.4		1	-1	4	211.5	-740.2
7	0	-4	532.8	-185.3	2	-3	-4	392.6	365.1		1	0	4	250.9	331.2
7	-1	-4	539.8	-109.3	2	-5	-4	468.2	-203.3		1	2	4	343.4	-55.5
7	-2	-4	550.7	305.2	2	-7	-4	542.1	192.7		1	4	4	426.9	288.3
6	5	-4	522.9	-339.8	1	8	-4	465.6	268.5		1	5	4	465.9	265.8
6	4	-4	506.2	-268.9	1	7	-4	425.9	-467.5	NA	1	6	4	504.3	-44.3
6	2	-4	486.1	43.0	1	6	-4	384.6	-80.8		1	7	4	542.4	245.8
6	-1	-4	495.0	270.1	1	4	-4	293.1	105.0		2	-8	4	474.2	-380.2
6	-2	-4	508.2	-122.0	1	2	-4	191.7	-98.3		2	-6	4	401.0	6.1
6	-3	-4	525.4	-26.2	1	1	-4	185.3	-189.9		2	-5	4	364.5	103.2
6	-4	-4	546.2	7.0	1	0	-4	231.7	-260.5		2	-4	4	329.9	999.3
5	5	-4	481.0	-97.5	1	-2	-4	332.2	86.1		2	1	4	337.3	-175.3
5	3	-4	446.7	154.1	1	-4	-4	418.6	-191.6		2	2	4	372.5	156.3
5	2	-4	437.8	-75.0	1	-6	-4	497.3	127.0		2	3	4	409.0	-281.3
5	1	-4	435.2	-187.3	0	-9	4	499.9	-17.7		2	4	4	445.8	-95.4
5	-3	-4	487.0	-260.6	0	-8	4	459.5	-734.5		2	5	4	482.2	257.0
5	-4	-4	511.0	-187.4	0	-6	4	376.3	-231.6		3	-7	4	460.2	-587.6
5	-5	-4	537.6	-156.0	0	-5	4	330.2	5.4		3	-6	4	428.5	709.1
4	7	-4	496.3	-158.8	0	-4	4	278.1	159.5		3	-4	4	373.1	-243.5
4	6	-4	467.2	276.2	0	-2	4	127.4	-2577.6	BS	3	1	4	381.8	58.0
4	5	-4	440.3	-180.9	0	-1	4	121.9	30.0		3	3	4	439.7	-232.3
4	-1	-4	405.4	206.8	0	0	4	212.2	-206.5		3	5	4	505.0	-260.2
4	-3	-4	451.2	130.2	0	1	4	275.5	-67.7		4	-7	4	488.6	101.5
4	-5	-4	509.1	-371.2	0	2	4	328.0	32.8		4	-6	4	461.8	166.8
3	5	-4	401.3	106.2	0	3	4	374.4	-26.0		4	-5	4	437.8	263.3
3	2	-4	331.8	29.5	0	5	4	457.9	-61.8		4	1	4	426.9	-108.8
3	-1	-4	360.3	203.5	0	6	4	497.0	59.5		4	2	4	449.0	278.0
3	-3	-4	418.9	-219.6	0	7	4	535.7	-106.2		4	3	4	474.6	-115.4
3	-5	-4	485.4	-199.0	0	8	4	573.8	-538.6		4	4	4	502.7	214.3
3	-6	-4	520.0	-112.5	0	9	4	611.8	2.6		5	-6	4	498.2	518.7
3	-7	-4	554.9	-178.3	1	-7	4	423.4	-580.4		5	-4	4	462.7	-664.5
2	7	-4	442.6	-280.8	1	-5	4	339.2	804.7		5	1	4	472.0	-61.4
2	5	-4	366.7	-30.9	1	-3	4	246.7	10.7		5	3	4	512.3	124.1
											6	-2	4	495.7	-140.9
											6	-1	4	497.9	354.9

APPENDIX C

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR THE (2:1) $SbCl_3$.1-CHLORONAPHTHALENE COMPLEX.

Scale= 1.0   F(000)=1152

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 2SBCL3.1-CHLORONAPHTHALENE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
14	0	-14	27	36	8	2	-8	74	79	16	0	-6	73	55	10	2	-5	47	50	8	2	-4	63	66
14	2	-13	23	34	10	2	-8	79	74	18	0	-6	41	33	12	2	-5	76	56	10	2	-4	113	111
14	4	-13	21	37	9	3	-8	88	92	7	1	-6	41	51	14	2	-5	59	39	12	2	-4	101	93
12	0	-12	44	69	11	3	-8	63	59	9	1	-6	25	34	16	2	-5	45	31	14	2	-4	70	63
14	0	-12	38	61	13	3	-8	40	37	6	2	-6	216	227	18	2	-5	19	15	16	2	-4	29	20
16	0	-12	31	44	15	3	-8	28	31	8	2	-6	157	166	7	3	-5	31	37	18	2	-4	22	16
13	5	-12	20	32	17	3	-8	26	25	10	2	-6	132	107	9	3	-5	26	33	5	3	-4	289	273
11	1	-11	42	57	13	5	-8	30	42	12	2	-6	46	44	6	4	-5	94	102	7	3	-4	182	175
13	1	-11	32	51	15	5	-8	34	39	14	2	-6	51	46	8	4	-5	91	97	9	3	-4	107	102
15	1	-11	22	36	17	5	-8	33	34	16	2	-6	27	26	10	4	-5	96	72	11	3	-4	35	51
11	3	-11	35	46	8	8	-8	29	32	7	3	-6	22	47	12	4	-5	87	69	13	3	-4	28	27
13	3	-11	32	44	7	1	-7	38	49	11	3	-6	47	49	14	4	-5	75	51	6	4	-4	41	36
12	4	-11	26	48	9	1	-7	48	56	13	3	-6	49	45	16	4	-5	38	31	12	4	-4	40	31
14	4	-11	22	39	11	1	-7	58	63	15	3	-6	42	39	7	5	-5	29	31	5	5	-4	88	99
16	0	-10	22	42	13	1	-7	58	58	6	4	-6	18	23	6	6	-5	99	97	7	5	-4	72	82
18	0	-10	25	33	15	1	-7	58	53	8	4	-6	56	41	8	6	-5	100	90	9	5	-4	30	28
20	0	-10	22	26	17	1	-7	43	36	10	4	-6	18	19	10	6	-5	73	71	11	5	-4	54	56
11	3	-10	43	47	8	2	-7	94	87	7	5	-6	50	49	12	6	-5	62	57	13	5	-4	35	35
13	3	-10	29	35	10	2	-7	59	55	9	5	-6	28	35	14	6	-5	47	39	15	5	-4	25	29
11	5	-10	48	66	12	2	-7	57	52	11	5	-6	22	35	16	6	-5	21	20	6	6	-4	33	27
13	5	-10	45	56	14	2	-7	28	29	17	5	-6	18	21	5	7	-5	50	52	10	6	-4	44	44
15	5	-10	30	36	16	2	-7	27	28	6	6	-6	54	56	5	9	-5	30	32	14	6	-4	25	32
9	1	-9	127	123	7	3	-7	21	14	8	6	-6	41	36	9	9	-5	17	24	5	7	-4	73	70
11	1	-9	92	94	9	3	-7	54	44	10	6	-6	56	60	4	0	-4	199	186	7	7	-4	65	61
17	1	-9	21	31	11	3	-7	21	26	12	6	-6	35	34	6	0	-4	149	141	11	7	-4	23	19
19	1	-9	21	25	8	4	-7	137	132	7	7	-6	27	26	10	0	-4	66	62	4	8	-4	23	28
11	3	-9	27	35	10	4	-7	106	99	6	8	-6	45	52	12	0	-4	71	67	6	8	-4	25	28
13	3	-9	31	35	12	4	-7	58	62	8	8	-6	47	53	14	0	-4	58	42	8	8	-4	46	48
10	4	-9	33	59	14	4	-7	34	43	10	8	-6	32	35	16	0	-4	45	27	10	8	-4	34	32
12	4	-9	22	47	16	4	-7	28	34	12	8	-6	23	28	18	0	-4	40	24	12	8	-4	29	30
13	7	-9	19	18	8	6	-7	89	93	5	1	-5	276	247	20	0	-4	22	14	3	1	-3	382	382
8	0	-8	120	122	6	0	-6	158	152	7	1	-5	212	199	5	1	-4	87	80	5	1	-3	328	300
10	0	-8	154	142	8	0	-6	107	114	9	1	-5	76	83	7	1	-4	48	48	7	1	-3	183	168
12	0	-8	97	96	10	0	-6	69	73	13	1	-5	34	41	9	1	-4	48	41	9	1	-3	165	143
9	1	-8	45	38	12	0	-6	76	68	6	2	-5	111	112	13	1	-4	16	15	11	1	-3	113	102
11	1	-8	38	46	14	0	-6	99	79	8	2	-5	79	81	6	2	-4	71	70	13	1	-3	67	61

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15  1 -3   26   28     7  9 -3   33   33     2  4 -2   59   66     6  2 -1   49   52     6  0  0   60   68
 4  2 -3   53   45     9  9 -3   30   32     4  4 -2   52   46    10  2 -1   21   33     8  0  0   53   61
 6  2 -3   20   29     3 11 -3   18   22     6  4 -2   23   22     1  3 -1  199  208    10  0  0   29   32
 8  2 -3   56   58     5 11 -3   21   21     8  4 -2   27   23     3  3 -1  136  144    12  0  0   13   32
10  2 -3   42   43     7 11 -3   26   29     3  5 -2  234  240     5  3 -1  134  130    14  0  0   23   32
12  2 -3   40   47     2  0 -2  178  163     5  5 -2  133  131     7  3 -1   69   83     1  1  0   53   59
14  2 -3   21   16     4  0 -2   66   79     7  5 -2   95   96     9  3 -1   83   91     3  1  0   12   26
16  2 -3   23   17     6  0 -2   98  101     9  5 -2   63   56    11  3 -1   17   20     5  1  0   60   88
 3  3 -3  164  172     8  0 -2   91   96    11  5 -2   61   54     2  4 -1  222  235     7  1  0   48   60
 5  3 -3  169  145    10  0 -2   89   98    13  5 -2   36   23     4  4 -1  146  151     9  1  0   55   62
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15  3 -3   12   21    18  0 -2   21   10     4  6 -2   22   29     1  5 -1   29   33     0  2  0  243  266
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 8  4 -3   49   48     3  1 -2   86   80     8  6 -2   21   15     5  5 -1   69   65     4  2  0   71   82
10  4 -3   61   64     5  1 -2  104   96    14  6 -2   21   19     7  5 -1   47   51     6  2  0   82  111
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16  4 -3   30   22    11  1 -2   31   33     7  7 -2   64   56     6  6 -1   61   64    12  2  0   31   39
18  4 -3   27   14    13  1 -2   17   16     9  7 -2   53   50     8  6 -1   57   61     1  3  0   10   14
 3  5 -3   26   34     2  2 -2  265  262    11  7 -2   57   40    10  6 -1   24   25     3  3  0   43   46
 7  5 -3   28   36     4  2 -2  255  247     2  8 -2   54   46    16  6 -1   19   14     5  3  0   39   53
 9  5 -3   15   14     6  2 -2  119  119     4  8 -2   30   37     1  7 -1   54   51     7  3  0   57   60
 4  6 -3   73   87     8  2 -2   25   32     6  8 -2   23   26     3  7 -1   46   35     9  3  0   71   77
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14  6 -3   34   30    16  2 -2   26   22     7  1 -1  178  187    11  7 -1   30   31    17  3  0   21   15
16  6 -3   31   21    18  2 -2   25   19     9  1 -1  168  170    13  7 -1   35   23     0  4  0   31   25
 3  7 -3   69   67     3  3 -2  129  130    11  1 -1  103   95     2  8 -1   57   52     2  4  0  100  111
 5  7 -3   97   89     5  3 -2  182  174    13  1 -1   67   58     8  8 -1   22   30     4  4  0   35   52
 7  7 -3   65   67     7  3 -2  143  146    15  1 -1   32   22     1  9 -1   38   44     6  4  0   28   33
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 4  8 -3   24   30    11  3 -2  114   99    19  1 -1   18    8     5  9 -1   55   57     1  5  0   15   12
 3  9 -3   41   44    13  3 -2   61   55     2  2 -1  263  279     7  9 -1   38   35     3  5  0  123  120
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   2SBCL3.1-CHLORONAPHTHALENE                               PAGE  3

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  7  5  0   145   137      7  3  1    63   100     16  0  2    14    11      0  6  2    54    59      7  3  3    17    30
  9  5  0    74    68      9  3  1    31    48     -1  1  2   154   169      2  6  2    63    69     -2  4  3    24    24
 11  5  0    36    38     13  3  1    17    17      1  1  2    70    65      4  6  2    45    43      0  4  3    56    65
  0  6  0    40    39      0  4  1   222   233      3  1  2    76   119      6  6  2    38    43      2  4  3   114   121
  2  6  0    64    71      2  4  1   206   207      5  1  2     8    29      8  6  2    31    39      4  4  3   122   129
  4  6  0    73    75      4  4  1   183   185      7  1  2    10    38     10  6  2    27    29      6  4  3    96   106
  6  6  0    55    51      6  4  1   159   169      9  1  2     7    19     -1  7  2    40    36      8  4  3    53    71
  8  6  0    32    42      8  4  1   100   117     13  1  2    16    20      1  7  2    47    37     10  4  3    41    56
  7  7  0    62    48     10  4  1    51    58     -2  2  2   266   262     -2  8  2    52    46     12  4  3    30    39
  9  7  0    35    33     12  4  1    19    22      0  2  2    84    93      0  8  2    61    62     14  4  3    16    21
 11  7  0    34    28     -1  5  1    28    33      2  2  2    50    50      2  8  2    76    65     -3  5  3    27    34
 15  7  0    21    14      9  5  1    23    23      4  2  2    91   128      4  8  2    54    49     -1  5  3    33    40
  0  8  0    61    60     11  5  1    24    25      8  2  2    35    79      6  8  2    58    52      1  5  3    91    91
  2  8  0    83    79      0  6  1    96   107     10  2  2    19    41     10  8  2    40    29      3  5  3    69    71
  4  8  0    71    70      2  6  1    33    38     12  2  2    14    21     12  8  2    22    23      5  5  3    35    41
  6  8  0    69    59      4  6  1    73    76     14  2  2    15    21      0 10  2    31    38     -2  6  3    51    63
  8  8  0    41    43      6  6  1    66    64     16  2  2    16    13      2 10  2    39    40      0  6  3    72    83
  0 10  0    44    45      8  6  1    76    73     -1  3  2   138   132      4 10  2    39    40      2  6  3    64    73
  2 10  0    38    39     10  6  1    36    40      1  3  2    34    40      6 10  2    26    26      4  6  3    78    78
 -1  1  1   179   183     12  6  1    21    24      3  3  2    27    26     -3  1  3   381   382      6  6  3    38    38
  7  1  1    31    48     -1  7  1    54    51      5  3  2    14    26     -1  1  3   179   176      8  6  3    32    35
  9  1  1    10    14      9  7  1    35    32      7  3  2    21    37      1  1  3   124   117     12  6  3    23    24
 11  1  1    31    35      0  8  1    56    56     13  3  2    16    18      3  1  3    64    72     -3  7  3    71    69
 13  1  1    33    37      2  8  1    64    58     -2  4  2    60    67      5  1  3    39    76     -1  7  3   116   107
 15  1  1    29    24      4  8  1    43    43      0  4  2    69    66     -2  2  3    39    46      1  7  3    68    50
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  0  2  1   216   226     -1  9  1    39    44      6  4  2    75    93      2  2  3   189   201      2  8  3    43    37
  2  2  1   245   277      9  9  1    30    26     10  4  2    13    28      4  2  3   111   154      4  8  3    44    39
  4  2  1   103   137     11  9  1    19    15     -1  5  2   208   213      8  2  3    18    46      6  8  3    51    42
  8  2  1    29    45     13  9  1    22    17      1  5  2   186   183     10  2  3    17    41     10  8  3    19    17
 10  2  1    23    28      2 10  1    18    24      3  5  2    38    35     12  2  3     9    10     -3  9  3    41    43
 14  2  1    11    16      4 10  1    22    29      7  5  2    33    34     -3  3  3   166   172     -1  9  3    57    63
 -1  3  1   200   207     -2  0  2   179   164      9  5  2    19    28     -1  3  3   255   247      1  9  3    43    46
  1  3  1   138   133      0  0  2   323   347     11  5  2    31    36      1  3  3   135   133      3  9  3    51    52
  3  3  1    27    22     10  0  2    27    32     13  5  2    19    21      3  3  3    78    91      5  9  3    26    28
  5  3  1   107   129     12  0  2    21    15     -2  6  2    22    22      5  3  3    49    70     -3 11  3    18    22
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 OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  2SBCL3.1-CHLORONAPHTHALENE                                      PAGE  4

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 -4  0  4  198  185      -1  5  4  148  151       8  2  5   23   51      -3  9  5   31   29       3  3  6  139  125
 -2  0  4  300  301       1  5  4  194  195      10  2  5   17   36      -1  9  5   41   44       5  3  6   64   67
  0  0  4   76   75       3  5  4  158  159      -3  3  5   34   29       1  9  5   38   39       7  3  6   40   49
  2  0  4  132  116       5  5  4  130  130      -1  3  5   97   78       3  9  5   43   41       9  3  6   23   34
  4  0  4  160  177       7  5  4   33   34       1  3  5  101   98       5  9  5   31   26      11  3  6   10   14
  6  0  4   48   74      -2  6  4   14   15       3  3  5  166  175       7  9  5   35   29      -6  4  6   18   22
 10  0  4   13   39       6  6  4   18   21       5  3  5   72   93       9  9  5   21   16      -4  4  6   14   16
 12  0  4   24   62       8  6  4   24   23       7  3  5   20   31      -3 11  5   24   26      -2  4  6   68   67
 14  0  4   12    8      10  6  4   17   20      -4  4  5   98  104      -1 11  5   21   25       0  4  6   43   45
 -3  1  4   26   28      -3  7  4   82   77      -2  4  5   52   54      -6  0  6  159  150       4  4  6   26   25
 -1  1  4   48   49      -1  7  4   49   39       2  4  5   16   19      -4  0  6  129  125      -3  5  6   47   49
  1  1  4   34   31       1  7  4   68   56       6  4  5   14   13      -2  0  6  164  150      -1  5  6   74   80
  3  1  4  100   99       3  7  4   39   33       8  4  5   25   32       0  0  6  123  116       1  5  6  118  119
  5  1  4   52   59       5  7  4   56   39      10  4  5   25   31       2  0  6  197  187       3  5  6  107  101
  7  1  4   27   67      -4  8  4   23   28      12  4  5   16   16       4  0  6   92   99       5  5  6   80   82
  9  1  4    5   28       6  8  4   32   22      -3  5  5   19   18       8  0  6   42   42       7  5  6   53   54
 -2  2  4   17    8      10  8  4   27   20      -1  5  5   12   13      10  0  6   13   26       9  5  6   40   46
  0  2  4  135  130       4 10  4   20   24       1  5  5   23   30      12  0  6   12   26      11  5  6   15   14
  2  2  4  188  187       6 10  4   22   19       5  5  5   25   40      -5  1  6   73   63      -6  6  6   52   57
  4  2  4   84  101       8 10  4   23   21       7  5  5   27   33      -3  1  6   42   52      -2  6  6   46   40
  6  2  4   22   39      -3 11  4   18   21       9  5  5   19   26      -1  1  6   53   48       0  6  6   30   36
  8  2  4   12   20      -5  1  5  274  247      -4  6  5   61   61       3  1  6   15   10      -5  7  6   18   19
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 12  2  4   13   26      -1  1  5  225  202       2  6  5   26   35       7  1  6   30   25      -1  7  6   57   58
 14  2  4   10   11       1  1  5  252  233       4  6  5   30   24       9  1  6   16   23       1  7  6   73   66
 -3  3  4  256  233       3  1  5  189  175       6  6  5   16   22      11  1  6    7   23       3  7  6   47   39
 -1  3  4  208  204       5  1  5  126  123       8  6  5   27   23      -6  2  6  214  227       5  7  6   35   31
  1  3  4  130  129       7  1  5   33   41      10  6  5   18   17      -4  2  6  168  168       7  7  6   18   14
  3  3  4  130  123       9  1  5   10   16      -5  7  5   48   52      -2  2  6  102   89       9  7  6   17   18
  5  3  4   56   73      11  1  5    8   39      -3  7  5   71   73       2  2  6   54   53      -4  8  6   52   56
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 -2  4  4   19   21      -2  2  5  104  101       1  7  5   87   81       8  2  6   22   33      -2 10  6   17   27
  2  4  4   33   34       0  2  5   77   77       3  7  5   87   78      -5  3  6   84   86       0 10  6   20   22
  4  4  4   12   24       2  2  5   16   11       5  7  5   36   33      -3  3  6  137  136      -7  1  7   37   48
 10  4  4   16   28       4  2  5   21   29       7  7  5   30   39      -1  3  6  222  207      -3  1  7  130  120
 -3  5  4  134  147       6  2  5   44   61      -5  9  5   30   32       1  3  6  197  174      -1  1  7  212  189
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  2SBCL3.1-CHLORONAPHTHALENE                                     PAGE  5

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 3  1  7  108   95     -1  7  7   22   21      3  3  8   76   71     -2 10  8   20   28     -5  5  9   19   18
 5  1  7   75   56      1  7  7   34   33      5  3  8   72   65     -9  1  9  125  122     -4  6  9   76   79
 7  1  7   64   51      3  7  7   65   53      7  3  8   47   46     -7  1  9  122  108     -2  6  9   89   89
 9  1  7   43   45      5  7  7   55   48      9  3  8   19   22     -5  1  9   59   52      0  6  9   85   74
11  1  7   18   19      7  7  7   43   39     11  3  8   12   10     -3  1  9   32   36      2  6  9   51   43
-6  2  7   61   77     -1  9  7   20   24     -6  4  8   36   39     -1  1  9   28   49      4  6  9   47   37
-4  2  7  103  100      3  9  7   25   19     -4  4  8   32   25      3  1  9   56   61      6  6  9   24   26
-2  2  7  141  133      5  9  7   22   20      0  4  8   20   26      5  1  9   56   49     -5  7  9   30   42
 0  2  7  179  152      7  9  7   22   18      2  4  8   23   20      7  1  9   36   38     -3  7  9   43   53
 2  2  7  114  107     -8  0  8  119  123      4  4  8   22   26      9  1  9   19   12      9  7  9   18   12
 4  2  7   54   60     -6  0  8  103   87      1  5  8   21   22     11  1  9   12    7     -8  0 10   57   62
-7  3  7   19   14     -4  0  8   82   90      3  5  8   27   32     -8  2  9   39   30     -6  0 10  102  110
-5  3  7   18   24     -2  0  8  156  144      5  5  8   50   48     -6  2  9   23   37     -4  0 10  110  118
-1  3  7   42   39      0  0  8  182  163      7  5  8   40   40     -4  2  9   71   60     -2  0 10   81   91
 1  3  7   34   43      2  0  8  150  135      9  5  8   22   22     -2  2  9   60   65      0  0 10   64   64
 3  3  7   53   52      4  0  8   67   58     -6  6  8   66   66      0  2  9   94   78      2  0 10   86   65
 5  3  7   20   27      6  0  8   60   49     -4  6  8   55   51      2  2  9   90   75      4  0 10   93   70
 7  3  7   40   49      8  0  8   25   33     -2  6  8   54   54      4  2  9   92   69      6  0 10   56   58
 9  3  7   18   29     10  0  8   18   19      2  6  8   23   26      6  2  9   50   48      8  0 10   39   25
11  3  7   11   12     -5  1  8   27   34      4  6  8   27   25      8  2  9   21   26     10  0 10   15    9
-6  4  7  141  121     -3  1  8   55   63      6  6  8   18   17     -9  3  9   19   27     -9  1 10   61   71
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-2  4  7   87   88      1  1  8   23   32      1  7  8   29   24     -1  3  9   20   34     -5  1 10   61   55
 0  4  7   95  100      3  1  8   13   13      3  7  8   21   24      1  3  9   26   45     -3  1 10   21   22
 2  4  7   72   69     -8  2  8   73   77      5  7  8   36   27      3  3  9   17   15      1  1 10   28   35
 4  4  7   32   37     -6  2  8  128  111      7  7  8   24   21      5  3  9   27   25      3  1 10   29   27
 6  4  7   17   16     -4  2  8  109  121     -8  8  8   27   32      7  3  9   19   26     -6  2 10   48   42
 8  4  7   10   20     -2  2  8  174  178     -6  8  8   36   42     -8  4  9   62   73     -4  2 10   71   71
-5  5  7   24   21      0  2  8  170  161     -4  8  8   50   61     -6  4  9  105  103     -2  2 10  108   92
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 5  5  7   16   24      4  2  8   27   30      0  8  8   42   42     -2  4  9  138  120      2  2 10   72   66
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-4  6  7  108  103     -7  3  8   95   97      4  8  8   30   24      2  4  9   49   46      6  2 10   48   47
-2  6  7   93   88     -5  3  8   47   55      6  8  8   17   17      4  4  9   48   46      8  2 10   24   20
 0  6  7   80   73     -1  3  8   33   35     -6 10  8   18   19      6  4  9   36   33     -9  3 10   58   57
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 2SBCL3.1-CHLORONAPHTHALENE

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  H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

 -7  3 10   72   70     2  2 11   33   35     2  0 12   48   53    -3  5 12   40   40   -10  0 14   35   57
 -5  3 10   95   99     4  2 11   46   38     4  0 12   30   40    -1  5 12   36   34    -8  0 14   45   68
 -3  3 10  105   99     6  2 11   28   26     6  0 12   38   25     1  5 12   44   41    -6  0 14   33   53
 -1  3 10   78   76     8  2 11   24   17     8  0 12   23   15     3  5 12   34   39    -3  1 14   34   37
  1  3 10   25   35   -11  3 11   35   46    -7  1 12   46   65   -10  6 12   18   30    -1  1 14   41   41
 11  3 10   10    9    -9  3 11   28   37    -5  1 12   65   75    -5  7 12   23   33     1  1 14   33   29
 -4  4 10   62   60    -5  3 11   26   30    -3  1 12   63   58    -3  7 12   18   21   -10  2 14   18   30
 -2  4 10   52   56    -3  3 11   37   40    -1  1 12   46   40    -7  1 13   51   63    -8  2 14   30   36
  0  4 10   20   23     1  3 11   21   19   -12  2 12   23   21    -5  1 13   61   68    -4  2 14   17   31
 -9  5 10   45   59    -6  4 11   23   37     0  2 12   28   39    -3  1 13   59   65    -3  3 14   31   37
 -7  5 10   36   39    -4  4 11   47   53     2  2 12   54   47    -1  1 13   74   69    -1  3 14   42   46
 -3  5 10   50   53    -2  4 11   66   63     4  2 12   18   29     1  1 13   70   64     1  3 14   36   38
 -1  5 10   46   54     0  4 11   71   68     6  2 12   24   22     3  1 13   39   46     3  3 14   21   26
 -2  6 10   33   35     2  4 11   77   63     8  2 12   15   11     5  1 13   28   26     5  3 14   21   16
  0  6 10   32   30     4  4 11   41   44    -9  3 12   28   29    -9  3 13   27   39    -5  5 14   27   37
  2  6 10   38   37     6  4 11   16   18    -7  3 12   47   49    -7  3 13   33   45    -3  5 14   22   39
 -2  8 10   22   28     8  4 11   14   12    -5  3 12   61   65    -5  3 13   24   32    -1  5 14   31   39
  0  8 10   32   35    -7  5 11   22   29    -3  3 12   64   62    -1  3 13   17   16    -3  1 15   35   45
  2  8 10   33   35    -2  6 11   29   22    -1  3 12   60   60     1  3 13   27   25    -1  1 15   38   48
  4  8 10   24   24     0  6 11   36   35     1  3 12   64   51     5  3 13   16   18     1  1 15   24   40
 -9  1 11   62   62     2  6 11   45   40     3  3 12   50   45   -10  4 13   31   49     3  1 15   36   29
 -7  1 11   85   89     4  6 11   43   35     5  3 12   17   23    -8  4 13   35   56     5  1 15   19   19
 -5  1 11  128  128     1  7 11   32   36     0  4 12   34   21    -6  4 13   36   53   -10  2 15   25   44
 -3  1 11  132  126     3  7 11   23   26     2  4 12   33   27     2  4 13   22   33    -8  4 15   25   48
 -1  1 11   78   75    -7  9 11   24   40    -9  5 12   38   53     6  4 13   19   18    -6  4 15   35   50
  1  1 11   28   39   -12  0 12   41   68    -7  5 12   43   63   -14  0 14   25   34    -4  4 15   30   45
  0  2 11   30   26     0  0 12   42   63    -5  5 12   45   59   -12  0 14   35   44    -2  4 15   32   41
1  SBCL3.CLN   Cc
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NON-
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   2SBCL3.1-CHLORONAPHTHALENE                                     PAGE  1

      H  K  L   FO   FC        H  K  L   FO   FC        H  K  L   FO   FC        H  K  L   FO   FC        H  K  L   FO   FC

     14  2-14   32   30       13  1-10   88   38   UB 9  3 -9   28   30       12  4 -8   27   22       10  6 -7   86   61
     13  1-13   31   14       15  1-10   32   21       15  3 -9   40   27       14  4 -8   40    7       12  6 -7   31   26
     15  1-13   37   25       17  1-10   71   15       17  3 -9   35   23       16  4 -8   35   11       14  6 -7   69   15
     16  2-13   97   28       19  1-10   87    9       19  3 -9   32   17       18  4 -8   32   11       16  6 -7   84   15
     15  3-13   37   15       10  2-10   29   21       21  3 -9   41    8        9  5 -8   46   33       18  6 -7   47   12
     18  0-12   44   26       12  2-10   34   18   SG14  4 -9   32   36       11  5 -8   87   37       20  6 -7   53   11
     13  1-12   49   22       14  2-10   27   21       16  4 -9   70   30       19  5 -8   47   22        9  7 -7   34   30
     15  1-12   93   16       16  2-10   41   18       18  4 -9   86   24       10  6 -8   34   23   UB11  7 -7   27   28
     12  2-12   30   23       18  2-10   36   18       20  4 -9   48   17       12  6 -8   27   14       15  7 -7   35   16
     14  2-12   36   26       20  2-10   33   15       11  5 -9   34   19       14  6 -8   41   11       17  7 -7   32   14
     16  2-12   29   24       15  3-10   33   25       10  6 -9   48   10       16  6 -8   36   13        8  8 -7   48    8
     18  2-12   44   21       17  3-10   72   20       12  6 -9   90   12       18  6 -8   33   12       12  8 -7   33   18
     13  3-12   50   24       19  3-10   88   17       14  6 -9   33   10        9  7 -8   48   28       14  8 -7   71   18
     15  3-12   94   24       12  4-10   34   12       16  6 -9   72   15       11  7 -8   90   19        9  9 -7   35   10
     14  4-12   36   10       14  4-10   28   10       18  6 -9   88   13       13  7 -8   33   16       11  9 -7   28   16
     16  4-12   30    2       16  4-10   42    8       10  8 -9   50   22       15  7 -8   72   12       13  9 -7   43   15
     15  5-12   96   27       18  4-10   37    7       13  9 -9   30   24       19  7 -8   49    9       15  9 -7   37   17
     14  6-12   37   17       20  4-10   34    5   UB14  0 -8   39   57       12  8 -8   28   19        9 11 -7   37   10
     19  1-11   37   22       17  5-10   73   26   UB16  0 -8   34   39       14  8 -8   43   15       20  0 -6   30   15
     12  2-11   48   19       19  5-10   90   19       18  0 -8   31   29       16  8 -8   37   13       22  0 -6   30    8
     14  2-11   91   26       12  6-10   35   21       20  0 -8   39   19       19  1 -7   38   18       11  1 -6   29   25
     16  2-11   33   24       14  6-10   29   20       22  0 -8   32   12       21  1 -7   31   12       15  1 -6   77   23
     18  2-11   73   20       16  6-10   43   16       24  0 -8   33    9       23  1 -7   31    8       18  2 -6   37   16
     15  3-11   28   27       13  7-10   94   23   UB13  1 -8   31   37       18  2 -7   45   14       20  2 -6   30   10
     17  3-11   43   12       12  8-10   36   12       15  1 -8   67   26       20  2 -7   50    9        9  3 -6   82   35
     16  4-11   34   28       14  8-10   30   10       17  1 -8   82   18       13  3 -7   38   21       17  3 -6   44   26
     18  4-11   74   21       20 10-10   37    6       19  1 -8   46   10       15  3 -7   33   21       19  3 -6   49   15
     13  5-11   36    5   UB13  1 -9   27   58   UB12  2 -8   26   31       17  3 -7   31   19       21  3 -6   42    9
     15  5-11   29    8       15  1 -9   40   37       14  2 -8   39   21       21  3 -7   31    8       12  4 -6   38   12
     17  5-11   44    7       23  1 -9   33   10       16  2 -8   34   20       20  4 -7   51   15       14  4 -6   33   22
     16  6-11   35   16       10  2 -9   46   23       18  2 -8   31   20       22  4 -7   44    9       16  4 -6   30   17
     13  7-11   37   16       12  2 -9   86   32       20  2 -8   40   13        9  5 -7   32   11       18  4 -6   38    8
     12  8-11   52    7       14  2 -9   32   21       22  2 -8   32    9       11  5 -7   26   14       13  5 -6   66   25
 UB10  0-10   28   47       16  2 -9   69   17       21  3 -8   53   12       13  5 -7   39   11       15  5 -6   80   23
 UB12  0-10   34   57       20  2 -9   48   13       23  3 -8   45    7       15  5 -7   34   10       19  5 -6   31   14
 UB11  1-10   47   57       22  2 -9   54    9   UB10  4 -8   33   43       17  5 -7   31   11       14  6 -6   34   13
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NON-

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 2SBCL3.1-CHLORONAPHTHALENE

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
16	6	-6	31	9	15	9	-5	32	12	8	6	-3	29	23	16	2	-1	25	13	10	8	0	29	13
18	6	-6	39	9	7	11	-5	36	20	18	6	-3	40	11	13	3	-1	24	7	12	8	0	36	7
20	6	-6	32	7	9	11	-5	29	10	11	7	-3	33	22	10	4	-1	51	20	14	8	0	29	4
9	7	-6	86	24	11	1	-4	43	12	13	7	-3	30	24	12	4	-1	28	17	1	9	0	46	5
11	7	-6	31	21	15	1	-4	41	14	6	8	-3	85	12	16	4	-1	26	17	3	9	0	85	35
13	7	-6	68	20	17	1	-4	46	6	8	8	-3	31	6	18	4	-1	31	12	5	9	0	31	21
15	7	-6	83	16	4	2	-4	15	6	10	8	-3	66	16	13	5	-1	24	4	4	10	0	27	40
17	7	-6	47	12	20	2	-4	28	7	16	8	-3	50	7	12	6	-1	41	25	6	10	0	40	25
19	7	-6	53	8	15	3	-4	42	28	11	9	-3	34	15	14	6	-1	46	11	8	10	0	34	23
14	8	-6	35	17	17	3	-4	46	16	13	9	-3	31	15	4	8	-1	83	13	14	10	0	31	6
16	8	-6	32	15	10	4	-4	26	7	15	9	-3	39	10	6	8	-1	30	15	2	12	0	36	12
9	9	-6	90	14	14	4	-4	29	10	6	10	-3	89	25	14	8	-1	48	14	14	12	0	33	3
14	10	-6	37	12	16	4	-4	36	10	8	10	-3	32	11	11	9	-1	30	21	1	13	0	51	5
SG 11	1	-5	26	37	18	4	-4	29	7	SG 12	0	-2	19	44	13	9	-1	38	18	12	2	1	24	10
SG 15	1	-5	29	35	22	4	-4	56	3	15	1	-2	31	4	15	9	-1	30	8	11	3	1	19	19
17	1	-5	36	24	17	5	-4	48	16	17	1	-2	26	6	4	10	-1	88	9	15	3	1	18	9
UB 13	3	-5	32	39	UB 8	6	-4	25	40	19	1	-2	31	5	6	10	-1	32	13	12	4	1	30	19
17	3	-5	37	17	16	6	-4	37	12	19	3	-2	44	7	3	11	-1	35	6	14	4	1	25	6
19	3	-5	29	7	UB 9	7	-4	30	35	10	4	-2	22	10	15	11	-1	32	8	16	4	1	30	3
9	5	-5	25	10	13	7	-4	80	21	12	4	-2	20	11	16	0	0	18	17	1	5	1	21	2
11	5	-5	38	8	15	7	-4	44	18	14	4	-2	24	14	3	1	0	25	25	SG 3	5	1	17	31
13	5	-5	33	8	17	7	-4	50	11	16	4	-2	27	9	15	1	0	20	11	5	5	1	25	25
15	5	-5	30	15	16	8	-4	39	17	18	4	-2	27	6	17	1	0	29	3	SG 7	5	1	21	47
17	5	-5	38	10	9	9	-4	32	17	17	5	-2	38	12	16	2	0	18	4	13	5	1	19	12
18	6	-5	50	10	8	10	-4	28	17	SG 12	6	-2	29	32	1	3	0	21	13	14	6	1	26	14
7	7	-5	33	15	10	10	-4	41	14	8	8	-2	38	8	UB 8	4	0	21	47	3	7	1	25	17
13	7	-5	34	19	6	12	-4	36	4	10	8	-2	33	10	12	4	0	24	14	SG 5	7	1	37	39
15	7	-5	31	19	17	1	-3	19	14	12	8	-2	30	25	14	4	0	19	1	7	7	1	31	22
6	8	-5	46	5	19	1	-3	27	10	14	8	-2	38	16	13	5	0	31	16	11	7	1	35	16
8	8	-5	87	14	18	2	-3	38	10	16	8	-2	30	12	15	5	0	26	15	12	8	1	47	3
10	8	-5	31	15	9	3	-3	25	12	7	9	-2	31	6	10	6	0	20	16	1	9	1	33	18
12	8	-5	68	6	UB 11	3	-3	22	30	4	10	-2	34	19	12	6	0	25	11	3	9	1	26	8
18	8	-5	52	10	20	4	-3	46	9	6	10	-2	27	8	1	7	0	44	10	7	9	1	33	14
7	9	-5	34	17	11	5	-3	31	26	8	10	-2	40	18	3	7	0	81	16	-1	11	1	30	6
11	9	-5	41	15	13	5	-3	29	11	12	2	-1	28	32	5	7	0	29	14	3	11	1	28	2
13	9	-5	35	12	15	5	-3	34	15	14	2	-1	31	10	13	7	0	46	9	13	11	1	32	4

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NON-
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   2SBCL3.1-CHLORONAPHTHALENE                      PAGE  3

    H  K  L    FO    FC      H  K  L    FO    FC      H  K  L    FO    FC      H  K  L    FO    FC      H  K  L    FO    FC

   -1 13  1    31     3      7  9  3    30    15  MI 11  3  5    12    15     -5  1  7    22     6  UB -8  6  8    29    36
SG 10  0  2    12    32      9  9  3    37     6  MI  0  4  5    20    36      6  2  7    21    26     -7  7  8    47    18
   14  0  2    12     9     11  9  3    29     0      4  4  5    41    26  SG  8  2  7    17    24     -5  7  8    87    11
    5  1  2    16    14      2 10  3    31     9      3  5  5    21    20     10  2  7    18    16     -1  7  8    65    12
MI  7  1  2    22    23      4 10  3    67    18     -2  8  5    85    31  UB -3  3  7    17    23     -5  9  8    90     7
MI  9  1  2    14    21     -1 11  3    35    12      0  8  5    30    37     -7  5  7    28    10     -3  9  8    32     3
SG 11  1  2    17    22     -3 13  3    32     3      2  8  5    65    28      1  5  7    22     7     -8 10  8    31    15
    9  3  2    19    21  MI  9  1  4    11    23      4  8  5    77    36      3  5  7    20    17      6 10  8    30    11
   15  3  2    24    13  MI 11  1  4    10    13      8  8  5    46     8      4  6  7    29    16  MI  1  1  9    19    56
    4  4  2    20    18     13  1  4    14    10      0 10  5    32     1      6  6  7    31    14     -7  3  9    32    11
SG  8  4  2    15    23     -4  2  4    15     4     -5 11  5    30    20      8  6  7    26     5     -3  3  9    37    28
    5  5  2    43    21     14  2  4    20     9     -4 12  5    51    10  UB -7  7  7    28    30     -9  5  9    29    18
   12  6  2    19    15     16  2  4    14     3      6  0  6    13    40     -5  7  7    33     9     -7  5  9    33     9
    3  7  2    29    18     11  3  4    17     4      1  1  6    34    28     -3  7  7    26    13     -1  5  9    32    32
    5  7  2    44    19     13  3  4    20     7  MI  0  2  6    20    33     -6  8  7    47     2      1  5  9    28    23
    7  7  2    53    26     -4  4  4    18    10  SG 10  2  6    10    17     -4  8  7    87    13      3  5  9    25    26
    9  7  2    41    22  SG  6  4  4    15    29     11  3  6    20    12     -2  8  7    31    14     -8  6  9    47    14
UB  8  8  2    29    36  SG  8  4  4    19    33  UB  2  4  6    21    33      0  8  7    66    30     -6  6  9    87    44
   -1  9  2    46     6      9  5  4    30    21  UB  6  4  6    19    36      2  8  7    78    34     -9  7  9    30    19
    1  9  2    85     8     11  5  4    25     4  SG  8  4  6    15    24      6  8  7    47    14     -7  7  9    34    24
    3  9  2    31    16     -4  6  4    27     7     -5  5  6    44    14     -7  9  7    30    10     -1  7  9    33    14
   -2 10  2    29    20  SG  4  6  4    22    27     13  5  6    18     8     -5  9  7    34    23      3  7  9    36    25
   -1 11  2    49     2      7  7  4    29    27     -4  6  6    32    15     -3  9  7    27    22      5  7  9    28    26
   -2 12  2    31     5      9  7  4    32    13      2  6  6    22    22      1  9  7    34    17     -8  8  9    49    15
    9  1  3    10     1     -2  8  4    32    16  SG  4  6  6    20    23     -6 10  7    50     9     -4  8  9    32    10
   11  1  3     9     7      2  8  4    38    25      8  6  6    19    12      0 10  7    69     6     -2  8  9    68    10
    9  3  3    16     4  SG  4  8  4    32    39  UB -6  8  6    29    52     -7 11  7    31     8      4  8  9    48    10
UB  7  5  3    19    30      1  9  4    31    13  UB -2  8  6    26    39     -5 11  7    36     5     -7  9  9    36    19
    9  5  3    24    20      5  9  4    79    10      2  8  6    32     8     -3 11  7    29     9     -5  9  9    28     8
   11  5  3    19    13     -4 10  4    29    17      4  8  6    29     6      5  1  8    24     9     -3  9  9    41     5
   10  6  3    31    17     -2 10  4    34     5      8  8  6    28    14      7  1  8    17     3      1  9  9    31    12
    5  7  3    22    13      0 10  4    27     6      3  9  6    80    12     -3  3  8    21    12     -8 10  9    51    10
    7  7  3    20    14      2 10  4    40     7     -6 10  6    30    25  UB -8  4  8    28    46     -2 10  9    71    10
    9  7  3    25    20     -4 12  4    31     1      2 10  6    34    14     -7  5  8    46    18     -1  1 10    53    13
   -2  8  3    45    21  SG -5  3  5    18    33      8 10  6    30     5     -3  5  8    30    26    -10  2 10    29    19
    0  8  3    83    29  UB  5  3  5    15    95     -6 12  6    32     5     -1  5  8    63    36     -8  2 10    33    13
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    NON-
    OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   2SBCL3.1-CHLORONAPHTHALENE                     PAGE  4

    H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

SG  3  3 10   31   37   -10  8 10   31    7    -4  6 11   68    8   -11  5 12   50   39   -12  4 13   51   39
SG  5  3 10   25   31    -8  8 10   35   11   -11  7 11   31   18   -12  6 12   31   20     0  4 13   48   41
    7  3 10   29   18    -6  8 10   28   19    -9  7 11   36   18    -8  6 12   28   24   -13  5 13   32    6
  -10  4 10   29   14    -4  8 10   41   28    -7  7 11   28   18    -6  6 12   41   13   -11  5 13   36    2
   -8  4 10   33   11    -5  9 10   33   11    -1  7 11   31   26    -4  6 12   35   10    -9  5 13   29    4
UB -6  4 10   26   34    -6 10 10   29    9   -10  8 11   51    8    -2  6 12   31   26   -12  6 13   52   11
    2  4 10   25    6 UB-11  1 11   29   56    -8  8 11   94   12    -9  7 12   94   24   -10  6 13   95    6
UB -5  5 10   31   42 UB  3  1 11   19   31    -9  9 11   37   30    -7  7 12   33   29   -13  1 14   51   19
    5  5 10   26   20 UB  5  1 11   18   34 SG-10  0 12   34   39   -10  8 12   37    9   -11  1 14   94   24
  -10  6 10   30   13   -10  2 11   47    9    -6  0 12   39   15    -8  8 12   29   11   -14  2 14   32   30
   -8  6 10   34   20    -8  2 11   87   26 SG -4  0 12   33   50    -6  8 12   43   10   -12  2 14   36   26
UB -6  6 10   27   37 UB -6  2 11   31   43   -11  1 12   49   23   -13  1 13   31   14     0  2 14   29   26
UB -4  6 10   39   46    -4  2 11   65   31     1  1 12   45    9 SG -9  1 13   28   37   -13  3 14   52   17
    4  6 10   28    9    -7  3 11   27   23   -10  2 12   34   10   -12  2 13   50   30   -11  3 14   95   22
   -9  7 10   49   28   -10  4 11   48   37    -8  2 12   27    6   -10  2 13   91   23   -12  4 14   37   16
   -7  7 10   90   18    -8  4 11   88   19    -6  2 12   39   15     0  2 13   47   32   -10  4 14   29   18
   -5  7 10   32   25   -11  5 11   30    9 SG -4  2 12   33   38     2  2 13   38   28     0  4 14   30    8
   -3  7 10   68   28    -3  5 11   33   11   -10  4 12   35   23   -13  3 13   31   12   -11  5 14   96   14
   -1  7 10   80   29    -8  6 11   90   11    -8  4 12   28   21   -11  3 13   36   18    -1  7 15   32   17
    3  7 10   47   14    -6  6 11   32    9    -4  4 12   34   12
1   2SBCL3.1-CHLORONAPHTHALENE

                             UB=means Unequal Backgrounds,MI=Minimun observed Inten-
                             sity used in computing Fo's, SG=Sigma@Greater than  ob-
                             served intensity.
```

APPENDIX D

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR THE (1:1) $SbCl_3$.1-IODONAPHTHALENE COMPLEX REFERRED TO THE HALF CELL.

Scale=1.0 F(000) =444

```
            CALCULATED STRUCTURE FACTORS FOR    SBCL3.1-IODONAPHTHALENE                          PAGE  1

 H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

 1 -7 -3   75   52     2 -1 -3   91   73     4  3 -3   62   12    10 -4 -2   66   55     7  0 -2  104  128
 2 -7 -3   74   53     3 -1 -3   55   55     6  3 -3  113  120    11 -4 -2   61   48     9  0 -2   59   33
10 -6 -3   76   89     4 -1 -3   95   91     8  3 -3  101   91     1 -3 -2   93   75    10  0 -2   69   55
11 -6 -3   67   54     5 -1 -3  101  102     9  3 -3   95   78     2 -3 -2   77   68    11  0 -2   63   42
13 -6 -3   74   76     6 -1 -3  100  105    11  3 -3   77   93     5 -3 -2  100  112    12  0 -2   67   66
 2 -5 -3   76   70     7 -1 -3   61   79     1  4 -3  121  127     6 -3 -2   65   56     3  1 -2   94   89
 3 -5 -3   97  104     9 -1 -3   86   89     3  4 -3  110   94     7 -3 -2   90   90     4  1 -2   66   38
 8 -5 -3   77   52    10 -1 -3   76   77     4  4 -3   66   21     9 -3 -2   59   59     7  1 -2   81   73
 9 -5 -3   81   72    11 -1 -3   71   50     6  4 -3  104   95    10 -3 -2   70   76     8  1 -2   85   75
10 -5 -3   71   47    14 -1 -3   70   56     8  4 -3   77   63    11 -3 -2   77   84    10  1 -2   60   33
12 -5 -3   71   45     4  0 -3   86   70     1  5 -3  101   82     1 -2 -2  122  140    11  1 -2   77   98
14 -5 -3   75   79     5  0 -3   75   51     2  5 -3   81   54     2 -2 -2   90   92    13  1 -2   68   66
 1 -4 -3   69   33     6  0 -3  115  113     3  5 -3   69   40     3 -2 -2   94  114     1  2 -2   86   50
 2 -4 -3   57   34     7  0 -3   76   45     4  5 -3   70   45     4 -2 -2   65   77     3  2 -2  124  156
 3 -4 -3   71   47     9  0 -3   62   33     5  5 -3   76   47     5 -2 -2   76   88     4  2 -2   75   32
 6 -4 -3   85   67    10  0 -3  103  106     7  5 -3   79   74     6 -2 -2   88   89     5  2 -2   92   69
 7 -4 -3   77   51    12  0 -3   78   65     1  6 -3   62   44     7 -2 -2   81   79     6  2 -2  118  117
 9 -4 -3   88   93    13  0 -3   76   62     2  6 -3   86   72     8 -2 -2   66   59     7  2 -2   56   19
11 -4 -3   81   85     3  1 -3   84   50     4  6 -3   82   73     9 -2 -2   62   46     8  2 -2   92  110
14 -4 -3   79   90     5  1 -3  118  113     5  6 -3   72   58    10 -2 -2   64   42     9  2 -2   85   43
 1 -3 -3  107   84     6  1 -3   63   63     7  6 -3   77   81    11 -2 -2   75   64    10  2 -2   74   43
 5 -3 -3   79   76     7  1 -3   90   84     2 -7 -2   68   48    12 -2 -2   64   54    11  2 -2   71   73
 6 -3 -3   94   85    10  1 -3   94  100    10 -7 -2   73   80     1 -1 -2  114  122     1  3 -2  107   91
 7 -3 -3   61   54    12  1 -3   77   62     2 -6 -2   73   50     3 -1 -2  107  103     3  3 -2  121  132
 9 -3 -3   91   89     1  2 -3   63   23     9 -6 -2   75   68     4 -1 -2   70   50     5  3 -2   57   30
10 -3 -3   70   50     2  2 -3  120  147    11 -6 -2   73   62     5 -1 -2   92   85     6  3 -2   57   43
 1 -2 -3  104  106     3  2 -3   74   46     1 -5 -2   82   70     6 -1 -2   50   40     7  3 -2   77   68
 4 -2 -3   75   34     4  2 -3   87   43     8 -5 -2   71   69     7 -1 -2  115  138     8  3 -2   76   60
 5 -2 -3   90   84     5  2 -3  113   93     9 -5 -2   74   86     8 -1 -2   54   36     9  3 -2   62   29
 6 -2 -3   85   52     6  2 -3   82   55    11 -5 -2   75   77     9 -1 -2   60   48    10  3 -2   64   27
 8 -2 -3   71   67     7  2 -3   70   46     1 -4 -2   94  113    10 -1 -2   73   77    12  3 -2   72   71
 9 -2 -3   70   57     8  2 -3   68   19     2 -4 -2   56   63    11 -1 -2   60   63     2  4 -2   99   73
10 -2 -3   91   88    10  2 -3   69   50     5 -4 -2   81   67    12 -1 -2   74   95     3  4 -2   66   48
13 -2 -3   71   56    11  2 -3   71   58     6 -4 -2   87  101     3  0 -2   80   74     4  4 -2  101   97
14 -2 -3   77   71     1  3 -3   85   59     7 -4 -2   64   42     4  0 -2   84   80     5  4 -2   61   33
 1 -1 -3  110  117     2  3 -3  117  105     9 -4 -2   75   70     5  0 -2   95  101     6  4 -2   64   30
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   SBCL3.1-IODONAPHTHALENE                          PAGE  2

 H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

 7  4 -2   88   98     5 -2 -1   64   51     7  3 -1   60   48     6 -5  0   63   62     2 -1  0   68   29
 9  4 -2   67   67     9 -2 -1   79  104     8  3 -1   70   24     7 -5  0   61   65     3 -1  0  100   76
 1  5 -2   79   63    12 -2 -1   65   74    11  3 -1   67   24     8 -5  0   89   90     4 -1  0  104   78
 2  5 -2   71   81     1 -1 -1   83   89     2  4 -1   72   77     9 -5  0   66   61     5 -1  0  118  123
 3  5 -2   65   75     3 -1 -1   70   71     4  4 -1   75   80    12 -5  0   70   62     6 -1  0   76   57
 4  5 -2   92  107     4 -1 -1   87  104     5  4 -1   66   57     2 -4  0   59   36     7 -1  0   92   77
 6  5 -2   63   42     7 -1 -1   89  103    11  4 -1   76   29     3 -4  0   84   46     8 -1  0  122  142
 7  5 -2   71   72     9 -1 -1   74   64     1  5 -1   66   55     4 -4  0  113   92    10 -1  0  114   93
 3  6 -2   67   61    13 -1 -1   69   71     5  5 -1   69   84     5 -4  0   87   60    11 -1  0   62   25
 3  7 -2   65   69     3  0 -1   58   48     1  6 -1   70   75     7 -4  0   68   53    13 -1  0   71   69
 2 -7 -1   69   43     4  0 -1   50   45     5  6 -1   65   45     9 -4  0   76   87     3  0  0  131  152
 1 -6 -1   74   85     5  0 -1   88   84     2 -9  0   70   89    12 -4  0   72   77     4  0  0   81   53
 1 -5 -1   63   73     6  0 -1   69   56     3 -8  0   72   58    14 -4  0   66   52     5  0  0  111  101
 6 -5 -1   77   78     7  0 -1   51   34     6 -8  0   77   65     1 -3  0  105   91     6  0  0   79   42
 7 -5 -1   71   78     8  0 -1   83  102     8 -8  0   79   83     2 -3  0  117  112     8  0  0   63   51
10 -5 -1   61   71    10  0 -1   57   65    11 -8  0   68   77     3 -3  0   55   64     9  0  0   88   84
11 -5 -1   60   63    11  0 -1   73   83     1 -7  0   78   71     4 -3  0  123  143    11  0  0   76   64
12 -5 -1   64   94    13  0 -1   74   90     3 -7  0   83   89     5 -3  0   57   74    12  0  0   68   60
 2 -4 -1   90  117     2  1 -1   49   17     6 -7  0   71   55     6 -3  0   70   69     1  1  0   93   78
 6 -4 -1   70   81     4  1 -1   67   58     7 -7  0   66   37     7 -3  0   54   67     3  1  0  101   56
 7 -4 -1   74   80     5  1 -1   99  126     8 -7  0   64   55     8 -3  0   76   71     4  1  0  116  138
 8 -4 -1   65   62     6  1 -1  100  105     9 -7  0   69   35     9 -3  0   80   81     6  1  0   99  111
 2 -3 -1   80   95     8  1 -1   73   82    12 -7  0   72   72    10 -3  0   59   36     7  1  0   58   52
 3 -3 -1  101   99     9  1 -1   64   43     2 -6  0   75   39    12 -3  0   70   46     8  1  0   58   46
 4 -3 -1   61   62    11  1 -1   63   19     3 -6  0   82   57     1 -2  0  101   92     9  1  0   91  112
 5 -3 -1   57   56     3  2 -1   75   86     4 -6  0   78   67     2 -2  0  103   94    11  1  0   87   83
 6 -3 -1   72   70     4  2 -1   80   78     6 -6  0   62   41     3 -2  0   58   36    12  1  0   73   50
 7 -3 -1   76   79     5  2 -1   93   95     7 -6  0   75   89     4 -2  0  136  159    14  1  0   82   69
 8 -3 -1   68   62     6  2 -1   66   20     8 -6  0   66   66     5 -2  0   57   27     0  2  0   96   83
 9 -3 -1   57   53     7  2 -1   71   80     9 -6  0   72   89     6 -2  0   64   22     1  2  0  111  110
10 -3 -1   56   54     8  2 -1   80   36    10 -6  0   63   53     7 -2  0   71   34     3  2  0   68   55
12 -3 -1   59   68     1  3 -1  103  135    12 -6  0   70   72     8 -2  0   97   86     4  2  0  107   87
 1 -2 -1   59   38     2  3 -1   80   78     2 -5  0   76   72     9 -2  0   57   31     6  2  0   87   92
 2 -2 -1  113  131     4  3 -1   87  108     3 -5  0   86   82    10 -2  0   74   59     9  2  0   74   62
 3 -2 -1   61   43     5  3 -1   54   56     4 -5  0   88   77    11 -2  0   61   28    11  2  0   66   38
 4 -2 -1   97  119     6  3 -1   58   66     5 -5  0   69   56    13 -2  0   78   95     0  3  0   73   49
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR    SBCL3.1-IODONAPHTHALENE                    PAGE  3

 H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

 1  3  0  110   95     6 -6  1   64   52     7 -2  1   88   87     2  3  1   93  119     2 -5  2   64   63
 3  3  0   58   20     8 -6  1   68   42     8 -2  1   75   62     5  3  1   62   57     3 -5  2   67   51
 4  3  0   65   55     9 -6  1   71   67    10 -2  1   79   86     6  3  1   61   68     4 -5  2   60   30
 5  3  0   85   90    10 -6  1   63   54     3 -1  1   59   38     7  3  1   63   54     5 -5  2   86   61
 7  3  0   82   70     0 -5  1   65   52     4 -1  1   74   50     0  4  1   56   43     6 -5  2   80   72
 8  3  0   70   62     1 -5  1   68   38     6 -1  1  101  124     1  4  1   65   63     7 -5  2   64   37
10  3  0   68   78     2 -5  1   71   40     7 -1  1   55   21     2  4  1   74   68     8 -5  2   64   30
 0  4  0   90   78     3 -5  1   67   45     8 -1  1   66   40     3  4  1   64   49     9 -5  2   63   42
 1  4  0   74   65     4 -5  1   72   69     9 -1  1   67   76     4  4  1   67   43    10 -5  2   68   68
 2  4  0   81   82     5 -5  1   74   70    11 -1  1   67   85     6  4  1   64   58    11 -5  2   68   48
 4  4  0   62   62     6 -5  1   69   90    12 -1  1   64   24     7  4  1   65   63    12 -5  2   65   61
 5  4  0   78   80     9 -5  1   72   73     2  0  1   81   64     2  5  1   73   96     0 -4  2   59   22
 7  4  0   66   67    10 -5  1   62   54     3  0  1   73   71     4  5  1   64   68     1 -4  2  107   82
 0  5  0   68   69     1 -4  1   87  111     4  0  1   82   94     2  6  1   65   65     2 -4  2  111   88
 1  5  0   82   83     3 -4  1   62   72     5  0  1   55   47     1 -8  2   73   93     3 -4  2   52   18
 2  5  0   65   38     4 -4  1   72   88     6  0  1  106  149     4 -8  2   75   74     4 -4  2   88   63
 3  5  0   66   49     5 -4  1   65   77     7  0  1   58   33     6 -8  2   67   68     5 -4  2  115  123
 4  5  0   62   44     6 -4  1   79   88     8  0  1   70   68    10 -8  2   67   52     7 -4  2  110  119
 6  5  0   65   56     8 -4  1   60   32     9  0  1   73   78     0 -7  2   69   59     8 -4  2   67   48
 7  5  0   66   46     9 -4  1   65   61    11  0  1   68   77     1 -7  2   72   66     9 -4  2   59   32
 0  6  0   73   64    10 -4  1   65   60     1  1  1  100  117     2 -7  2   64   41    10 -4  2   73   92
 1  6  0   65   37     1 -3  1  107  127     2  1  1   72   68     3 -7  2   62   24    12 -4  2   73   69
 2  6  0   69   82     2 -3  1   66   35     3  1  1   80   71     4 -7  2   62   38     0 -3  2  103   91
 0  7  0   67   72     4 -3  1   84   70     4  1  1   70   45     6 -7  2   75   59     2 -3  2  130  133
 2  7  0   77   91     5 -3  1   88   99     6  1  1   91  106     9 -7  2   71   72     3 -3  2   62   27
 0 -8  1   69   77     6 -3  1   60   37    10  1  1   70   80    10 -7  2   70   81     4 -3  2  103   75
 0 -7  1   64   59     7 -3  1   68   52     0  2  1   60   15    11 -7  2   68   61     5 -3  2  112  119
 3 -7  1   65   54     8 -3  1   79   76     1  2  1   58   55     0 -6  2   67   51     7 -3  2   87   70
 4 -7  1   73  101    10 -3  1   93  130     2  2  1  100  134     1 -6  2   83   85     8 -3  2   63   32
 6 -7  1   64   68    11 -3  1   62   50     3  2  1   53   44     2 -6  2   67   63     9 -3  2   61   33
 7 -7  1   69   71    12 -3  1   63   59     4  2  1   79   73     4 -6  2   65   59    11 -3  2   80   79
 9 -7  1   67   75     0 -2  1  104  126     5  2  1   74   90     6 -6  2   85   79     0 -2  2   59   18
 0 -6  1   72   82     2 -2  1  108  162     6  2  1   58   62     8 -6  2   69   45     1 -2  2  128  124
 3 -6  1   74   75     3 -2  1   87  111     7  2  1   71   91     9 -6  2   77   66     2 -2  2   48   31
 4 -6  1   69   71     4 -2  1   71   55     0  3  1   58   68    11 -6  2   71   56     3 -2  2  110  109
 5 -6  1   69   65     5 -2  1  104  154     1  3  1   69   77     1 -5  2  102  106     4 -2  2   64   22
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR   SBCL3.1-IODONAPHTHALENE                              PAGE  4

  H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC     H  K  L   FO   FC

  6 -2  2   94   98     0  2  2   65   72     4 -7  3   68   48     3 -3  3  123  126     7  0  3   70   52
  7 -2  2   61   33     1  2  2   71   67     8 -7  3   72   37     5 -3  3   91   75     9  0  3   71   45
  8 -2  2   86   91     2  2  2   88   87     1 -6  3   73   42     6 -3  3   87   76     0  1  3   87   58
  9 -2  2   70   64     3  2  2   77   84     2 -6  3   83   49     8 -3  3   92   99     1  1  3   96   61
 11 -2  2   81   94     4  2  2   76   61     3 -6  3   88   63    10 -3  3   86   52     3  1  3   94   73
  3 -1  2  130  165     7  2  2   68   58     6 -6  3   69   49    11 -3  3   83   65     4  1  3   82   56
  4 -1  2   64   54     8  2  2   70   68     7 -6  3   88   79    13 -3  3   78   67     5  1  3   85   77
  5 -1  2   57   47     0  3  2   76   57    12 -6  3   73   69     0 -2  3  131  127     0  2  3   73   63
  6 -1  2  106  115     1  3  2   59   20     0 -5  3   88   63     1 -2  3   84   73     1  2  3  102  102
  8 -1  2   89   86     2  3  2   64   59     1 -5  3   79   35     3 -2  3  138  156     3  2  3   71   68
  9 -1  2   60   28     3  3  2   69   74     2 -5  3  122  124     5 -2  3   98   67     4  2  3   69   80
 11 -1  2   64   52     4  3  2   84   93     4 -5  3  101   82     6 -2  3   68   37     5  2  3   78   80
 12 -1  2   70   70     0  4  2   60   71     5 -5  3  100   76     7 -2  3   74   55     0  3  3   59   37
  1  0  2  117  115     2  4  2   64   51     7 -5  3   92  118     8 -2  3   68   43     1  3  3   89   78
  3  0  2  109  118     4  4  2   72   73     9 -5  3   72   42     9 -2  3   79   63     3  3  3   59   23
  4  0  2   61   32     0  5  2   67   52     0 -4  3  106   62    12 -2  3   66   80     4  3  3   69   58
  7  0  2   89   95     3  5  2   69   70     1 -4  3   88   43     2 -1  3   57   51     5  3  3   71   54
  8  0  2   59   44     0  6  2   80   87     2 -4  3  121  122     3 -1  3   66   42     0  4  3   90   72
  9  0  2   74   69     2  6  2   66   49     3 -4  3   77   54     4 -1  3  101   87     2  4  3   69   45
 10  0  2   70   72     3  6  2   74   89     4 -4  3   86   49     6 -1  3   96   69     3  4  3   74   62
 12  0  2   78   91     0  7  2   72   59     6 -4  3   83   50     7 -1  3  108  111     5  4  3   82   98
  0  1  2   73   70     2 -8  3   73   35     7 -4  3   90   60     9 -1  3   91   94     0  5  3   93  103
  1  1  2   56   63     3 -8  3   72   51     8 -4  3   94   94     1  0  3  101   89     2  5  3   76   57
  2  1  2  104  119     4 -8  3   73   30     9 -4  3   65    8     2  0  3  100   83     5  5  3   68   64
  3  1  2   56   62     6 -8  3   71   63    11 -4  3   91  100     3  0  3   96   78     0  6  3   65   35
  4  1  2   99   98     7 -8  3   77   74     0 -3  3   94   56     4  0  3   81   79     1  6  3   75   71
  5  1  2   77   50     1 -7  3   77   62     1 -3  3   97   46     5  0  3   65   50     1  7  3   81   84
  7  1  2   70   79     3 -7  3   91   89     2 -3  3   58   28
1  SBCL3.IN1  P1
```