Structural Aspects of Group(IV) Amines and Ketimines.

By

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"You boil it in sawdust: you salt it in glue:
You condense it with locusts and tape:
Still keeping one principal object in view-
To preserve its symmetrical shape."

THE HUNTING OF THE SNARK

Lewis Carrol

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Abstract

In this work the structural aspects of M-N bonded systems of GroupIV(a) and (b) have been investigated.

1) GroupIV(a) : A novel heterocycle containing alternating atoms of titanium and nitrogen has been synthesised, and the solid state structure proved by X-ray Crystallographic methods. The titanium atom, which appears four-coordinate in solution, exhibits the unusual coordination number of five in the solid state, achieved via intermolecular chlorine bridges. The more usual octahedral geometry is found in the pyridine adduct of the ring.

The X-ray structure was not straightforward and many approaches were used, including the Patterson method, direct methods (using the X-RAY SYSTEM programmes of Phaser), and direct methods hand applied in two dimensions, with only partial success. Another direct methods approach, MULTAN, finally produced a reasonable solution and the discovery of disorder in the molecule led to the final result.
The structure shows that the dimeric rings are planar, with rather short Ti-N bond lengths, indicative of substantial d_π-p_π orbital interaction.

2) GroupIV(b) : Structural investigations have been carried out on the series of diphenylketimines $M(NC(C_6H_5)_2)_4$, (M = Si,Ge and Sn). The results show that the only major difference between the structures is in the M-N=C angle, which is sufficient to cause the three analogues to

crystallise in different space groups with increasing symmetry as the normal sp^2 angle of 120° is approached. The variations in this angle support sustantial d_{π}-p_{π} bonding in the M-N bond for M = Si, rather less for M = Ge and the effect is undetectable for M = Sn.

CONTENTS

CONTENTS (continued)

LIST OF TABLES

The page numbers refer to the page in the text preceding the Table, except for Tables in Appendix B, which are individually numbered.

TABLE

LIST OF TABLES (continued)

CHAPTER 1

Introduction:

(M-N) Bonded Systems of Group IV.

1.1.(M-N) Bonded systems of Group IV(b)

There is an extensive chemistry of compounds containing a nitrogen atom bound to a Group IV(b) element. Excluding carbon, these elements contain vacant, accessible nd orbitals, which affect their chemical behaviour and much of the sustained interest in the M-N bonded systems revolves around possible intermolecular multiple bonding using these orbitals.
The vast majority of the reported work involves silicon, although research into the germanium and tin analogues is increasing, and several comprehensive reviews have been published[1-4].

Nitrogen has a lone pair of electrons, and the orbital which contains these may interact with the empty d orbitals on M, provided that the symmetry is correct. The extent of interaction will depend on the overlap integrals but unfortunately these cannot be accurately calculated.

The concept of d orbital involvement in π-bonding was first developed on a theoretical basis by Craig et al.[5]. He suggested that d_{π}-p_{π} overlap is relatively insensitive to the diffuseness of the orbitals concerned, because in a π bond the electrons lie off the internuclear axis and are closer to the donor atom. Appreciable overlap may therefore occur even with the more diffuse d orbitals. However, all experimental evidence indicates that overlap is greatest for silicon, with more compact d orbitals, and decreases down the group as the orbitals expand.
The primary problem is the evaluation of meaningful d_{π}-p_{π}

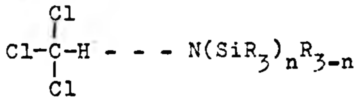
overlap integrals. The d orbitals are not properly described by Slater-type orbitals[6] which do not account for radial nodes. There are no accurate calculations, but on the basis of hydrogen-like wavefunctions the radial node of a 4d orbital occurs at about the same distance from the nucleus as the 3d radial maximum, and is therefore expected to be very inefficient at π-bonding[7].

There are problems in defining π-bonds strictly for tetrahedral molecules. Individual atom pairs must be considered, excluding the rest of the molecule. Consideration of the d orbital symmetry implies that the most favorable interactions will occur when the lone pair on nitrogen occupies an orbital of high p character. Maximum overlap will thus be achieved with planarity of the nitrogen atom. Ebsworth[8] has shown that the planarity of the donor atom is not essential, and substantial overlap can occur when the lone pair occupies an sp^3 orbital. Thus a molecule such as $P(GeH_3)_3$[9], with a non-planar skeleton, may still have some p_π-d_π orbital interaction.

The theoretical aspects of d orbital involvement have been reviewed[10-15], but predictions are limited owing to the impossibility of correctly describing the unoccupied d orbitals. Experimentally the extent of π-bonding may be deduced from the decrease in the basicity of the nitrogen atom as the lone pair is delocalised, or by determination of the M-N bond strength.

The basicity of an amine can be measured by its tendency towards adduct formation. The hydrogen-bonding capacity of silylamines, with respect to chloroform as reference acid;

i.e.



$$\mathrm{Cl{-}C(Cl)_2{-}H - - - N(SiR_3)_nR_{3-n}}$$

has been measured using infrared techniques[16]. Because ν(C-D) occurs in a cleaner area of the spectrum, and is therefore more easily distinguished, deuterochloroform is generally used. Some results are given in Table 1.1. As can be seen, silylamines show considerably lowered basicity compared with alkylamines, and successive silylation further lowers the donor capacity of the amine. The ratio of the shifted to unshifted ν(CD) peak gives a relative measure of the steric accessibility of the nitrogen electrons for donation. From these values it may be seen that whilst the donor strength of the trimeric ring is about the same as its acyclic equivalent, $(Me_3Si)_2NH$, the nitrogen lone pair is sterically more accessible.

Pitt and Fowler[17] have investigated the effect of silyl substitution of amines on their u.v. absorption spectra, (see Table 1.2). Successive silylation of ammonia results in a hypsochromic shift. The absorption is due to the transition of the nitrogen lone pair, possibly into the Si-N σ^* orbital. The shift to higher energy on increased silylation is caused by the stabilisation of the nitrogen lone pair via delocalisation. There is also a contribution from the partial rehybridisation of the nitrogen from tetrahedral sp^3 to planar sp^2; the increase in s character of the Si-N σ-bond increases the energy of the σ^* orbital.

TABLE 1.1

AMINE	ν(CD)(cm^{-1})	Ratio Unshifted:Shifted
$(CH_3)_3CNHC_2H_5$	89	1:100
$(CH_3)_3SiN(CH_3)_2$	62	1:12
$(CH_3)_3SiN(C_3H_7)_2$	77	1:1
$((CH_3)_3Si)_2NH$	30	1:1
$((CH_3)_3Si)_2NCH_3$	39	2:1
$((CH_3)_2SiNH)_3$	31	1:4

TABLE 1.2

Pitt and Fowler u.v (isooctane)

AMINE	λmax mμ	ε
Et_3SiNH_2	208.8	1780
$(Et_3Si)_2NH$	205.5	1810
$(Me_3Si)_2NH$	203.7	2870
$(Me_3Si)_3N$	200.4	4850
$PhNH_2$	233.7, 287.5	9130, 1860
$PhNHSiMe_3$	239.8, 291.0	10700, 1860
$PhN(SiMe_3)_2$	234.0, 265.0	3250, 445
$(Me_2SiNH)_3$	201.8	6160
$(Me_2SiNH)_4$	201.1	7730
n-$Me_7Si_3NH_2$	213.0	6420
n-Me_7Si_3NH	217.5	13200

Quantitatively, the decrease in basicity of amines on silylation may be determined by measuring the decrease in heats of mixing with chloroform[18]. Table 1.3 shows some sample results.

The frequencies of M-H stretching modes have been found to be a sensitive probe for the estimation of M-X d_π-p_π interaction[19,20] in compounds of the type X_3MH. There is found to be a linear correlation between the silicon and germanium analogues, indicating that the main features of the interaction are similar, but the effect is much smaller for germanium.

Photoelectron spectroscopy is a very valuable technique for investigations into possible π-bonding. The excitation of an electron from a non-bonding orbital causes no significant change in equilibrium bond lengths. By the Franck-Condon principle excitation occurs predominantly to the vibrational ground state of the molecular ion, and gives rise to a strong vibrationless component. In contrast, excitation of an electron in a bonding or antibonding orbital results in a change in equilibrium bond lengths. Excitation to various vibrational levels occurs and hence the band width increases and vibrational structure becomes apparent. Studies on Group IV(b) halides[21-23] indicate that multiple bonding is most important for silicon and that there is some d orbital participation in germanium and tin halides.

Structural data has proved useful in estimating the degree of π-orbital interaction. A most striking example of the

TABLE 1.3

Heats of Mixing **[cals/mole]**

AMINE	Heat of Mixing
n $C_4H_9NH_2$	714
$(n\ C_4H_9)_2NH$	810
$(C_2H_5)_2NH$	866
$(C_2H_5)_3N$	870
$(CH_3)_3SiNHCH_3$	355
$(CH_3)_3SiN(CH_3)_2$	359
$(C_2H_5)_3SiNH_2$	272
$((CH_3)_3Si)_2NH$	28
$((CH_3)_2SiNH)_3$	196

effect of multiple bonding can be seen in the molecule trisilylamine[24]. The nitrogen atom in this molecule is planar, as compared with the analagous trimethylamine which has pyramidal nitrogen[25]. This planarity was first thought to be due entirely to d_{π}-p_{π} bonding, with the nitrogen rehybridised to sp^2. However the same structure is not observed for the phosphorus, arsenic or sulphur analogues[26,27]. This must be due in part to the different sizes of the respective 2p, 3p and 4p orbitals, the 2p orbital being smaller and less diffuse is able to form a more effective overlap with the 3d orbitals of silicon. However other effects, such as ionic character, must be taken into account. The polar nature of the Si-N bond leads to a net (δ+) charge on silicon and mutual repulsion tends towards a planar configuration which will be stabilised by π overlap.

The results of all these investigations are consistent with the participation of d orbitals in internal π-bonding in M-N bonded systems. The effect is greatest when M is silicon and very small for germanium and tin. This trend is reflected in the reactivity of the compounds. Thus the silazanes are much less susceptible to hydrolysis than their germanium and tin analogues. The tin amines are particularly sensitive to traces of moisture and it has been suggested that reaction occurs via electrophilic attack at nitrogen and so possibly π-bonding is important for the stability of these compounds.

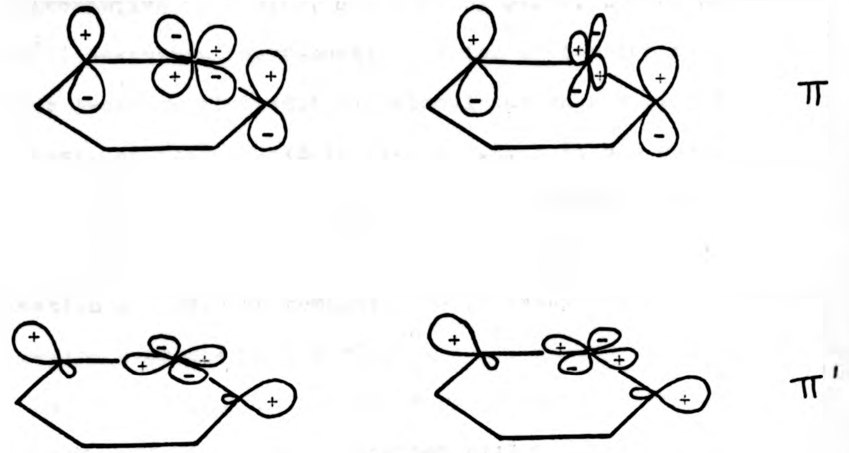
1.2. Cyclic Amines

There are no stable derivatives of Group IV(b) from silicon to lead containing formal p_π-p_π double bonds. Instead cyclic or polymeric structures are preferred, because the bond energy of (M=X) must be less than twice that of (M-X). It has been suggested that np orbitals with n greater than 2 are so diffuse that π overlap is poor[28].

Cyclic amines which exhibit the Group IV elements in their characteristic hybridisation state are well known, particularly for silicon[29-31]. The most favourable cyclic compounds are those containing alternating nitrogen atoms, in which the bonding is to some extent polar, which increases the bond energy. Providing the characteristic hybridisation is preserved, an element A may be replaced with an element A' in a heterocyclic system $(AB)_n$, formed by regular alternation, if A and A' have similar electronegativities. This is found especially for nitrogen and oxygen. Thus complete series are known such as : M_3N_3; M_3N_2O; M_3NO_2; M_3O_3.[32,33]

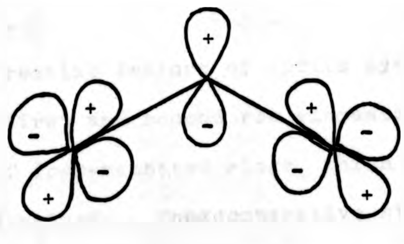
Various bonding schemes have been suggested for alternating cyclic systems of the type $(M-N)_x$ where M has vacant d orbitals. Craig and Paddock[34,35] have proposed a model in which d_π-p_π conjugation occurs throughout the ring. The symmetry properties of the d orbitals allow overlap with the p orbitals on nitrogen in a plane perpendicular to the ring (π) or in the local plane of the ring (π') forming aromatic type molecular orbitals. These interactions are schematically illustrated in Figure 1.1.

Figure 1.1



π and π' conjugation throughout the ring.

Figure 1.2



Three-centre 'island' delocalisation.

Also exocyclic π-bonding may occur between ring atoms and substituents. This type of bonding is less sensitive to non-planarity than the true aromatic p_π-p_π analogue and is not necessarily restricted to the $(4n+2)\pi$ electron systems.

An alternative mechanism, proposed by Dewar, Lucken and Whitehead[36], describes the π-bonding system as forming non-interacting 3-centre 'islands' of delocalisation covering the M-N-M linkage, as illustrated in Figure 1.2. It has been found that when the d orbitals are equally electronegative the 3-centre π-bonding accounts for 85-95% of the total delocalisation energy, the remaining 5-15% being due to delocalisation over the entire ring[37].

The extent of d_π-p_π bonding may vary between different systems because of different stereochemistries or other properties. Even in those systems which do not contain formal double bonds, such as the cyclic silazanes or siloxanes, the bonds are shorter than expected, suggesting some degree of delocalisation. For example, hexamethylcyclotrisilazane $(Me_2SiNH)_3$ has been found to be virtually planar with short Si-N bonds[38].

An interesting feature of cyclic systems based on alternating first and second row elements is the frequent occurrence of four-membered rings, which are normally considered strained. Their comparative stability is ascribed partly to the ability of such a system to minimise non-bonded repulsions. In addition to this there will be extra resonance stabilisation from the lack of perfect pairingof the ring bonds. It is probable that the assumption of perfect pairing of the ring σ-bonding orbitals fails for molecules with small ring angles. σ-Delocalisation thus becomes more important. Wherever comparative evidence is available it appears that the four-membered rings are chemically more reactive than corresponding six- or eight-membered rings[39].

1.3. The Group IV(b) Ketimines

Quite distinct from the previous examples of Group IV(b) amines, in which the nitrogen is formally sp^3 rehybridising towards sp^2 on interaction with the Group IV elements, are unsaturated systems where nitrogen is formally sp^2 and may approach sp in character on p_π-d_π delocalisation. This type of system includes the ketimines, isocyanates and isothiocyanates, in which the π system of the N=C group might be involved in d_π-p_π interaction with the vacant d orbitals. If such interaction occurs then both the π and π^* orbitals must be involved, but because of the difference in energies only one of these may be presumed to be dominant.

The first N-organosilyl ketimines were synthesised by Krûger in 1963[40], since when various Group IV(b) derivatives have been isolated. These compounds are reactive and undergo rapid hydrolysis to the parent ketimine:

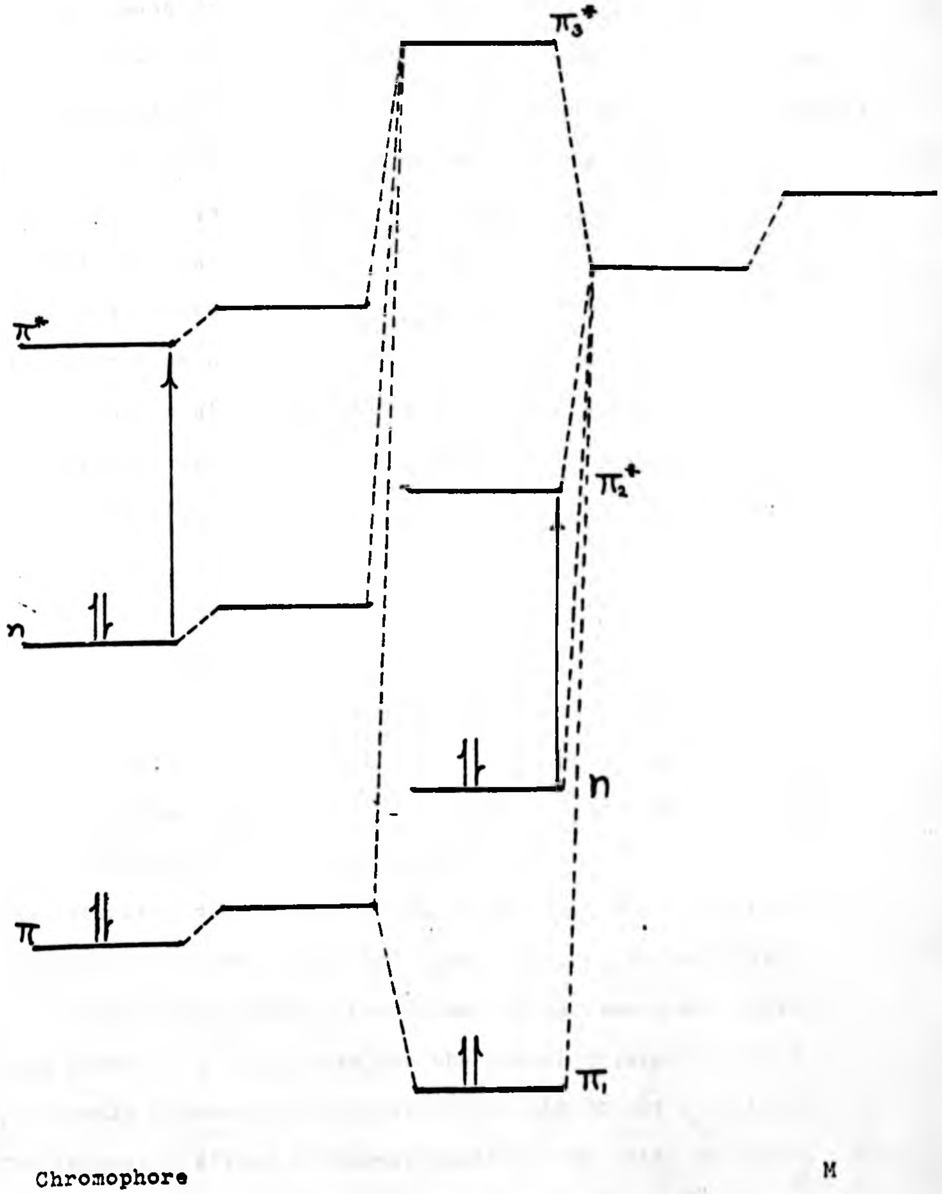
$$2R_3M(NCR_2) + H_2O \longrightarrow R_3MOMR_3 + 2HNCR_2$$

This tendency to hydrolysis increases with the number of ketimine groups and is hindered by bulky substituents on the metal.

West[41] has suggested a model for the effect of the metalloid substituent on the molecular orbital energy levels, and hence on the electronic transitions, of compounds of the type M-N=N-; M-N=C=; M-N=O; (see Figure 1.3). The vacant d orbitals on M can interact both with n and π^* levels. For most compounds the energy match of the d orbitals is better with π^*, causing resonant interaction with π^* and stabilising the excited state. A bathochromic shift of the $n \rightarrow \pi^*$ transition results. In some cases this resonant interaction is greater with the non-bonding, n, level, with the effect of π-bond formation. This probably explains the linearity of silyl isocyanate and isothiocyanate. The stabilisation of the n level in this case causes a hypsochromic shift of the $n \rightarrow \pi^*$ transition. There is thus always competition between inductive and π-bonding effects.

Chan and Rochow[42] have studied the electronic spectra of various ketimines of the Group IV(b) elements, with particular regard to the $n \rightarrow \pi^*$ transitions, which are low intensity, high energy bands. Silyl ketimines show a bathochromic shift of about 12,000cm^{-1} compared to the organic analogues, implying that d orbital interaction with the π^* orbital is greater than with the non-bonding orbital. Electron donor substituents on silicon cause no significant change in the $n \rightarrow \pi^*$ absorption maxima. This supports a bent C=N-Si linkage in which the n orbital has some s character and is directed away from the d orbitals. Such non-linearity of the nitrogen is found in other similar compounds;

Figure 1.3



bis(trimethylsilyl)carbodiimide, $Me_3SiN=C=NSiMe_3$, shows a dipole moment of 1.3 Debye units[43] where none is expected for a linear skeleton, and electron diffraction measurements for trimethylsilyl isothiocyanate and trimethylsilyl isocyanate show angles of 154° and 150° respectively at nitrogen[44]. The effect on the electronic spectra of changing the Group IV substituent was also studied. The relative order of $d_\pi - p_\pi$ bonding is known to be $Si > Ge > Sn \gg Pb$ or C[2,3,45-47]. Interpretation of the spectra must allow for the opposing effect due to electronegativities varying as $C > Si \sim Ge > Sn > Pb$[48]. The measured spectra are consistent with a combination of both these effects.

The intensity of the $n \rightarrow \pi^*$ absorption should be a sensitive indication of molecular geometry. Symmetry considerations show that the excitation of an electron from a non-bonding orbital of pure p character (p_y) (as found in a linear C=N-Si fragment) to a π^* orbital (from p_z) is forbidden. However with a C=N-Si angle of 120° the non-bonding electrons occupy an sp^2 orbital and the transition to π^* is allowed. Thus the intensity of the absorption varies with the geometry at nitrogen, and hence with the amount of $d_\pi - p_\pi$ interaction. In the series $Ph_2C=NMMe_3$ the intensity increases as $Si < Ge < Sn$. This trend is not observed for the phenyl derivatives of M, presumably because of competition for the vacant d orbitals. The inductive effect of substituents on the metal is very marked. Electron releasing groups tend to raise the energies of π, π^* and n orbitals, especially the latter as it is more directly affected, causing a bathochromic shift of the n→π* absorption.

Summarising, these results show that $d_{\pi}-p_{\pi}$ bonding is present in the Group IV(b) ketimines, although only to a small extent in the silicon compound and decreasing for the germanium and tin analogues. There is also substantial $d_{\pi}-\pi^*$ interaction, though no conclusions can be made as to the extent of $d_{\pi}-\pi$ orbital interaction.

1.4. (M-N) bonded Systems of Group IV(a)

Transition metal dialkylamides provide examples of covalent metal-nitrogen bonds, and they have been investigated with a view to elucidating the type of bonding that occurs. The field has been reviewed by Burger and Neese, and Bradley[49,50]. In MNR_2 systems the nitrogen lone pair can be used to bridge to another metal atom or alternatively there is the possibility of internal π-bonding.

The first transition metal dialkylamide, tetrakis(diphenylamino)titanium(IV), was reported in 1935[51], but until the 1960s few other derivatives were synthesised. The compounds are readily hydrolysed and this is a special case of the general reaction with an acid HL;

$$M(NR_2)_x + yHL \longrightarrow ML_y(NR_2)_{x-y} + yHNR$$

which has been explored by Lappert[52-56]. These compounds also readily undergo insertion reactions[57,58] and metathetical ligand exchange[49].

It is sometimes assumed that the high reactivity of these

M-N species must be due to weak M-N bonds with a tendency to ionic character as $\overset{+}{M}-\overset{-}{N}R_2$. However, the systems may be reactive owing to the presence of vacant, low energy orbitals on the metal which can interact with a nucleophile. The physical properties of the $M(NR_2)_x$ compounds support considerable covalency in the M-N bonds. The compounds are usually fairly volatile, and are often sublimed or distilled in vacuo, and are generally soluble in non-reactive organic solvents. The presence of strong infrared- and Raman-active bands ascribed to ν(M-N) also support the substantial covalent character of this bond[49,59]. Additional evidence is supplied by the electronic spectra which show large ligand field splitting energies, and the thermal stability implied by mass spectrographic measurements in which peaks due to parent molecular ions (e.g. $Ti(NMe_2)_4^+$ and $M(N(SiMe_3)_2)_2^+$) are found[60a,b].

Various crystal structures have been determined and the monomeric species invariably show trigonal planar nitrogen atoms, indicative of substantial π-bonding. In $W(NMe_2)_6$[61] the $C_2N-W-NC_2$ units are all coplanar. In the pentacoordinate nitrogen compounds $Nb(NMe_2)_5$ and $Nb(piperidide)_5$[62] the square pyramidal structures have the axial Nb-N bond shorter than the basal ones. Again all the nitrogen atoms are trigonal planar implying π overlap, although there is a possibility that this is due to steric congestion. It has been suggested that the longer bonds have only partial π-bonds formed from two d orbitals with the four nitrogen p_π orbitals.

A special class of dialkylamido species involvesthe bis(trimethylsilyl)amido group. These derivatives were first prepared by Bürger and Wannagat for the metals chromium, manganese, nickel, copper, iron and cobalt[63,64], and have unusually low coordination numbers. Using this ligand several three- and even two-coordinate transition metal species have been synthesised. The crystal structure of $Fe(N(SiMe_3)_2)_3$ has been reported by Bradley[65] and shows the FeN_3 unit to be trigonal planar and all the nitrogens are also trigonal planar. Similar structures are found for other three coordinate species. The planarity of the nitrogens does not necessarily imply π-bonding with the transition metal as interaction with the silicon d orbitals would have the same effect. However, the structure of $Cr(NPr^i_2)_3$ has been determined[66] and shows the $Cr-NC_2$ units to be planar and the Cr-N bond length to be somewhat shortened (1.87Å) suggesting significant orbital interactions.

Group IV(a) dialkylamides were first reported by Bradley in 1960, with the preparation of titanium(IV) and zirconium(IV) derivatives, and a hafnium analogue has also been prepared[67a,b]. Titanium(III) dialkylamides (also titanium(II) via disproportionation) were first prepared in 1969[68]. It is found that the N-phenyl derivatives are more stable to attack than N-alkyl ones, possibly because the aryl groups would enhance any ligand-metal π interaction.

Trimethylsilylamino derivatives of Group IV(a) have been prepared[69] and the electronic spectra and magnetism of the three-coordinate species have been investigated by Bradley[70]. He concludes that there is a certain amount of ligand to metal π donation into the empty metal d orbitals. This has the effect of raising the energy of the antibonding orbital, thereby increasing the M-N bond strength and decreasing the amount of π-bonding in the NSi_2 fragment.

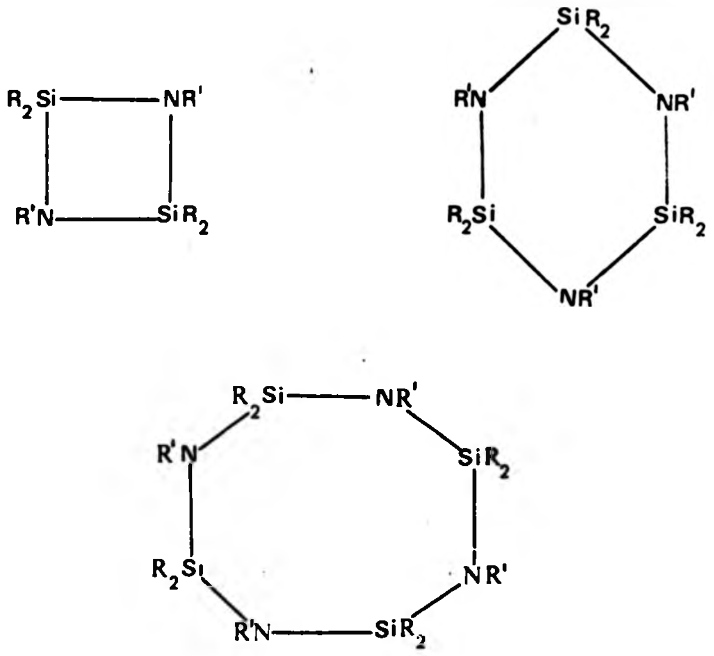
CHAPTER 2

The Synthesis and Properties of a Titanium-Nitrogen Ring System $(Cl_2TiNSiMe_3)_2$.

As mentioned in the previous chapter nitrogen containing heterocycles of Group IV(b) are well known, particularly those with alternating nitrogen atoms. Cyclic silazanes have been known since 1921 when Stock first prepared a compound analysed to be $(H_2SiNH)_n$ by the ammonolysis of dichlorosilane[71], although they were not fully characterised until 1948 when Brewer and Haber isolated well defined cyclosilazanes, $(R_2SiNH)_n$, (n = 3 and 4) from the ammonolysis of dimethyl- and diethyl-dichlorosilanes.[72] Research in more recent years has produced many well documented examples of dimeric, trimeric and tetrameric rings, (see Figure 2.1), with a wide range of substituents on both silicon and nitrogen. The chemistry of cyclogermazanes and cyclostannazanes has been much less studied but some authenticated examples of dimeric and trimeric rings are known[73-77], (see Figure 2.2).

The presence of the nitrogen lone pairs in these systems points to the possibility of adduct formation with a suitable Lewis acid. Delocalisation of the lone pair charge into the available Group IV(b) d orbitals will decrease the basicity of the nitrogen, however both π- and σ-donation are possible. Because the π system is non-continuous, owing to the d_π orbital symmetry, σ donation is more likely. Indeed there is no evidence for π donor properties of the cyclosilazanes although adducts in which the nitrogen acts as a σ donor are known. Examples of this kind of system are $MCl_3(Me_2SiNH)_3$, (M=V(III) and Ti(III), Ti(IV)), and $(MCl_3L)_2(Me_2SiNH)_4$, (M = Ti,V, and Cr; L = T.H.F or NMe_3[78,79]. A one:one adduct of

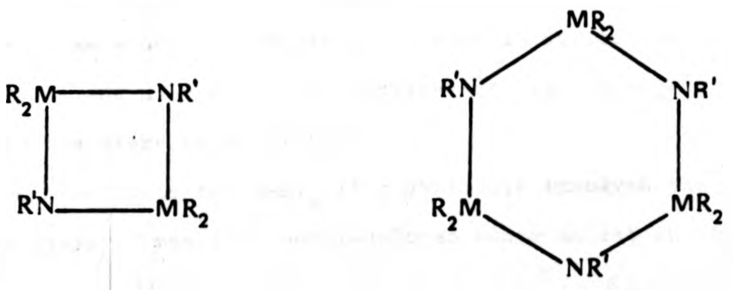
Figure 2.1



R = H, Me, Et, Ph, All, Vin, Bu^n, Bu^t, Pr^n, Pr^i, (4-$MeOC_6H_4$), OR.

R' = H, Me, Et, Bu^n, Bu^t, Ph, All, CH_2Ph, SiH_3, $SiMe_3$, $SiCl_3$, $SiEt_3$.

Figure 2.2



M = Ge : R = Me, Et, Bu, Ph, Cl ; R' = H, Me.

M = Sn : R = Me ; R' = Me, Et ; R = Bu^t ; R' = Me, CH_2Ph.

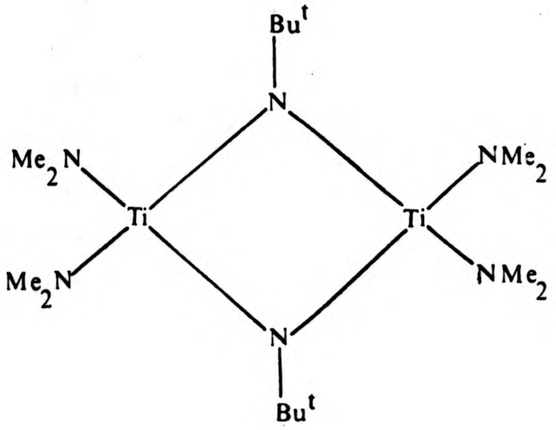
hexamethylcyclotrisilazane with tin tetrachloride has also been reported[80].

Interestingly, examples of cyclic systems, analagous to the cyclosilazanes, involving Group IV(a) elements are extremely rare. The only discrete Group IV(a)-nitrogen heterocycle prior to this work is the four-membered titanium nitrogen ring, shown in figure 2.3, formed during the ammonolysis of titanium amides, $Ti(NMe_2)_4$ and $Ti(NEt_2)_4$[81]. The reaction was repeated using a range of amines RNH_2 (R = Pr^n, Pr^i, Bu^i, Bu^s, Bu^t, Ph, and cyclohexyl) but in all cases except R = Bu^t the rings polymerise via nitrogen bridges. It was suggested that the size of the bulky tert-butyl group prevents effective intermolecular interaction. To date there have been no reported nitrogen containing heterocycles of zirconium or hafnium.

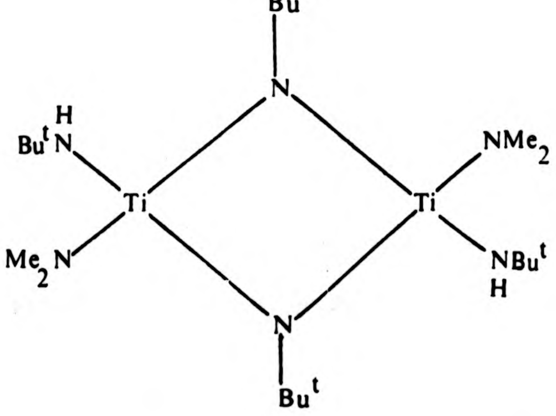
There is no obvious reason why the Group IV(a) elements should not form analogues to the cyclosilazanes. Ring compounds which contain alternating atoms of titanium and oxygen are known[82-85], and X-ray analysis has confirmed the cyclic nature of cyclotetra(μ-oxo-chloro-π-cyclopentadienyltitanium(IV), $(\pi\text{-}(C_5H_5)_2TiClO)_4$[86]. As discussed in the previous chapter elements of similar electronegativity can often replace each other in heterocyclic systems, and this is particularly true of oxygen and nitrogen. A discrete titanium nitrogen ring should therefore be attainable.

A good route to $(M\text{-}N)_x$ ring synthesis involves the ammonolysis of reactive metal-halogen bonds as set out in

Figure 2 . 3



Bu^t
N
Me₂N
Ti
Ti
NMe₂
Me₂N
NMe₂
N
Bu^t



Bu^t
N
H
Bu^t N
Ti
Ti
NMe₂
Me₂N
NBu^t
H
N
Bu^t

the following equations:

$$MCl_4 + RNH_2 \longrightarrow 1/n(MCl_2NR)_n + 2HCl$$

$$R_2MCl_2 + R'NH_2 \longrightarrow 1/n(R_2MNR')_n + 2HCl$$

The stability of the product cyclosilazanes to hydrolytic attack is known to be enhanced by silyl substituents on nitrogen. Unfortunately silylamines are well known for their decreased basicity and hence their reluctance to undergo adduct formation. However the silicon-nitrogen bond is readily cleaved and this is the driving force behind many silylamine reactions, particularly when the formation of a thermodynamically favourable product, such as trimethylchlorosilane, ensues.

Wannagat et al.[87] have investigated the reaction of titanium tetrachloride with hexamethyldisilane, $(Me_3Si)_2NH$, and its sodium salt. In both cases there is cleavage of the titanium-chlorine bond according to the equations:

$$TiCl_4 + (Me_3Si)_2NH \longrightarrow Cl_3TiNHSiMe_3 + SiMe_3Cl$$

$$TiCl_4 + (Me_3Si)_2NNa \longrightarrow Cl_3TiN(SiMe_3)_2 + NaCl$$

Treatment of the product, $Cl_3TiN(SiMe_3)_2$ with pyridine gives a compound of the formula $Cl_2py_2TiNSiMe_3$ for which the imide structure shown in figure 2.4 is postulated.

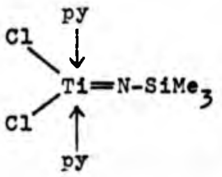


Figure 2.4

Titanium(IV) chemistry is dominated by tetrahedral or octahedral geometry.[87a] Established pentacoordinate compounds are known but not in abundance. The five-coordinate structure in Figure 2.4 might be expected to attain the more usual octahedral conformation by cyclisation. This would also avoid the formation of a formal titanium-nitrogen double bond. No other examples of such bonds to titanium have been reported.

It was decided to investigate the possible synthesis of cyclic titanium amines. On comparison with the cyclosilazane work the most obvious choice of starting materials are titanium(IV) chloride and bis(π-cyclopentadienyl)dichlorotitanium(IV). Both are readily available and have the advantage of being relatively easy to manipulate. Titanium-chlorine bonds are very reactive and many chlorinated titanium(IV) compounds are extremely sensitive to moisture because of this (especially the parent compound $TiCl_4$). In order to alleviate this problem the bis(π-cyclopentadienyl) compound was chosen for the first attempts. The reaction of this with primary organic amines is known to be complex, with some cleavage of the titanium-cyclopentadienyl linkage[88]. Tris(trimethylsilyl)amine was therefore selected as the amine source, but even under vigorous conditions the starting materials showed no sign of reaction. The reason for this must lie in the presence of the cyclopentadienyl groups, which can accept electron density from the metal, thus making the metal-chlorine bond less susceptible to attack. A more nucleophilic amine might be able to overcome this, as the initial adduct formation would be more favourable. The lithium salt of trimethylsilyl(*tert*-butyl)amine was then reacted with bis(π-cyclopentadienyl)dichlorotitanium(IV). As expected lithium chloride was immediately precipitated, however, there was no sign of evolution of trimethylchlorosilane, required by the reaction,

$$\pi\text{-}(C_5H_5)_2TiCl_2 + SiMe_3(Bu^t)NLi \longrightarrow 1/n(\pi\text{-}(C_5H_5)_2TiNBu^t)_n + LiCl + SiMe_3Cl$$

even under harsh conditions, and no isolable product could be obtained from the reaction mixture. This reaction was repeated using the lithium salts of ethylamine and *tert*-butylamine; again lithium chloride was deposited but no product could be isolated.

The use of the bis(π-cyclopentadienyl) derivative was then given up in favour of the more reactive titanium tetrachloride. This was found to react, although extremely slowly, with tris(trimethylsilyl)amine according to the following equation:

$$2TiCl_4 + 2N(SiMe_3)_3 \longrightarrow (Cl_2TiNSiMe_3)_2 + 4Me_3SiCl$$

The product, *catena*-di-μ-chloro-bis-μ-(trimethylsilylamino)-di-(chlorotitanium(IV), was formed as yellow-orange needle crystals in good yield.

Two chlorines have been removed from each titanium atom as volatile trimethylchlorosilane, but the exact mechanism is open to conjecture. The possibilities are that either one or both of the chlorines are lost via solvolysis to give respectively $Cl_3TiN(SiMe_3)_2$ or $Cl_2Ti(N(SiMe_3)_2)_2$. In the first instance intramolecular elimination of trimethylchlorosilane followed by dimerisation would yield the product. In the second case the $Cl_2Ti(N(SiMe_3)_2)_2$ could react with a further molecule of titanium tetrachloride, i.e. intermolecular elimination would result in product formation. In an effort to distinguish which intermediate was being formed the reaction was halted at various intervals. However it was not possible to isolate either of the possible amides from the reaction mixture. The solubility of the intermediate parallels that of the product, and so this was always present as an impurity.

The yellow-orange crystalline product is extremely sensitive to hydrolysis and decomposes without melting at $T \geqslant 415^{o}K$ to a brown amorphous solid. It exhibits limited solubility in benzene, cyclohexane, chloroform and dichloromethane. Heating in vacuo to $600^{o}K$ causes decomposition to an almost black, polymeric material approximating to $(ClTiN)_x$, i.e. loss of a further molecule of trimethylchlorosilane.

Cryoscopic and vapour pressure osmometric molecular weight determinations were denied by the insufficient solubility of the compound. The mass spectrum was measured but the thermal instability of the molecule prevented detection of the parent molecular ion. The highest m/e value measured was 206, which corresponds to the $(Cl_2TiNSiMe_3)^+$ fragment.

An X-ray crystal structure analysis unambiguously showed the crystals to be composed of planar, dimeric titanium-nitrogen rings, polymerised via chlorine bridges (see Figure 4.2). The crystallographic aspects of the structure are reported in Chapter 4.

Spectral Data

Infrared

Both solid and solution (dichloromethane) infrared spectra were obtained, and band assignments are given in Table 2.1. The titanium-nitrogen stretching mode has been reported[89,90,91] to occur between 580 and 670 cm^{-1}. The band at 640 cm^{-1} is tentatively assigned to this mode. The relatively high energy could be due to substantial overlap of the nitrogen p_π and titanium d_π orbitals.

The titanium-chlorine stretching frequencies should be informative with regard to the coordination number of the titanium atom[92-94]. For tetrahedral chlorotitanium(IV) compounds $\nu(\text{Ti-Cl})_{\text{terminal}}$ occurs in the region 470 to 490 cm^{-1}, whereas similar absorptions for octahedral analogues are normally found in the region 370 to 400 cm^{-1}. The solid phase spectrum of the cyclotitanazane shows a strong band at 427 cm^{-1}, attributable to $\nu(\text{Ti-Cl})_{\text{terminal}}$, which is indicative of pentacoordination. The band at 231 cm^{-1} is assigned to a bridging $\nu(\text{Ti-Cl})$ mode on the basis of previous assignments.

The solution spectrum is virtually identical to the solid phase one, except in the region of $\nu(\text{TiCl})$ frequencies. The bridging (TiCl) stretching mode is no longer observed and $\nu(\text{Ti-Cl})_{\text{terminal}}$ has shifted to 470 cm^{-1}, indicating a change in the geometry of the titanium atom towards tetra hedral. The species in solution therefore appears to be monomeric, with four-coordinate titanium (see Figure 2.5).

TABLE 2.1.

INFRARED SPECTRAL DATA (cm^{-1})

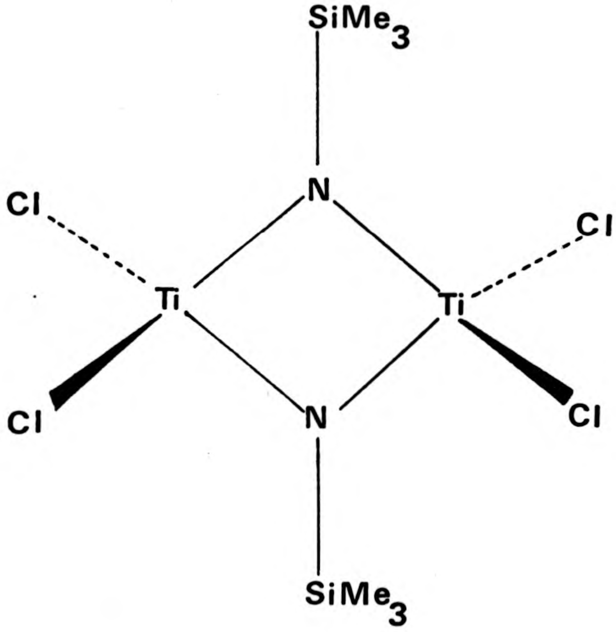
$(Cl_2TiNSiMe_3)_2$ and Sublimate B		Sublimate A		Pyridine Adduct	Mode
Solid	Solution	Solid	Solution	Solid	
				3102 w*	
				3062 w*	
				3042 w*	
2948 w	2965 w	2978 w	2965 w	2948 m	$\nu_{as}(CH_3)$
2919 sh				2820 sh	
2785 w	2910 w	2920 w	2910 w	2787 w	$\nu_s(CH_3)$
				2746 w	
				1603 s*	
				1482 w*	
				1442 w*	
1403 w	1410 m	1406 m	1410 m		$\delta_{as}(CH_3)$
	1265 sh	1265 sh	1265 sh	1250 m*	
1244 s	1252 s	1252 s	1252 s	1239 m	$\delta_s(CH_3)$
				1212 m*	
				1151 m*	
				1069 m*	
				1041 m*	
1014 w	1070 w	1012 w	1070 w	1011 m*	
	986 w		986 w		
886 m	896 s	894 m	896 s	946 s	$\nu_{as}(Si\text{-}N)$
844 vs	847 s	845 vs	847 s	833 s	$\rho_{as}(CH_3)$
827 s	826 s	826 s	826 s		
756 s	759 s	758 s	759 s	753 s*	$\nu_s(Si\text{-}C)$
698 m	698 m	698 m	698 m	692 s*	$\rho_s(CH_3)$
670 m	670 m	670 m	670 m	670 w	$_{as}(SiC_3)$
				654 w*	
640 s	641 s	643 s	641 s	636 s	$\nu(Ti\text{-}N)$
624 m	624 m	624 m	624 m	620 sh	$\nu_s(SiC_3)$
				428 m*	
427 s	468 s	470 s	468 s	371 s	$\nu(Ti\text{-}Cl)$(terminal)
356 m	356 m	352 m	356 m	350 s	
276 m		276 m		258 m	$\delta(Si\text{-}N)$
231 w					$\nu(Ti\text{-}Cl)$(bridging)

* = due to coordinated pyridine.

s = strong vs = very strong m = medium w = weak sh = shoulder.

Bands have been assigned on the basis of known vibrational modes of the starting materials[98,99,103-105].

Figure 2.5



^{1}H n.m.r.

The proton n.m.r. spectrum was measured using dichloromethane as both solvent and internal reference (4.50τ). As expected a singlet peak was obtained at 9.43τ, which is slightly downfield from the starting material, tris(trimethylsilyl)amine resonance (9.59τ; dichloromethane solution). This deshielding effect can be rationalised in terms of π-bonding between the nitrogen and the titanium.

Electronic Spectrum

The absorptions occurring in the electronic spectrum are recorded in Table 2.2. The bands are due to charge transfer transitions from the lone pairs on chlorine and nitrogen. Possible transitions are chlorine(π)$\rightarrow$titanium(d); nitrogen(n)$\rightarrow$silicon(d); and nitrogen(n)$\rightarrow$titanium(d).

Sublimation

Attempts to purify the cyclotitanazane via sublimation resulted in two different components; a yellow amorphous powder, A, sublimes slowly at 363-373°K, and above 373°K an orange microcrystalline component, B, also collects on the cold finger. The cyclotitanazane decomposes rapidly above 410°K and slowly at the temperatures required for sublimation. The extremely slow sublimation necessary for the separation of A and B was thus accompanied by considerable loss of material. Elemental analyses of the products, A and B, were identical with that of the parent cyclotitanazane. Furthermore, all solution spectra (infrared, ^{1}H n.m.r. and electronic) were identical with the solution spectra of the parent cyclo-

TABLE 2.2

Electronic Spectral Data (cyclohexane solution; λ_{max} cm^{-1})

$(Cl_2TiNSiMe_3)_2$	Sublimate A	Sublimate B
45500 s	45500 s	45500 s
44200 sh	44200 sh	44200 sh
40800 sh	40800 sh	40800 sh
33300 sh	33300 sh	33300 sh
25500 m	25500 m	25500 m

s = strong; m = medium; sh = shoulder

titanazane. The solid phase infrared spectra, (see Table 2.1) show some differences in the region of titanium-chlorine stretching modes. The crystalline sublimate, B, exhibits the same bands as the cyclotitanazane, indicating a penta-coordinate species polymerised via chlorine bridge bonds. Sublimate A however shows no band due to a bridging ν(Ti-Cl) mode, and $\nu(\text{Ti-Cl})_{\text{terminal}}$ occurs at 470 cm^{-1}, indicating a four-coordinate species similar to that existing in solution.

Behaviour in Solution

Samples of the ring were dissolved in dichloromethane, (as a neutral solvent) and in ether (as a weakly coordinating solvent). The solvents were then removed under vacuum and the resultant solids were pumped for several hours to complete dryness. The solid phase infrared spectra were then measured. The sample retrieved from the dichloromethane solution was microcrystalline and the spectrum was identical to that of the original five-coordinate bridged species. The sample from the ethereal solution was non-crystalline, and appeared identical to sublimate A, the non-bridged, discrete ring. Presumably the ether, coordinated to the titanium in solution, hinders the formation of intermolecular chlorine bridges.

Adduct Formation

It was decided to investigate the donor ability of the cyclotitanazane ring nitrogens similar to that demonstrated in the cyclosilazanes. The ring is expected to be a weak σ-donor, as the solid state structure shows substantial delocalisation of the nitrogen lone pair. The species in solution is thought to be four-coordinate from infrared evidence. The distortion of the tetrahedral angle to accomodate a ring which is planar (or nearly so) might be stabilised by solvation. Alternatively, the ring skeleton may be puckered, relieving the angle strain by weakening the π-orbital interaction: increased basicity of the nitrogen would result, with the possibility of donation to a suitable Lewis acid. Titanium tetrachloride is known to form adducts with the cyclosilazanes but failed to react with the cyclotitanazane in the temperature range required to avoid decomposition of the ring. A π-bonded complex might be preferred if there is a high degree of delocalisation. (π-Bicyclo(221)hepta-2,5-diene)tetracarbonyl-molybdenum(0), $C_7H_8Mo(CO)_4$, might be a good system for this kind of adduct formation. The diene is easily displaced leaving two cis-coordination sites available. The mild conditions normally required for substitution reactions also favour its use[95-97].

$(CO)_4$Mo(norbornadiene) was allowed to react with the cyclotitanazane at ambient temperatures. Careful work-up under strict anhydrous conditions yielded a brown solid, completely insoluble and probably polymeric, and also an olive-green powder which was soluble in a wide range of organic solvents. This green compound was extremely sensitive to traces of air and moisture, and appeared to be unstable, decomposing to a light brown polymeric powder. Adequate characterisation of this compound was therefore not achieved.

Lewis Acid Behaviour

Octahedral geometry is very common in titanium(IV) chemistry. The cyclotitanazane has the ability to react with donor ligands to form a six-coordinate complex, and in fact is extremely soluble in coordinating solvents such as pyridine, acetonitrile or tetrahydrofuran. This contrasts with the limited solubility demonstrated in non-coordinating solvents.

It was decided to investigate the cyclotitanazane/pyridine system as a direct comparison to Wannagat's work, in which the titanium imide species was postulated (see Figure 2.4). The reaction was carried out in benzene using an excess of pyridine. The product, formed over a few hours, was precipitated as chunky orange crystals which were soluble in dichloromethane, pyridine, acetonitrile and to a small extent in benzene. Decomposition without melting occurs at $T > 373^{\circ}K$ to a brown solid with loss of pyridine. As with the parent cyclotitanazane hydrolysis is rapid via attack at the titanium-chlorine bond. Elemental analysis agrees with the empirical formula $C_{13}H_{19}Cl_2N_3SiTi$ for the compound which is consistent with a bis-pyridine adduct formulation similar to the Wannagat compound (Figure 2.4). A molecular weight determination to prove the integrity of the ring skeleton was attempted by cryoscopic and vapour pressure osmometric methods. However, unsatisfactory results were obtained, probably because of the hydrolytic instability of the compound.

Spectral Data

The solid phase infrared spectrum (see Table 2.1) shows all the bands expected for coordinated pyridine[98,99], in addition the original cyclotitanazane vibrations appear, with only the titanium-chlorine stretching region showing a major shift. The band due to the bridging ν(Ti-Cl) vibration is missing altogether, and the terminal ν(Ti-Cl) mode occurs at 371 cm^{-1}, within the range for octahedral coordination of the titanium.

The proton n.m.r. spectrum (dichloromethane solution) shows a complex multiplet around 1.0 τ due to the pyridine moieties, and a singlet peak at 9.52 τ. There is thus a small upfield shift of .07 τ from the free cyclotitanazane. The ratio of the integrated intensities of the two peaks is 9.0 : 10.0 (trimethylsilyl :pyridine protons), which is consistent with a bis-pyridine adduct.

The similarity between the spectra of the pyridine adduct and the parent cyclotitanazane suggests that ring cleavage has not taken place. The adduct is therefore proposed to be bis-μ-[trimethylsilylamino]-bis-(dichlorodipyridine-titanium(IV)), $(py_2Cl_2TiNSiMe_3)_2$, shown in Figure 2.6, and not the imide structure put forward by Wannagat, shown in Figure 2.7 for comparison.

Figure 2.6

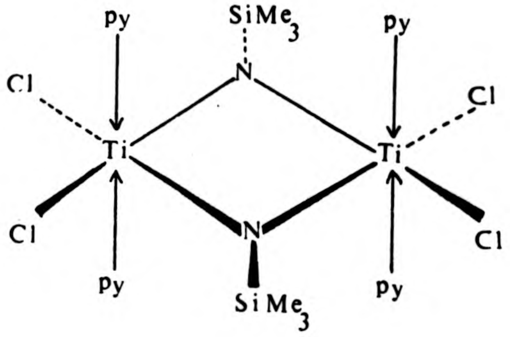
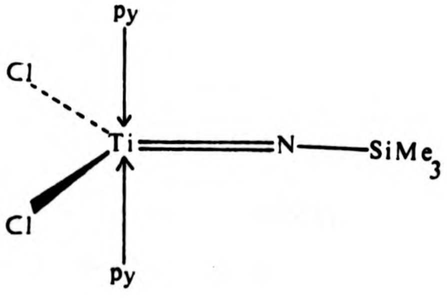


Figure 2.7



Experimental

Due to extreme air-moisture sensitivity of the products and many of the reactants special techniques were necessary. Materials were handled under an inert atmosphere or under high vacuum.

All glassware was thoroughly washed in chromic acid and dried by baking in an oven at 400°K for several hours, and whenever possible flamed out under vacuum prior to use.

All materials were purified prior to use.

BENZENE: Supplied by Koch Light Laboratories Ltd., Colnbrook. It was stored over sodium wire and when required was heated under reflux over CaH_2 or $LiAlH_4$ and distilled under a normal pressure of nitrogen.

DICHLOROMETHANE: Supplied by Hopkin and Williams Ltd., Essex. This was heated under reflux over P_2O_5 and distilled under a normal pressure of nitrogen.

n-HEXANE: Supplied by B.D.H. Chemicals Ltd., Poole. This was stored over sodium wire and prior to use was heated under reflux over CaH_2 or $LiAlH_4$ and distilled under a normal pressure of nitrogen.

CYCLOHEXANE: Supplied by B.D.H. Chemicals Ltd., Poole. Purified as n-hexane.

MOLYBDENUM HEXACARBONYL: Supplied by Koch Light Laboratories Ltd.. Purified by sublimation under vacuum.

$(CO)_4Mo$(norbornadiene): Prepared by the method of Pettit[101].

PYRIDINE: Supplied by Fisons Scientific Apparatus Ltd., Loughborough. This was distilled under a normal pressure of nitrogen over KOH pellets.

TITANIUM TETRACHLORIDE: Supplied by Hopkin and Williams Ltd., Essex. This was stored over copper powder to remove traces of iron and vanadium impurities and distilled in vacuo when required.

TRIS(TRIMETHYLSILYL)AMINE: This was prepared by the method of Lehn[100] and purified by distillation under reduced pressure.

Analyses

Chlorine was determined by the Volhard method[102]. A small quantity of sample (about 0.1gm) was hydrolysed with aqueous nitric acid made up to 50mls in a graduated flask. Determinations were carried out on 10ml aliquots. Silver nitrate solutions were standardised against sodium chloride using potassium chromate as indicator; potassium thiocyanate solutions were standardised against silver nitrate with ferric ion as indicator

Elemental analyses for carbon, hydrogen and nitrogen were carried out professionally at the A. Bernhardt Microanalytical Laboratories, Mullheim, Germany.

Spectral Measurements

1) Infrared Spectra (4000-200 cm^{-1}): Recorded on a Perkin-Elmer 621 Grating Infrared Spectrophotometer. Calibrations were taken at three points, 2850, 1601, and 1028 cm^{-1} from a 0.05mm polystyrene film. Samples were run as nujol or hexabutadiene mulls held between caesium iodide plates. Solution spectra were recorded with the samples held in potassium bromide windowed infrared solution cells.

2) Proton Nuclear Magnetic Resonance Spectra (60MHz): Recorded on a Perkin Elmer R 12 Spectrophotometer.

3) Electronic Spectra: Recorded on a Cary 14 Spectrophotometer. Solution spectra were measured using special sealed 1cm silica cells (see Appendix A).

Experimental Details

1) Preparation of $(Cl_2TiNSiMe_3)_2$

Titanium tetrachloride (3 moles i.e. excess) was distilled into a glass reaction vessel containing tris(trimethylsilyl)-amine (1 mole) and dry benzene. On warming to 293°K a yellow solution was apparent, which gradually deepened over a few days to red and some red crystalline material was precipitated. As the reaction proceeded more of this was produced and the product began to be deposited as yellow-orange needles. Three months (at 293°K) was required for total conversion to the product. The solid was filtered and washed with n-hexane. A sample of the crystalline material was sealed under nitrogen into a glass vial to be used for the crystal structure analysis, and the remainder was extracted with dry dichloromethane, (yield = 65%). Fractional distillation of the filtrate gave 2 moles of trimethylchlorosilane (B.P. 59-60°).

Melting point: Decomposes at $T \geqslant 415^{\circ}K$.

Analysis: Required for $(Cl_2TiNSiMe_3)_2$; Cl=34. 5 %; N=6.8 %; C=17. 5% ; H=4. 4 %. Obtained results were; Cl=34.6 %; N=6.9 %; C=17. 5%; H=4.4 %.

2) Reaction of $(Cl_2TiNSiMe_3)_2$ with $(CO)_4Mo$(norbornadiene).

$(CO)_4Mo$(norbornadiene) was prepared from molybdenum hexacarbonyl and excess norbornadiene (bicyclo(2.2.1)hepta-2,5-diene), in petroleum ether[101]. Recrystallisation from petroleum ether gave a good yield of yellow plate-like crystals of $(CO)_4Mo$(norbornadiene). This (1 mole) and $(Cl_2TiNSiMe_3)_2$ (1.5 moles) were allowed to react in benzene in an evacuated glass reaction vessel. The reaction was left for some weeks and then careful filtration yielded a green-brown solution and a light brown solid, insoluble in all organic solvents and probably polymeric. The solution, after cautious work-up gave an olive green powder which proved to be extremely sensitive to air and moisture, and adequate characterisation was not achieved.

3) Preparation of the pyridine adduct of $(Cl_2TiNSiMe_3)_2$.

Dry pyridine (3 moles) was distilled into a glass reaction vessel containing $(Cl_2TiNSiMe_3)_2$ (1 mole) and benzene. The orange solution deposited an orange crystalline solid over a few days. Careful anhydrous work-up yielded the product, which was recrystallised from dichloromethane/hexane (yield = 95%).

Melting point: Decomposes at $T \geqslant 393^\circ K$.

Analysis: Required for $(py_2Cl_2TiNSiMe_3)_2$; Cl=19.5 % ; N=11.5 %; C=42.8 %; H=5.2 %. Results obtained were; Cl=19.8 %; 11.5% ; C=42.6 %; H=4.8 %.

CHAPTER 3

Crystallographic Techniques.

Crystal structure analyses have been carried out on the cyclic amines catena-di-μ-chloro-bis-μ-(trimethylsilylamino)-di-(chlorotitanium(IV), $(Cl_2TiNSiMe_3)_2$, and nonamethylcyclotrisilazane, $(Me_2SiNMe)_3$, and the diphenylketimenes $M(NC(C_6H_5)_2)_4$ (M=Si, Ge and Sn); the results are discussed in Chapters 4 and 5. The techniques used during these structure determinations are set out and discussed below. The general background and mathematics behind the theory has been described in various books[106-110] and so will not be covered in any detail.

3.1. Data Collection

The first step in any crystal structure analysis is to determine the space group and unit cell vectors, and to this end initial Weissenberg or Precession photographs were taken. Observations on symmetry and systematic absences provided a basis for the selection of a space group and unit cell dimensions were approximately measured.

Intensity data were collected by diffractometer throughout the investigation. Data for the cyclotitanazane, $(Cl_2TiNSiMe_3)_2$, were collected on a Stoe 2-Circle Weissenberg Diffractometer, equipped with a graphite monochromator. Initial centring was carried out manually (see Chapter 4.1. for details). All other determinations used a computer controlled Automatic Syntex $P2_1$ 4-Circle diffractometer, which was also equipped with a graphite crystal as monochromator.

The coordinates of several (up to fifteen) Friedel pairs of spots, obtained from a rotation photograph, were fed into the centring programme and accurately located by refinement. These were then used to generate sets of possible axial vectors; the choice of vectors defined the orientation matrix to be used. This matrix was then refined by using higher angle (2θ) reflections. Reflections were scanned using the 2θ method in which both the counter (2θ circle) and the crystal (ω circle) are rotated at relative angular rates given by:

$$\Delta 2\theta = 2\Delta\omega$$

A maximum 2θ value of 130° (Cu K_α radiation) or 50° (Mo K_α radiation) and variable scan rates dependent on reflection intensity were employed. Coincidence corrections were applied automatically to particularly intense reflections with the number of counts not exceeding 50,000. The background radiation was measured for half the time taken to measure each peak.

Standard reflections were collected at intervals so as to check for variations in intensity due to decomposition. When a crystal showed signs of decomposition during data collection the structure factors were rescaled on the basis of the drop in intensity of the standards. The scaling expression is:

$$\text{Scale} = 1.0(1.0 + \alpha T)(1.0 + \beta T\frac{\sin\theta}{\lambda})$$

Where T = exposure time in hours and α and β are the coefficients to be determined.

After collection the data must be reduced to the form of Structure Factors (Fs) where $F \propto \sqrt{I}$ and I is the measured intensity. Polarisation and Lorentz factors must be accounted for and corrections for background must be made. The Lorentz factor is dependent on the method used to collect the data. For general inclination geometry the axis of rotation makes an angle $(\pi/2) - \mu$ with the incident X-ray beam and a reciprocal lattice point P on the nth layer (perpendicular to the axis of rotation). The semi-angle of the cone of diffraction for the nth layer reflections is $(\pi/2) - \nu$, and Υ is the projection on the zero layer of the 2θ angle between the incident and reflected beams. The Lorentz factor is given by:

$$L^{-1} = \cos\mu\cos\nu\sin\Upsilon$$

For equiinclination Weissenberg geometry, as in the Stoe 2-Circle diffractometer, $\mu = -\nu$ and the expression reduces to:

$$L^{-1} = \cos^2\nu\,\sin\Upsilon$$

The geometry of the 4-Circle diffractometer is similar to that of the zero layer Weissenberg case, in which $\mu = \nu = 90^\circ$ and $\Upsilon = 2\theta$. The expression becomes:

$$L^{-1} = \sin 2\theta$$

The polarisation factor for monochromatised radiation is given by either

$$P = \frac{(\cos^2 2\theta_m \cos^2\varepsilon)\cos^2 2\theta + \cos^2 2\theta_m \sin^2\varepsilon + \cos^2\varepsilon + \sin^2\varepsilon\cos^2 2\theta}{1 + \cos^2 2\theta_m}$$

$2\theta_m$ = the Bragg angle for the monochromator

$\sin\varepsilon = \tan\mu\cot\theta$ where μ is the inclination angle for the Weissenberg geometry, or by

$$P = \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{1 + \cos^2 2\theta_m}$$

with 'parallel' setting of the monochromator.

The raw data from the Stoe diffractometer was fed into the programme DATPRO and that from the Syntex was fed into SYNDAT. These programmes process the data into the corrected structure factor form.

A systematic error in intensity data arises through absorption of radiation by the crystal. The diffracted beam is attenuated to the extent:

$$I = I_o e^{-\mu\tau}$$

I = measured intensity

I_o = incident intensity

τ = the total distance travelled through the crystal

μ = the linear absorption coefficient given by:

$$\mu = \rho \sum_n (P_n/100)(\mu/\rho)_{E_n,\lambda}$$

P_n = percentage of element in the compound

μ/ρ = mass absorption coefficient for the element E_n at wavelength λ.

The crystal must be described and measured as exactly as possible[111]. The bounding faces (which are not necessarily crystallographic planes) were measured by rotating the crystal using a Nonius orienter on which a dial indicates the angle of rotation. As each face was eclipsed the rotation angle ψ_A was noted and the scale reading, D_A, where the face cuts the x,y line was measured by means of a Vickers Screw micrometer eyepiece attached to the microscope. The crystal was rotated about 180° and the process repeated to obtain ψ_B and D_B. The angle (θ) between the face and the rotation axis was also measured. The plane equation is then:

$$x\sin(\psi - \psi_o) + y\cos(\psi - \psi_o) \pm z\tan\theta = \tfrac{1}{2}(D_B - D_A)$$

The sign of the z term is determined by the intersection of the plane at + or - z (the rotation axis).

The corrected intensities are calculated by the programme ABSCOR[112]. The crystal is divided into polyhedra within which rays are entering or leaving through one face only.

Within these polyhedra the loci of constant absorption are planes; these may lie in any direction but their position is determined from the absorption of rays diffracted at the corners of the polyhedra. For each of the polyhedra the contribution to the total diffracted intensity (A_T) is found. The transmission ($e^{-\mu\tau}$) is given by A_T/V, where V is the crystal volume.

The absorption effect is most important for elements with high atomic number (Z) and for less penetrating radiation. In this work absorption corrections were only applied to the tin ketimine, $Sn(NC(C_6H_5)_2)_4$, for which Cu K_α radiation was used, (λ = 1.5418Å).

Binary data files were set up for each data set. This was done using the programmes SORTM (for the Stoe), SYNDAT (for the Syntex data) and DATRDN (for the X-RAY SYSTEM). These programmes make use of symmetry, unit cell contents, molecular $F_{(000)}$ and individual atomic scattering factors[113]. Should it become necessary the data may be transformed into a different space group at a later date.

3.2. Solution of the Structure

Deducing atomic positions from intensity data is made difficult by the fact that the amplitudes of the structure factors are known but their phases are not. Solving a structure depends on the determination of an approximately correct phase set.

3.2.1. The Patterson Method

Initial Phase determination is often attempted using the 'heavy atom' Patterson approach which has been successfully applied in this work. Patterson[114,115] showed that a fourier synthesis with $|F|^2$ as coefficients (and hence no phase problem) has peaks corresponding to all the interatomic vectors. The height of a Patterson peak is proportional to the product of the atomic numbers of the atoms which give rise to it, and so those between heavy atoms should be easily located.
The search may be made easier by referring to the Harker lines and sections for vectors between symmetrically equivalent atoms[116]. The positions of the Harker lines and planes may also be of help in ascertaining or checking the correctness of the space group. The heavy atom(s) once located serve to determine the phases and intensities of the reflections to a large extent, and a fourier synthesis based on the calculated phases and observed structure factor amplitudes should show the positions of the remaining atoms.

3.2.2. Direct Methods

An alternative approach used successfully here is direct methods of phase determination. All the crystals studied in this way belong to centrosymmetric space groups, thus limiting the possible phases to 0 or π, i.e. confining the problem to the assignment of a plus or minus sign to each structure factor amplitude.

The direct method approach relies on mathematical relationships in the form of inequalities or probabilities between the phases of the reflections. These may be hand applied or, more commonly, make use of a computer. Both methods have been successfully employed here.

The hand application of inequality relationships was used to elucidate the h,k,0 projection of the pseudo-subcell of the cyclotitanazane, $(Cl_2TiNSiMe_3)_2$, (see Chapter 4). The first step involved conversion of the 102 h,k,0 structure factors into normalised structure factors (Es), satisfying the criterion $\langle E^2 \rangle = 1$, following the method of Woolfson[117]. The Harker-Kasper inequality relationships[118,119]

$$s(h).s(h').s(h \pm h') = +1$$

were then applied to the highest E values. Two strong reflections, (0,12) and (2,11), were chosen to be origin determining and there phases were arbitrarily assigned as positive. These acted as the starting point for phase determination and those large Es directly related to these could also be assigned positive. When no further progress could be made in this way the next highest E value was given the sign symbol 'a' and the process repeated. The use of two further sign symbols 'b' and 'c' gave the final phasing of the 27 highest, unique Es in terms of +, a, b, c or their products. Several inequalities supported the relationship $a = c \neq b$, and also $a = +$. The assumption that $a = c = +$ and $b = -$ gave the distribution of +:- of 14:13. The fourier synthesis hand computed on this basis showed six atoms, which were assumed to be the two titaniums and four chlorines expected in the pseudo-subcell. Least squares refinement on this assumption gave an initial R value of .42 which rapidly improved on further refinement. After the addition of further atoms (presumed to be silicons and nitrogens) an R value of .128 (102 reflections) was reached.

The limitations of the above hand application of direct methods lie chiefly in the size of the structure that can be conveniently handled. Two computer approaches have been used to overcome this problem, namely the X-RAY SYSTEM programme 'Phaser' (NORMSF, SINGEN and PHASE) and the programme MULTAN (NORMAL and MULTAN I,II,and III). The first stages of each are similar, involving the normalisation of the structure factors and the setting up of sigma-2 relationships. The programmes PHASE and MULTAN II and III, however, differ in their approach to phase determination.

Initially the observed structure factor amplitudes are converted to normalised structure factors (Es); there are two main approaches to this. Temperature and scale factors may be obtained from a Wilson plot:

$$\ln\left(\frac{I_{rel}}{\sum_{i=1}^{n} f_{o_i}^2}\right) = \ln C - 2B\left(\frac{\sin^2\theta}{\lambda^2}\right)$$

The overall temperature factor B is obtained from the slope and the intercept gives C which is related to the required scale factor by:

$$k = \frac{1}{\sqrt{C}} = \frac{|F_{abs}|}{|F_{rel}|}$$

The normalised structure factors are defined in terms of unitary structure factors, which are in turn obtained from the observed structure factors:

$$U_{hkl} = \frac{F_{hkl}(\text{point})}{F_{000}} = \frac{F_{hkl}}{e^{-B\left(\frac{\sin^2\theta}{\lambda^2}\right)}\left(\sum_{i}^{n} f_{o_i}\right)}$$

and $$E^2_{hkl} = \frac{U^2_{hkl}}{\overline{U^2}}$$

also $$\langle E^2 \rangle = 1$$

The second approach to normalisation involves the use of 'K-curves', where K is derived from

$$F^2(h) = K(s).I(h)$$

where K(s) is the K value for a small $(\sin\theta)/\lambda$ interval, (s). $\langle E^2 \rangle$ is assumed to be 1.0 for both the overall case and for $(\sin\theta)/\lambda$ zones. K is computed for a number of $(\sin\theta)/\lambda$ intervals and the curve obtained gives the scale function for:

$$k\langle F^2 \rangle = 1.0$$

The normalised structure factors are thus obtained by setting:

$$E^2 = kF^2$$

NORMAL uses the Wilson plot only, but NORMSF provides a choice of both methods.

The advantage of Es over Us is that they allow normalisation of all classes of reflections to a common basis. Thus they may be scaled such that $\langle E^2 \rangle$ =1.0 for the data as a whole or for separate groups. Experimentally the intensities of the reflections in different parity groups may vary considerably in some structural analyses. NORMAL allows the separate scaling of each parity group to overcome this problem. Unfortunately, NORMSF does not include this facility and during the investigation of the cyclotitanazane (see Chapter 4) Phaser failed to produce a reasonable solution because of the variations in different parity group intensities.
Finally, both NORMAL and NORMSF give the statistical distribution of Es and compares this with the theoretical

centric and acentric cases.

SINGEN and MULTAN I (SIGMA-2) then set up the sigma-2 relationships, which are based on the Sayre equation[120]:

$$sE_h.sE_k.sE_{h-k} \approx +1$$

The component vectors satisfying the criterion

$$H1 + H2 + H3 = 0$$

$$K1 + K2 + K3 = 0$$

$$L1 + L2 + L3 = 0$$

are searched for, where Hn,Kn,Ln is the vector for the nth reflection. To restrict the number of combinations only the largest E values are used. The probabilities of the relationships are determined. During the search SINGEN calculates the phase shift resulting from any transformations of reflections to their asymmetric equivalents. SIGMA-2 standardises the indices so that all reflections lie in the same part of the reciprocal lattice; any phase shift due to this is determined.

The actual phase determination is approached differently by PHASE and MULTAN (II and III). PHASE is a single solution method specifically designed for the solution of centrosymmetric structures[121]. Phases are first sought for a set of 'generators', which are usually chosen to be thirty to seventy of the strongest E value reflections.

The sigma-2 relationships, $s_{h1}.s_{h2}.s_{h3} = n$, of probability P, where n is the phase shift (0 or π), are divided into two types. The relationships of the first kind are derived entirely from the generators, and those of the second kind are obtained by the elimination of a common non-generator from a pair of original relationships. The resultant lists are sorted in order of decreasing probability.

The phases of the generators are solved for directly, assuming all relationships are true and examining them in descending order of probability until a unique solution is obtained, involving just as many relationships as there are unknown generator phases.

In any phase determination it is necessary to specify an origin for the system as groups of phases may change sign with origin shift. Looking at the simplest centrosymmetric case, $P\bar{1}$, there are eight possible, distinct origin positions. Three reflections, chosen from different, linearly independent parity groups, are required to define a unique origin. Some phase determining programmes fix the origin at the beginning of the determination process, but both methods discussed here achieve this at a later stage.

When the unique set of relationships for the generators has been determined, if the origin determining reflections have not been assigned, it is found that an appropriate set of reflections cannot be solved for. These are then given signs (usually arbitrarily positive) as origin fixing reflections, before continuing to solve for the remaining ones.

Two 'pedigrees' are then set up; firstly for each reflection, showing which relationships were used in defining the phase, and also for each relationship, to show which phases are dependent upon it. The solution is tested on all relationships of the first and second kinds and the number of discrepancies noted. The unique feature of Phaser is that it is capable of refining and improving the solution. This minimises these discrepancies by identifying which relationship of those used in the solution for the generators is involved in most discrepancies. It is then deemed to be untrue (i.e. $s_h . s_k . s_{h-k} = -1$) and the process is repeated.

The MULTAN approach to phase determination is a multiple solution one, which depends on finding a good starting point. This would be a combination of known phases which would lead to new phases with maximum reliability.

Firstly, a small group of strongly interlinked reflections are obtained by the MULTAN II(CONVERGE) programme.
A measure of the reliability with which the phase may be determined using the tangent formula is given by the quantity α_h defined by[122]:

$$\alpha_h^2 = (\sum_{h'} K_{hh'} \cos(\Phi_{h'} + \Phi_{h-h'}))^2 + (_{h'} K_{hh'} \sin(\Phi_{h'} + \Phi_{h-h'}))^2$$

where: $K_{hh} = 2\sigma_3 \sigma_2^{-3/2} E_h E_{h'} E_{h-h'}$

and: $\sigma_h = \sum_{j=1}^{N} Z_j^n$

This equation is a general expression applicable to centric or acentric structures, and in the centric case the Φ terms reduce to 0 or π.

In the absence of phase information the value of α_h may still be estimated using the formula[123]:

$$\alpha_h^2 = \sum_{h'} K_{hh'}^2 + 2 \sum_{\substack{h' h'' \\ h' \neq h''}} K_{hh'} K_{hh''} \frac{I_1(K_{hh'}) I_1(K_{hh''})}{I_0(K_{hh'}) I_0(K_{hh''})}$$

Where I_1 and I_0 are modified Bessel functions.
The value of α_h is calculated for each reflection. The reflection with the smallest α_h is eliminated together with all its phase relationships. The remaining α_hs are updated and the process is repeated until the best starting set is obtained. As each reflection is eliminated those remaining are examined to ensure that they contain all the necessary

reflections for origin definition; if not, the reflection just eliminated is reinstated and becomes one of the reflections used to define the origin.

Clearly a knowledge of the phases of one or two reflections would be very valuable. CONVERGE therefore applies the Sigma-1 formula before the elimination procedure. The Sigma-1 formula for the centrosymmetric case is

$$s\left\{E_{2h2k2l}\right\} \approx s\left\{|E_{hkl}|^2 - 1\right\}$$

which must be modified for space group symmetry.

The starting set is then chosen to include the sigma-1 signed reflections, the origin fixing reflections and a selection of other 'good' reflections picked by CONVERGE. In this work usually three of these reflections were selected. Eight possible starting points are obtained by assigning plus and minus signs to each of these.

These starting points are developed into complete sets of phases using the sigma-2 relationships in the order indicated by CONVERGE (i.e. the reverse order of elimination. For each set of phases finally obtained 'figures of merit' are computed. In this work the absolute figure of merit (ABS FOM), which is related to α_h, was mainly used. This is a measure of the internal consistency of the set of phases and is given by

$$\text{ABS FOM} = \frac{\Sigma_h \alpha_h - \Sigma \alpha_r}{\Sigma \alpha_e - \Sigma \alpha_r}$$

where α_h is calculated from equation 1, α_e is the sum of estimated αs from equation 2 and α_r assumes random phases. Clearly this value should be a maximum for the correct solution, [illegible] in fact a correct set of phases will give a others picked by CONVERGE. E-maps from seven possible phase sets were then calculated (apart from the all plus solution). None of these, on examination, showed any structure that could serve as a starting point for structure determination.

The initial results from PHASE were examined with particular regard to the pedigrees of the phases and the relationships. In a $P\bar{1}$ structure the refinement facility of PHASE, based on minimising discrepancies, cannot be used, because of necessity the first solution found is the all plus case in which there are no discrepant relationships. The strategy used to identify the subgroups has been to examine the pedigree for a low probability relationship which might be invalid, which has a high degree of involvement and is related to some of the generators. An appropriate generator phase is defined as negative and serves as the basis for the negative subset.

This approach was effective in the analysis of the silicon ketimine, and the second attempt to form the subsets resulted in the phases used as the starting point for the structure determination. The phases of the generators are listed in Table 3.1., where they may be compared with the final, correct phases. Of the 76 common reflections 69 of the phases calculated by Phaser agree with those of the final solution. The Phaser pedigrees have been further examined in an attempt to find a possible phase set in better agreement with the correct one. One other possible starting point was found of which 70 of the phases were in agreement, but there was no choice leading to a completely correct solution.

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TABLE 3.1.

Comparison of MULTAN and PHASE Solutions for $Si(NC(C_6H_5)_2)_4$

h,k,l	MULTAN		PHASE	Correct Solution	h,k,l	MULTAN		PHASE	Correct Solution
	a	b				a	b		
3,-5,14	+	+	+	+	3,-9,10	+	-	-	-
3,-7,7	-	+	+	+	3,-3,15	-	-	-	-
1,-3,3	-	-	-	-	4,-9,-1	-	-	-	+
6,13,1	+	+	+	+	9,2,8	-	+	-	-
3,-7,9	+	-	-	-	0,11,-3	+	+	+	+
0,3,-4	+	-	-	-	0,10,0	+	+	+	+
4,13,7	+	+	-	+	1,-4,-8	+	+	-	-
10,-1,5	+	+	-	-	1,2,16	+	+	+	+
8,1,0	-	-	-	-	0,8,11	-	+	-	-
2,2,-2	-	-	-	+	6,-2,2	-	-	+	+
2,-2,5	-	-	+	+	4,10,-8	-	-	-	-
2,-4,0	+	+	-	+	0,10,-7	-	+	+	+
1,5,-7	-	+	-	-	5,7,-8	-	-	-	-
9,-3,3	-	+	+	+	6,-2,0	-	+	-	-
5,-12,-2	-	-	-	-	2,-6,-7	-	-	-	-
2,-6,11	+	+	+	+	4,-6,-9	+	-	+	+
6,-10,7	+	-	-	-	3,1,-2	-	-	-	-
3,-11,9	-	+	+	+	5,6,-4	-	+	+	+
3,-12,0	-	-	+	+	4,10,12	+	-	-	-
10,-1,-2	-	+	-	-	3,-5,8	+	-	-	-
2,3,-2	+	-	-	-	4,11,11	-	+	-	+
10,3,3	+	+	-	-	4,13,-4	+	+	+	+
3,-7,13	-	-	-	-	5,-3,2	-	+	+	+
1,-1,-4	-	-	+	+	0,4,1	-	-	-	-
1,2,5	+	-	-	-	0,2,1	+	+	-	-
1,6,7	-	+	+	+	6,-4,-7	+	+	-	-
3,-5,10	+	+	+	+	6,0,-5	-	-	-	-
1,8,-3	+	-	-	-	1,12,1	+	-	+	+
4,5,-7	-	-	+	+	4,-3,9	+	+	-	-
4,3,-11	+	+	+	+	0,4,11	-	+	+	+
9,4,5	+	+	+	+	6,-3,-7	-	-	-	-
4,3,-8	-	+	-	-	3,-12,2	-	+	-	-
3,-11,-2	+	+	-	-	2,11,-4	+	-	-	-
4,6,-5	-	+	+	+	5,-4,4	+	-	+	+
3,-7,-9	-	+	+	+	5,-9,8	+	-	+	+
5,-5,-5	+	+	+	+	3,10,0	+	-	-	-
5,-1,-12	+	+	+	-	0,3,10	-	-	-	+
1,2,6	+	-	-	-	2,-2,4	+	-	-	-

As has been noted previously the ABS FOM figure of merit given by MULTAN is not meaningful in cases of non-translational symmetry. This is demonstrated by the results (see Table 3.1.). The phase set with the highest value of ABS FOM (1.1283) is labelled 'a', and only 36 of the phases are correct. The MULTAN solution with the best agreement is labelled 'b', (ABS FOM = 1.0676); 49 of these phases are correct.

3.3. Refinement

A fourier synthesis using phases determined by either of the methods described above, gives possible atomic positions, and these are fed into the Least Squares refinement programmes SFLSR or CRYLSQ (X-RAY), which work by minimising the function $\sum_{hkl} w_{hkl}(|F_o| - |F_c|)^2$, where w_{hkl} is the weight to be applied to an observation and $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Positional parameters and temperature and scale factors were allowed to refine throughout the determinations.

In the initial stages each atom is assumed to have a spherical, isotropic, thermal motion. This modifies the atomic scattering factors so that :

$$f = f' \exp- \frac{B\sin^2\theta}{\lambda^2}$$

The isotropic temperature coefficient B is allowed to refine; consistently large or negative B values for a particular atom indicate that the atom may be unreliable.

More accurately the atomic motion may be described by a triaxial ellipsoid defined by the coefficients B_{11}, B_{22}, B_{33}, B_{12}, B_{13}, B_{23}, and the form factor expression becomes:

$$f = f'\exp(-\tfrac{1}{4}\, h^2B_{11}(a^*)^2 + k^2B_{22}(b^*)^2 + l^2B_{33}(c^*)^2$$

$$+ 2hkB_{12}a^*b^* + 2hlB_{13}a^*c^* + 2klB_{23}b^*c^*)$$

This is allowed for in the final stages of the refinement procedure.

The agreement between the calculated and observed structure factors is given in terms of a residual index R, where:

$$R = \frac{\sum\big|\,|F_o| - |F_c|\,\big|}{\sum |F_o|}$$

The final R value should be less than 0.10 for any reliance to be placed on bond distances and angles.

The calculated phases and observed F amplitudes are used to generate another fourier map which should ressemble the true molecule more closely. Further atomic parameters are assigned and the process is repeated until a satisfactory result is obtained.

In the final stages of refinement ΔF syntheses have proved valuable. As these are based on coefficients of $|F_o| - |F_c|$ they give information on the differences between the model and the true structure. Thus unlocated atoms will appear as peaks and incorrectly placed atoms as holes, or on a gradient between a peak and a hole. Hydrogen atoms may be found in this way, although these are easily obscured and the non-hydrogen atoms should be fairly well refined before this is attempted. In some cases, such as methyl groups, rotation causes the hydrogens to appear as a smear of low electron density and they cannot be located.

A difference synthesis also shows anisotropically vibrating atoms. At the atomic position the electron density shrinks in some directions and stretches along others in the true ellipsoidal distribution.

The interatomic bond distances and angles are calculated together with their standard deviations (σ). Throughout the text all structural values are followed with the standard deviation on the last significant figure in parentheses. Theoretically, differences of greater than 2σ should be considered significant, but in practice it is found that the standard deviations tend to be underestimated, and consequently differences of less than 3σ are considered insignificant.

CHAPTER 4

Crystallographic Studies of the Cyclic Amines $(Cl_2TiNSiMe_3)_2$ and $(Me_2SiNMe)_3$.

In this chapter the X-ray diffraction study of the cyclic amine catena-di-μ-chloro-bis-μ-(trimethylsilylamino)-di-(chlorotitanium(IV)), $(Cl_2TiNSiMe_3)_2$, is described and discussed; the preliminary results of the X-ray analysis of nonamethylcyclotrisilazane, $(Me_2SiNMe)_3$, are also presented.

4.1.1. Data Collection

Crystals of the compound were prepared as described in Chapter 2. Recrystallisation was attempted from dichloromethane but the resultant crystals were too small for use, and so the sample used in this analysis was taken directly from the reaction mixture.

The cyclotitanazane is extremely sensitive to traces of moisture, and so handling and mounting of the sample was accomplished using a modified nitrogen 'dry box' (described in appendix A), fitted with a microscope and a heating wire. The crystals are formed as yellow-orange needles and a single crystal, approximately 0.1mm in diameter, was selected and mounted in a 0.5mm Lindemann glass capillary. The crystal was oriented with the needle axis approximately parallel to the axis of the capillary. It was then affixed with a dab of silicon grease and the capillary was sealed with the aid of the hot wire. To ensure a perfect seal a drop of 'dental' sticky wax was applied.

Oscillation, zero and first layer equiinclination Weissenberg photographs, obtained about the needle axis, indicated a monoclinic system. Systematic extinctions were observed for h,0,l : l=2n+1 (glide plane) and 0,k,0 : k=2n+1 (screw axis), which are consistent with the choice of $P2_1/c$ as space group.

Data were collected on a Stoe 2-Circle Equiinclination Weissenberg Diffractometer, equipped with a graphite monochromator. The approximate unit cell dimensions, obtained from the preliminary photographs, were used to generate a set of diffractometer settings for several of the high intensity reflections, using the programme STOE. These were accurately located by manually operating the diffractometer, and then used to generate more accurate cell constant data. The unit cell dimensions are recorded in Table 4.1. The programme STOE was again used to produce a paper tape to control the diffractometer during data collection.

Data were collected using MoK_α radiation(λ=0.71069Å) on layers h,k,0 to h,k,8, to a maximum 2θ value of 60°. The total number of independent reflections was 4,955, of which 1,298 were considered observed, having $I/\sigma \geq 3.5$.

The crystal density was measured by flotation in a benzene/diiodomethane mixture. Mixtures were made up in a dry box using dried solvents; small crystals were dropped into the various solutions until one was found in which the crystal floated. The refractive index of this mixture was measured, and the density was found

TABLE 4.1

Data For $(Cl_2TiNSiMe_3)_2$

Cell Constants

a	17.74Å
b	18.52Å
c	11.46Å
α	90.00°
β	102.71°
γ	90.00°

Vol = 3671.3 $Å^3$

Experimental Details

Radiation MoK_α = 0.71069Å

Maximum $(\sin\theta)/\lambda$ = 0.587

Total reflections = 4955

Observed reflections $(I/\sigma(I) \geqslant 3.5)$ = 1298

Z=4

F(000) = 832

ρ_{calc} = 1.504

ρ_{obs} = 1.505

using a calibrated graph of refractive index versus density. It was found to be 1.504. The number of ($Cl_2TiNSiMe_3$) monomer units per unit cell is therefore sixteen.

The structure was assumed to be tetrameric, as this would give one molecule in each asymmetric unit. This assumption was supported by apparent pseudosymmetry. In addition to the absences for the screw axis (0,k,0; k=2n+1) and the glide plane (h,0,l; l=2n+1) there were further conditions for reflection nearly obeyed in the h,k,0 and h,0,l planes, namely k=2n (h,k,0) and h=2n (h,0,l). Thus h+k=2n, which is the condition required for a centred sub-cell. Only one strong reflection, (h,k,l =-5,0,4) contradicts this.

The dimeric model was at this stage discarded as being unlikely on steric grounds because of angle strain in the ring.

4.1.2. Solution of the structure.

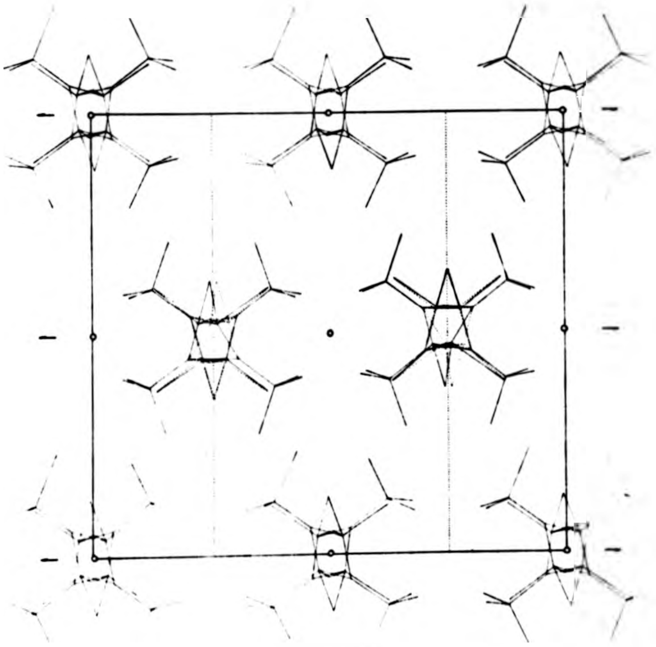
The first attempt at solving the structure used direct methods. The data was transferred to a binary data file and normalised by DATRDN and DATFIX. The direct methods programs NORMSF, SINGEN, and PHASE (X-RAY 70) were then used to generate a starting set of phases. No acceptable starting point was found from this, and the results showed clearly that the parity groups required normalisation. The average intensities of the various parity groups differed considerably, such that the hundred strongest normalised structure factors (E) only included three reflections from parity groups eoo and ooo. Unfortunately the facility for normalisation is not available within the program, and so this approach had to be abandoned.

A three dimensional Patterson map was obtained from the 1,289 observed reflections. There were a large number of intense peaks which could not be resolved. The problem here is that the structure contains too many relatively heavy atoms, namely four titaniums (Z=22), eight chlorines (Z=17) and four silicons (Z=14) in each asymmetric unit. Each atom gives rise to vectors by interaction with itself and with every other atom, and so in this situation the Patterson map is very confused. Attempts were made to solve it using the two dimensional h,k,0 vector map, but to no avail.

The next approach to the problem again involved the use of direct methods, hand applied to the h,k,0, projection of the centred pseudosubcell. From this a set of atomic coordinates (x,y,0) were located and subjected to least squares refinement using the program SFLSR. This two dimensional refinement gave an R value of .128 (102 reflections). However, the molecule could not be recognised from the electron density distribution. The packing diagram (figure 4.1), illustrating the h,k,0 projection of the final structure shows the substantial overlap of atoms that in fact occurs in this projection. A similar approach was applied to the h,0,1 projection, and another set of atomic coordinates was found (x,0,z). The common coordinates (x) matched fairly well with those previously obtained.

There now appeared to be two groups of atoms, one

Figure 4.1



Packing Diagram for $(Cl_2TiNSiMe_3)_2$ showing the unit cell contents projected along **c** .

centred around (0,0,0) and one around (1/2,1/4,0). On inspection this proved to be inconsistent with a tetrameric model if the spacegroup is $P2_1/c$. The tetramer at (0,0,0) would be satisfactory, containing a centre relating the two halves, but at (1/2,1/4,0) the two halves of the molecule would have to be related by the C-glide, i.e. a Z-shift of 5.73Å between them.

The two dimensional symmetry of the h,k,0 projection is pgm, consistent with $P2_1/c$ or $P2_1/m$. It can be rearranged to pmm which agrees with P2/m and P2/c. With extra pseudosymmetry the subgroups $P2_1$, P2, Pc and Pm are also possible spacegroups. These eight spacegroups were examined for consistency with the assumption of tetrameric rings. P2 was the only one not to split the two halves of one of the molecules by a half unit cell translation. The data was transformed to P2 (SORTM) and a least squares refinement was attempted using the atomic parameters from the h,k,0 and h,0,l projection maps. Unfortunately the atoms formed pairs with very similar x coordinates. Several permutations were therefore possible, and all those giving coherent ring structures were fed into the SFLSR program for least squares refinement. The R factors were all unsatisfactory, indicating incorrect choice of spacegroup.

At this point another attempt at three dimensional direct methods was begun. For this the program MULTAN was used, which has the has the facility for normalising the parity groups which had been required previously. The normalisation run showed the ratio for the eee:ooo groups to be 2.65:1. The final statistics pointed strongly to a centrosymmetric spacegroup, and so the data was resorted into $P2_1/c$. Encouragingly of the seven possible electron density distributions the one with the best MULTAN figure of merit agreed closely with the previously obtained h,k,0 projection map. The three dimensional map showed clearly that a tetrameric structure could not be fitted to the located atom positions. However the fourier map could now be almost fully explained in terms of dimeric $(Ti-N)_2$ units stacked around (0,0,0). Based on this an R value of .240 was reached.

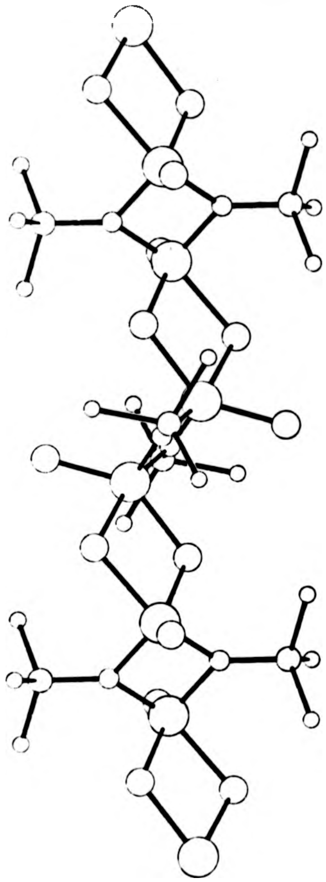
The final solution came with the discovery of disorder in the molecule centred around (1/2,1/4.0), involving the titanium atoms and half the chlorine atoms. When allowance had been made for this, and the temperature factors of the titanium and chlorine atoms, and the silicon atoms from the disordered molecule had been allowed to refine anisotropically, the R factor improved to a final value of .090.

Tables of observed and calculated structure factors are given in appendix B, as are the final atomic positions and lists of bond distances.

4.1.3. Discussion.

The molecule is shown in figure 4.2. The titanium atom adopts the unusual coordination number of five, by

Figure 4.2



$(Cl_2TiNSiMe_3)_2$: The ordered chain.

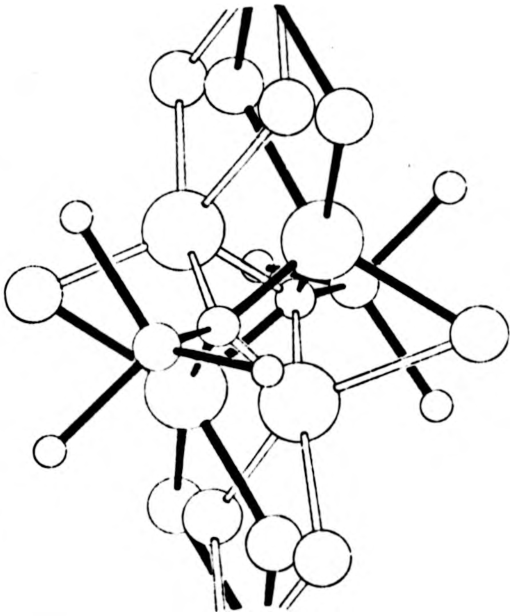
polymerising via inter molecular chlorine bridges, parallel to the c axis. Each ring is inclined by about 45° from the chain axis, alternately up and down so that titanium atoms on adjacent rings approach close enough for double chlorine bridges to be formed between each pair of them. The stacking of the rings is such as to align the trimethylsilyl and terminal chlorine groups at a distance of 5.73Å.

Figure 4.3 shows one unit of the disordered chain. One form is shown by the molecule with black bonds, and superimposed on this is another molecule linked with white bonds. The population of each is 0.5. The nitrogen atoms, trimethylsilyl groups and terminal chlorines remain fixed, but the titanium atoms and bridging chlorines move to give rings with the ring planes approximately normal to each other, with each inclined at about 45° to the c axis. Externally these two chains are not altered by the disorder, and so no interchain forces prevent it.

The spacegroup symmetry ($P2_1/c$) is only satisfied by a disordered structure, as the disordered atoms of one unit are related by the glide plane, to the disordered atoms of the other, superimposed unit of the adjacent ring.

The position of the atoms in the ordered chain were refined more easily than those of the disordered chain. The bond distances and angles to be discussed will therfore be taken from the ordered molecule. A complete list of bond distances and angles is included in appendix B.

Figure 4.3



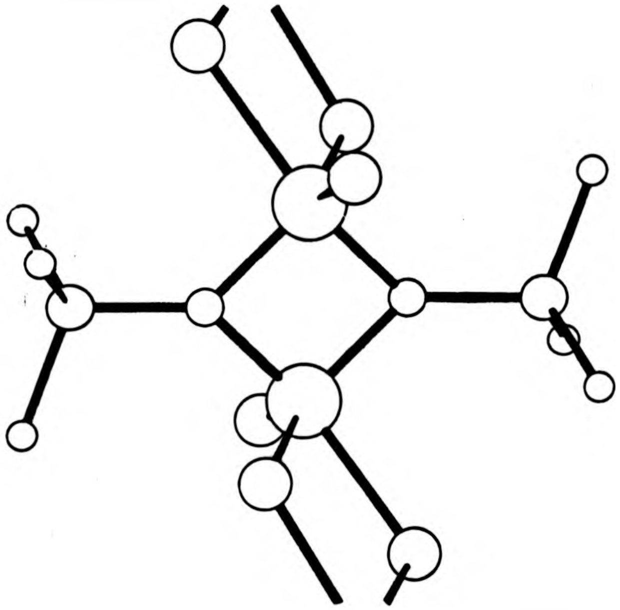
$(Cl_2TiNSiMe_3)_2$: One unit of the disordered chain. The two conformations are distinguished by the use of black and white bonds.

A single unit from the ordered chain is shown in figure 4.4. The most notable features of the structure are the four-membered rings which are planar, rigorously so for two of the four independent examples. The geometry about the titanium is best described as trigonal bipyramidal (axial angles are 159°(1) and 164°(1)). The axis is described by one of the nitrogen atoms and one of the bridging chlorines. The remaining nitrogen, bridging chlorine and terminal chlorine all lie in the equatorial plane; the largest equatorial angle is 137.3°(4) and lies between the two chlorines.

Authenticated five coordinate structures are rare for titanium(IV), apparently because it can normally achieve octahedral geometry via bridging atoms. An example of this is shown by the chlorine bridges in diethylaminotitaniumIV-trichloride[125], and di-μ-chloro-bis(dichloroacetonylacetone)-titanium(IV)[126]. Five-coordination does occur in $(TiCl_2(OX)_2)_2$ (X = Et or Ph) with oxygen bridges. The geometry of this species may also be described as trigonal bipyramidal with an axial distortion very similar to that of the cyclotitanazane, with axial angles averaging to 159.5° (X = Et) and 167° (X = Ph).

Titanium-nitrogen bond distances differ markedly between the axial and equatorial positions, as the axial Ti-N bond averages to 1.96Å (4) whereas the equatorial Ti-N distance averages to 1.76Å (3). Some difference is to be expected due to the non-equivalence of the trigonal bipyramidal hybrid orbitals. A difference of 0.15Å is

Figure 4.4



$(Cl_2TiNSiMe_3)_2$: One unit of the ordered chain.

found in a four-membered phosphorus nitrogen ring $(Cl_3PNCH_3)_2$ in which the phosphorus atom adopts an approximately trigonal bipyramidal geometry with one axial and one equatorial nitrogen. The difference in axial and equatorial bond lengths in trigonal bipyramidal structures has been suggested to account for this[129,130]; at least partially. The five-coordinate alkoxy titanium(IV) species mentioned above shows a similar discrepancy in titenium-oxygen distances, with bond lengths of 1.96Å (axial) and 1.77Å (equatorial).
The Ti-N bond length in diethylaminotitanium(IV) trichloride is reported to be 1.852Å, and some degree of multiple bonding is suggested as this is considerably shorter than the hypothetical value of 1.96Å for a pure Ti-N single bond. The extremely short alternate Ti-N bonds of 1.76Å found in the cyclotitanazane, together with the planarity of the ring, indicate considerable interaction between the p_π-orbitals on nitrogen and the d_π-orbitals on titanium.

The internal ring angles average to 86° (2) at titanium and 94° (2) at nitrogen. The deviation from the 90° that is predicted on the Dewar, Lucken and Whitehead model (see Conclusion) may be to allow the larger titanium atoms greater separation. Across the ring the Ti..Ti distance is 2.72Å (2) and the distance between the nitrogens is 2.5Å (1).

The terminal chlorine-titanium bonds are 2.217Å (10) and 2.209Å (10), which are slightly longer than the value of 2.185Å reported for titanium tetrachloride.[131] This may be rationalised by assuming decreased acidity of the titanium due to the attachments to nitrogen. Some effect may be due to the rehybridisation required to accomodate penta-coordination. These bond lengths are comparable to those of2.219Å and 2.209Å found in the five-coordinate species $(Cl_2Ti(OPh)_2)_2$.

The bridging chlorine-titanium distance varies between 2.427Å (10) and 2.501Å (10). This may be compared to the values for bridging chlorine distances of 2.419Å and 2.509Å found in $(Cl_3Ti(C_5H_7O_2))_2$, and 2.456Å and 2.496Å found in Cl_3TiNEt_2.

The nitrogen atom is planar despite the strain caused by the small internal ring angle, thus indicating at least some multiple bonding in the silicon-nitrogen bond. The extent of π-orbital interaction is however in doubt as the Si-N bond lengths vary considerably. In the ordered molecule the lengths are 1.728Å (34) and 1.862Å (38), and in the disordered molecule they are 1.712Å and 1.809Å (35). None of these bond lengths differ by greater than 3σ from the mean value of 1.791Å, but because of the individual variations this distance does not give information about the extent of multiple bonding.

The trimethylsilyl group appears to be essentially normal, with a Si-C bond lengths averaging to 1.89Å (5), which is comparable with the standard distance of 1.875Å[130].

Figure 4.1 shows the molecular packing within the unit cell, projected along c. The ordered molecule is positioned about a symmetry centre which leads to the strict planarity of this ring. The two conformations of the disordered molecule are shown around $(\frac{1}{2},\frac{1}{4},0)$ and are differentiated by the use of solid and dotted lines. The chains form columns parallel to the c axis, with molecules inclined by about 45°, alternately up and down, to allow for the formation of chlorine bridges. The bulky trimethylsilyl groups and the terminal chlorines occupy the space between the rings, and are stacked almost vertically above one another. The distance between them of 5.73 Å (i.e. c/2) is too great for significant interaction, and packing effects must be the major reason for this.

4.1.4. Conclusion

Pentacoordination in Titanium(IV)

This novel titanium-nitrogen ring compound (A), $(Cl_2TiNSiMe_3)_2$, provides an example of pentacoordinate titanium(IV), a coordination which has proved elusive with few of the proposed examples authenticated. In the vast majority of titanium(IV) compounds the metal atoms adopt tetrahedral or octahedral geometry, the latter being predominant. The occurrence of a few five-coordinate species suggests that it is not necessarily energetically unfavourable, but that an octahedral environment is normally preferred.

In A possible reasons for the pentacoordination can be deduced. The structure indicates substantial π-bonding between the nitrogen and the titanium, which is probably the cause of the planarity of the ring. The internal ring angles of about 90° which follow from this would give severely distorted tetrahedral geometry about the titanium. Octahedral geometry with cis nitrogens would be a better arrangement, but for this both chlorine atoms would be required to form intermolecular bridges (implying a three-dimensional polymeric structure) and this would clearly be sterically very crowded. The five-coordinate trigonal bipyramidal structure would also allow approximately 90° ring angles, with one axial and one equatorial nitrogen atom; the steric crowding is relieved and so this structure is preferred.

A puckered trimeric structure would more easily accomodate tetrahedral geometry of the titanium, but the dimeric (planar) structure favours substantial π-bonding. As mentioned in Chapter 1 four-membered heterocycles frequently occur despite the small ring angles required, because of the increased importance of σ-delocalisation. The presence of π-bonding will enhance the stability of such a system.

The bridging link is easily broken to allow two pyridine molecules to attach to each titanium, which thus achieves the normal coordination number of six, when there is less overcrowding.

π-Bonding in Cyclic Titanium Amines

The planarity of the solid state structure implies considerable π-orbital interaction and this is confirmed by the shortened bond lengths. The stucture may be compared to that of the dimeric cyclosilazane $(Me_2SiNSiMe_3)_2$[137], which is also strictly planar. In this molecule the bond lengths indicate substantial d_π-p_π bonding both internally, around the ring, and externally with the N-silyl group.

Multiple bonding of the nitrogen with silicon is found to be much greater than with the heavier GroupIV(b) elements. This is attributable to the relative compactness of the 3d orbitals over the 4d and 5d ones, which thus allow more effective overlap with a π-donor orbital. Titanium(IV) is similar to silicon in the availability of vacant 3d orbitals which can act as π-acceptors. In titanium the 3d orbitals may be slightly lower in energy than in silicon because of the increase in atomic number; d-orbitals are known to be more sensitive to changes in effective nuclear charge than the s or p orbitals[5,14,159,160]. The presence of electronegative substituents such as chlorine, will increase the effective nuclear charge, and this will cause some contraction of the 3d orbitals. The energy match with the nitrogen lone pair orbitals should be improved by this contraction. The cyclotitanazane should therefore exhibit considerable π-delocalisation, and the structure confirms this.

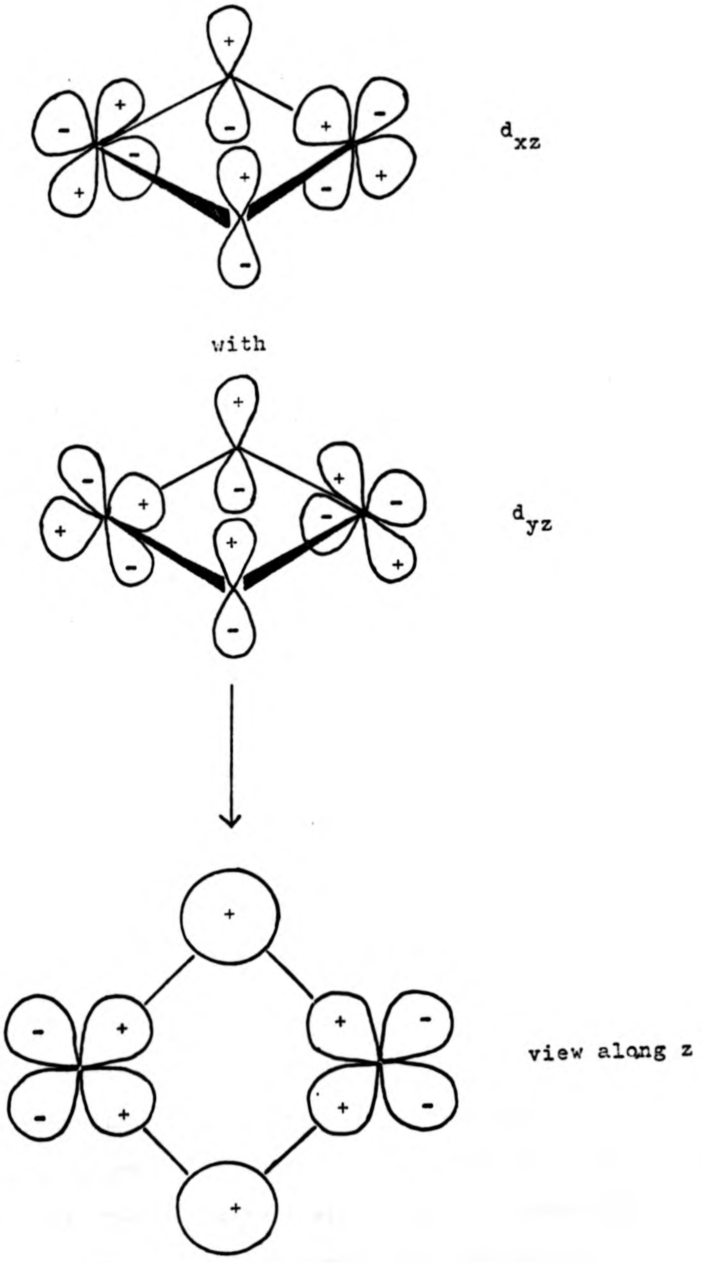
The best description of the π-bonding around the ring skeleton is probably given in terms of the three-centre 'island' delocalisation, as described by Dewar et al[36]. Two of the d orbitals normally considered available to trigonal bipyramidal structures, d_{xz} and d_{yz}, may combine to give:

$$d_{\pi}^{a} = 2^{-\frac{1}{2}}(d_{xz} - d_{yz}) \qquad \text{(antibonding)}$$

$$d_{\pi}^{b} = 2^{-\frac{1}{2}}(-d_{xz} - d_{yz}) \qquad \text{(bonding)}$$

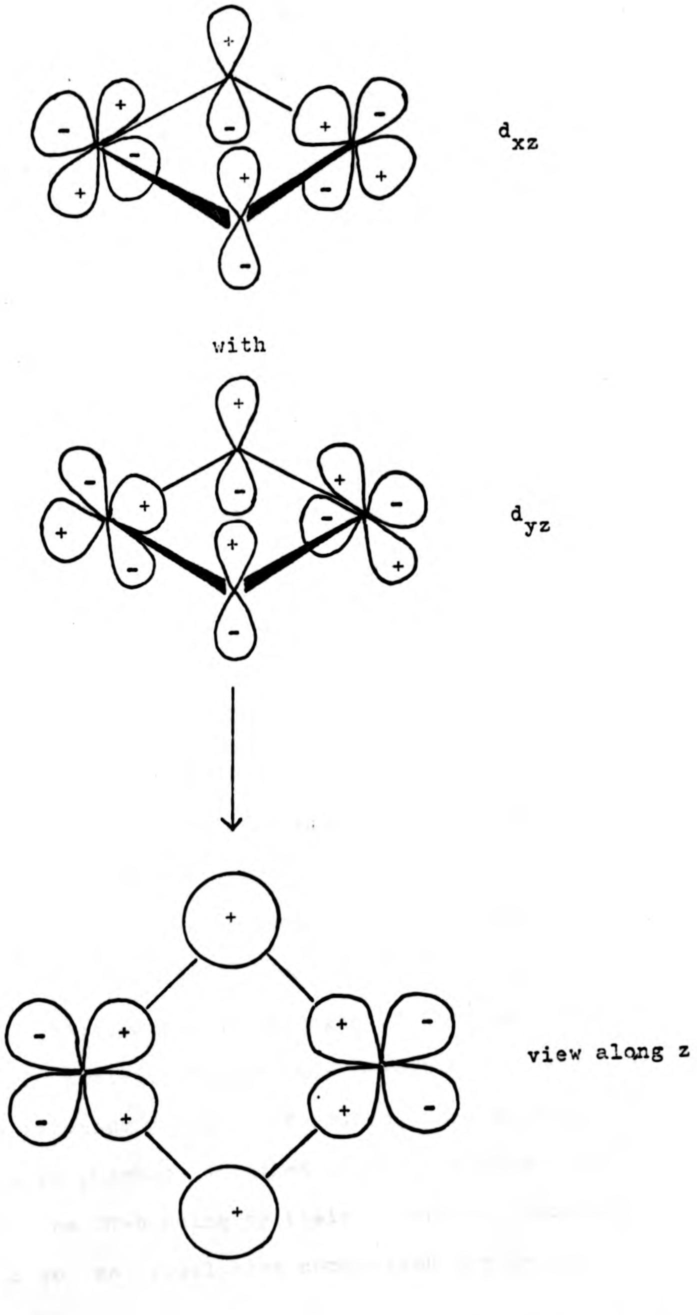
The bonding scheme is pictorially represented in Figure 4.5.

Figure 4.5



π-Bonding scheme proposed for the cyclotitanazane, $(Cl_2TiNSiMe_3)_2$

Figure 4.5



π-Bonding scheme proposed for the cyclotitanazane, $(Cl_2TiNSiMe_3)_2$

Optimum conditions require internal ring angles of 90° and d_{xz} and d_{yz} orbitals of equal energies. If the energies of these orbitals differ (as expected for trigonal bipyramidal hybridisation) the π-system is expected to be progressively concentrated in alternate bonds, which is the situation found experimentally. Unfortunately, orbital energies for trigonal bipyramidal titanium(IV) have not been calculated, but nonetheless this model is consistent with the observed results.

It would be interesting and informative to determine the structures of analagous titanium(IV) and silicon systems in order to compare the relative 3d orbital energies. The silicon analogue of the cyclotitanazane, $(Cl_2SiNSiMe_3)_2$ has not yet been reported although other cyclic chlorosilazanes are known.

Recently, the titanium(IV) diisocyanate $(\pi\text{-}(C_5H_5)_2TiNCO)_2$ has been reported together with its X-ray structure[161]. This is a monomeric, four-coordinate species, and the nitrogen atoms are very nearly linear with angles of 171.8°(3) and 175.7°(3). Similar silicon isocyanates, e.g. trimethylsilylisocyanate, Me_3SiNCO[44], and tetrakis(isocyanato)silane, $Si(NCO)_4$[151], have angles at nitrogen of 154° and 146.4° respectively, implying rather less π-orbital interaction than in the titanium case. Of course, the presence of π-cyclopentadienyl groups attached to the titanium atom can enhance the π-bonding by their electron acceptor ability and so no conclusive comparison can be made.

Further synthetic work needs to be done on cyclotitanazane systems. Varying the substituents on both the titanium and the nitrogen should have an effect on the extent of π-interaction in the titanium-nitrogen bond, and this will then influence the chemical behaviour as well as the structural properties.

4.2. Nonamethylcyclotrisilazane - Preliminary Results

Multiple bonding ($d_{\pi}-p_{\pi}$), as found in the cyclotitanazane is also known to occur in the cyclic silazanes. Attempts to determine the extent of delocalisation around the ring, and the effect of the ring geometry, have led to conflicting results. Vibrational analyses on trimeric rings suggest planar (D_{3h}) molecular symmetry[132,133], whereas ^{1}H n.m.r. spectral data support a non-planar conformation[134-136]. An X-ray structural analysis on the dimeric ring $(Me_2SiNSiMe_3)_2$[137] shows the ring skeleton to be planar. Electron diffraction studies of hexamethylcyclotrisilazane, $(Me_2SiNH)_3$, show the ring to be puckered[38]. Non-planar rings are also found for octamethylcyclotetrasilazane, $(Me_2SiNH)_4$, by X-ray studies. This structure has the unique feature of both 'chair' and 'boat' conformations occurring together[138].

It would be informative to determine the structure of the N-methyl derivative of the trimeric or tetrameric ring in order to investigate the inductive effect of the alkyl group on the ring skeleton. To this end a crystal structure analysis of nonamethylcyclotrisilazane, $(Me_2SiNMe)_3$, was initiated.

The sample was prepared by the method of Lienhard and Rochow[139] and purified by sublimation under reduced pressure. The melting point of the compound is quoted as 36°C (309°K). Because of the low melting point handling the crystals at ambient temperatures proved difficult. The dry box was cooled by passing the inlet nitrogen through a coil dipped in liquid nitrogen. The crystals were then mounted in the usual way (but without the use of the hot wire to seal the capillary) and stored in a refrigerator prior to use.

4.2.1. Data Collection

Initial oscillation and zero level Weissenberg photographs showed hexagonal symmetry and approximate unit cell dimensions were measured. Data were collected by diffractometer (4-circle Syntex $P2_1$). The accurate cell constants (see Table 4.2) and the orientation matrix were determined as described in Chapter 3. Because of the tendency of the sample to melt a large crystal was chosen for the data collection. CuK_α radiation (λ =1.5418) was used via the 2θ scan mode. The maximum 2θ value was limited to 115° in order to reduce the total number of reflections. A variable scan speed was employed with a minimum rate of 5° in 2θ per minute.

The crystal needed recentring twice during the first 336 reflections as melting caused it to slip in the tube.

TABLE 4.2

Cell constants

		σ
a	15.655Å	.005
b	15.645Å	.003
c	11.530Å	.002
α	89.99°	.01
β	90.01°	.02
γ	120.00°	.02
Vol	2445.6$Å^3$	.97

Experimental details

Radiation CuK_α = 1.5418Å

Maximum $(\sin\theta)/\lambda$ = 0.5460

Total reflections = 1105

Observed reflections $(I/\sigma(I) \geqslant 3.0)$ = 882

After this the tube was opened and more silicone grease was applied to hold the crystal in position. The intensity drop of the three standards increased from this point, but the orientation of the crystal remained unchanged. A further 769 were collected over 1½ hours, by which time the intensities of the standards had dropped to 50% of their initial values. The overall data quality was clearly low.

The last 769 reflections were rescaled on the basis of the intensity drop of the standards. The coefficients of the scaling equation;

$$F = F_{obs}(1.0 + \alpha T)(1.0 + \beta T \frac{\sin\theta}{\lambda})$$

were thus determined as $\alpha = .029$ and $\beta = .058$. The maximum rescaling factor (calculated on F) is 1.79. The total number of reflections collected was 1105.

A space group could not yet be selected. The data clearly have h,k,l ≠ k,h,l, indicating Laue group 6/m. The reflection 0,0,3 is the only one to violate the condition 0,0,l : l=2n; it has $I/\sigma(I)$ of 13.5. If this reflection truly exists then the space group is one of P6, $P\bar{6}$, or P6/m. However, it was considered more likely to be spurious, implying the possible space groups $P6_3$ or $P6_3/m$.

A Patterson synthesis was calculated and examined for possible Harker lines and sections. Possible Harker planes were found at x,y,0 and x,y,½, with a Harker line at 0,0,z. This is consistent with space group $P6_3/m$. Attempts to solve the Patterson were unsuccessful; the interatomic vectors point to the presence of only two molecules in each unit cell.

After this the tube was opened and more silicone grease was applied to hold the crystal in position. The intensity drop of the three standards increased from this point, but the orientation of the crystal remained unchanged. A further 769 were collected over 1[illegible] hours, by which time the intensities of the standards had dropped to 50% of their initial values. The overall data quality was clearly low.

The last 769 reflections were rescaled on the basis of the intensity drop of the standards. The coefficients of the scaling equation;

$$F = F_{obs}(1.0 + \alpha T)(1.0 + \beta T\frac{\sin\theta}{\lambda})$$

were thus determined as α = .029 and β = .058. The maximum rescaling factor (calculated on F) is 1.79. The total number of reflections collected was 1105.

A space group could [illegible] be selected. The data clearly [illegible] h,k.l ≠ k,h,l. [illegible] group 6/m. The [illegible] c [illegible] only no [illegible] the condition 0.0.[illegible] n [illegible] of 13.5. If this [illegible] h [illegible] group is one of P6, P$\bar{6}$, or P6/m. However, [illegible] a [illegible] more likely [illegible] conditions [illegible] the [illegible] l [illegible] P6_3 or P[illegible]

A Patterson synthesis was calculated and examined for possible Harker lines and sections. Possible Harker planes were found at x,y,0 and x,y,$\frac{1}{2}$, with a Harker line at 0,0,z. This is consistent with space group P6_3/m. Attempts to solve the Patterson were unsuccessful; the interatomic vectors point to the presence of only two molecules in each unit cell.

The crystal density calculated on this assumption is only 0.36, which is extremely low, and the R factor calculated on a possible silicon position was .75.

Direct methods was then applied to the problem via MULTAN in both P6/m and $P6_3/m$. The normalisation run supported the centric nature of the space group. Two of the last eliminated reflections were chosen for the starting set together with the origin determining reflections and the sigma-1 signed reflections, for each space group. Four possible phase sets were produced in each case and all were examined. Atomic positions from the two best solutions from each run (P6/m and $P6_3/m$) were fed into the least squares refinement programme CRYLSQ, however, the high R values ($R > .65$) indicated that they were all incorrect.

The failure to solve this structure is almost certainly due to the inferior quality of the data collected and the limited number of acceptable reflections. Cryogenic apparatus is obviously needed for a data collection of this sort, but unfortunately such apparatus was not available.

CHAPTER 5

Crystallographic Studies of the Group IV(b) Diphenylketimines $M(NC(C_6H_5)_2)_4$ (M = Si, Ge and Sn).

The crystal and molecular structures of the series of tetrakis(diphenylketimines) $M(NC(C_6H_5)_2)_4$ (M = Si, Ge and Sn) have been studied and the results are discussed in this chapter.

All three samples were supplied by K. Wade[140], and were prepared by the method of Chan and Rochow[42] from the lithium salt of diphenylketimine and the appropriate Group IV(b) halide:

$$4Ph_2C{=}NLi + MX_4 \longrightarrow 4LiX + (Ph_2CN)_4M$$

M = Si, Ge or Sn.

The products were obtained as yellow crystals which are moisture sensitive, especially for M = Sn. The samples were re-crystallised from n-hexane. The silicon and germanium compounds formed ill-defined, chunky crystals, whereas the tin compound took on a bipyramidal shape.

The samples were mounted in Lindemann glass capillaries in a dry box, as described in Chapter 4.1. Particular precautions against traces of moisture were required when handling the tin isocyanide, and the capillaries were baked at 360°K for several hours under vacuum prior to use.

Tables of atomic coordinates, temperature factors, bond lengths and angles, and observed and calculated structure factors are included in Appendix B.

5.1. Data Collection

5.1.1. Tetrakis(diphenylketimino)silane $Si(NC(C_6H_5)_2)_4$

Preliminary precession photographs showed no symmetry elements, indicating a triclinic system.

Data were collected using the Syntex $P2_1$ 4-Circle Diffractometer. Accurate cell constants and the crystal orientation matrix were determined by use of the automatic centring procedure described in Chapter 3. The unit cell dimensions are given in Table 5.1. The 2θ scan mode was employed for the observations using MoK_α radiation ($\lambda = 0.71069$Å). Because of the size of the unit cell, and hence the large number of reflections to be collected, the maximum 2θ value was limited to 40° for the first 500 reflections, and then reduced to 35°. A total of 5208 reflections (a complete hemisphere of the reciprocal lattice) were measured. 2327 of these were considered observed, with $I/\sigma(I) \geqslant 3.5$.

Solution of the Structure

An accurate density determination was not performed because of the experimental difficulty. The assumption of four molecules in each unit cell would give a crystal density of $1.16gcm^{-3}$, and this was thought to be the only plausible value. Of the two possible triclinic space groups the centrosymmetric $P\bar{1}$ was chosen.

In the absence of any atoms heavier than silicon the direct methods approach was adopted using MULTAN. The initial normalisation used group scattering factors based on rigid phenyl rings. The final statistics agreed with the choice of a centrosymmetric space group. MULTAN produced seven sets of phases other than the all plus solution, and

TABLE 5.1

Data For Si(NC(C_6H_5)$_2$)$_4$

CELL CONSTANTS		STANDARD DEVIATIONS
a	12.342Å	.006
b	18.100Å	.008
c	19.586Å	.015
α	86.89°	.05
β	82.72°	.05
γ	84.06°	.04
Vol	4312.82Å^3	4.51

Experimental Details.

Radiation MoK$_\alpha$ λ = .71069Å

Maximum (Sinθ)/λ =.4803

Total Reflections = 5205

Observed Reflections (>3.5σ) = 2327

Z = 4

F(000) = 1632.0

ρ_{calc} = 1.16gcm^{-3}

each of these were used as a basis for the calculation of E maps. However in all these maps only one 'heavy' atom, attributable to silicon, could be found instead of the two expected for the asymmetric unit.

The X-RAY SYSTEM programmes of Phaser were then applied to the problem, and this is discussed in Chapter 3. The second attempt at division into subsets provided a workable starting point, and the E map based on these phases showed two 'heavy' atoms and several possible rings.

The first stages of least squares refinement proved to be difficult. Inaccuracies in the phasing resulted in slight errors in atomic positions. The problem was augmented by the large number of atoms in the structure; each asymmetric unit contains two silicons, eight nitrogens, one hundred and four carbons and eighty hydrogens.

Initially the positions of the silicons, nitrogens and the carbons of ten of the sixteen phenyl rings were taken from the E map and fed into the programme CRYLSQ. The inevitable errors in the atomic parameters caused a large overall error, reflected in the R value of .563, which prevented effective refinement.

Idealised phenyl ring positions were calculated (RIGBOD) from the carbon atoms and using these the R factor improved to .500. However this still proved too inaccurate to serve as a basis to improve the phasing. Most of the carbons were therefore discarded and only those atoms which were well-defined in the E map were used. These included the silicons, nitrogens and twenty of the carbon atoms. On the basis of these atom positions CRYLSQ gave an R value of .480. A fourier map calculated from the refined phases showed all these atoms as well as defining more clearly the positions of fifteen more carbons. With these included the R factor improved to .408. The process was repeated until all the remaining carbon atoms had been located. The R value was .082 at this stage. The positions of the phenyl hydrogens were then calculated (using the programme BONDAT) and these were allowed to refine. For the final stages the core atoms, silicon, nitrogen and non-phenyl carbon, were allowed to refine anisotropically, and the phenyl rings were refined as rigid bodies, with interatomic distances of 1.395Å (C-C) and 0.95Å (C-H). The final R value obtained was .067 (2327 reflections).

5.1.2. Tetrakis(diphenylketimino)germane $Ge(NC(C_6H_5)_2)_4$

Oscillation, zero and first layer Weissenberg photographs show the crystal to be monoclinic, and therefore not isostructural with the silicon analogue.

Data were collected using the Syntex $P2_1$ Diffractometer. The orientation matrix was established by the procedure outlined in Chapter 3, with the vectors chosen to fit a monoclinic system, (see Table 5.2.). MoK_α radiation was used ($\lambda = 0.71069$) via the 2θ scan mode to a maximum 2θ value of 50°. 4260 reflections were collected, up to reflection 8,10,2, but a malfunction of the Syntex computer prevented completion of the collection. The molybdenum tube was replaced by a

TABLE 5.2

Data For $Ge(NC(C_6H_5)_2)_4$

CELL CONSTANTS		STANDARD DEVIATIONS
(1) Before transformation - body centred.		
a	18.339Å	.003
b	11.971Å	.001
c	18.587Å	.002
α	*90.01°	.009
β	100.03°	.01
γ	*90.00°	.01
Vol	4127.75$Å^3$	.86
(2) After transformation (C_2/C).		
a'	24.050Å	.002
b'	11.971Å	.001
c'	18.839Å	.003
α'	*90.00°	.01
β'	130.44°	.008
γ'	*90.01°	.008
Vol	4127.75$Å^3$	.86

*Required to be 90° but not constrained with least squares refinement of cell constants.

Transformation Matrix

$$\begin{matrix} 1.00 & 0.00 & 1.00 \\ 0.00 & 1.00 & 0.00 \\ -1.00 & 0.00 & 0.00 \end{matrix}$$

Experimental Details.

Radiation $MoK_{\alpha}:\lambda$ = .71069Å(4260 reflections)

$CuK_{\alpha}:\lambda$ = 1.5418Å(3607 reflections)

Total reflections collected = 7867

Maximum $(\sin\theta)/\lambda$ =.5955

Observed reflections ($I > 3\sigma(I)$) =2189

Z = 4

F(ooo) = 1648.0

ρ_{calc} = 1.28gcm^{-3}

copper one, and the second half of the data was collected using CuK$_\alpha$ radiation (λ = 1.5418Å) to a maximum 2θ value of 130°. 3607 reflections were collected in this way to make the total number of measurements 7867. However, inspection of the data revealed that a condition for reflection of h,k,l : h+k+l = 2n (implying I-centring) was obeyed by all but 5 weak reflections. The monoclinic system contains no 'standard'[141] body-centred cells, and so the data required transformation to a 'standard', face-centred form. The new vectors were chosen such that a' = a + c; b' = b; and c' = a. The lattice condition was therefore transformed to h',k',l': h'+k' = 2n. An additional absence was now obvious, namely h'0l' : l'$\neq$ 2n. These absences are consistent with choice of space group C2/c or Cc. Since these are indistinguishable at this stage the unit cell and the data were transformed (SYNDAT) into the higher symmetry group of C2/c. Excluding the lattice absences 3933 reflections were examined, of which 2189 were considered observed, having I/σ(I)$\geqslant$3.0. Table 5.2 gives the unit cell dimensions before and after transformation, and the transformation matrix used.

Solution of the Structure

The number of molecules in the unit cell was deduced to be four from consideration of the unit cell volume (4126Å^3) and comparison with the silicon analogue. On this assumption the crystal density was calculated to be 1.28 gcm^{-3}. The space group C2/c contains eight general equivalent positions, and so the value(Z = 4) implies that the molecules are centred about a special position.

A three-dimensional Patterson synthesis, calculated on the observed data, located the germanium atoms on the special positions (4e) $0,y,\frac{1}{4}$; $0,y,\frac{3}{4}$; $\frac{1}{2},\frac{1}{2}+y,\frac{1}{4}$; and $\frac{1}{2},\frac{1}{2}+y,\frac{3}{4}$. Initial phasing was accomplished on the basis of the heavy atom alone, for which the least squares programme SFLSR gave an R value of .542. Despite this high value the phases were defined well enough to locate all the remaining atoms, other than hydrogen, by a fourier synthesis. Positional and temperature factors (isotropic) were allowed to refine together with the scale factors for the two sections of data. The intensity difference was such that the scale factors refined to final values of .96092 (molybdenum radiation) and .34235 (copper radiation).

At this stage the R value was .221. The programme RIGBOD was used to determine the positions of the phenyl hydrogen atoms. These were allowed to refine and the temperature factors of all other atoms (germanium, nitrogen and carbon) were allowed to become anisotropic. As the germanium lies on a special position not all coefficients are unconstrained. In this case two of the cross terms, B12 and B23, reduce to zero[142].

Up to this point unit weights were applied to all observations and an R value of .064 (2189 reflections) was reached. The use of a weighting scheme, in which the weight given to each observation is inversely proportional to the square of its standard deviation, marginally improved the R value to .058.

5.1.3. Tetrakis(diphenylketimino)stannane $Sn(NC(C_6H_5)_2)_4$

This compound is extremely moisture sensitive, so much so that despite all precautions the mounted crystals had very limited lifetime. For this reason it was decided to use the diffractometer (Syntex $P2_1$) for preliminary investigations rather than standard photographic procedures.

The initial results from the centring procedure pointed to a tetragonal space group, thus eliminating any possibility of the compound being isomorphous with the silicon or germanium analogues. The Laue group was chosen to be 4/m because of the difference in intensities of equivalent reflections ($|F(hkl)| \neq |F(\bar{h}kl)|$). The variation in intensities was considered too great to be caused entirely by absorption of radiation by the crystal. Random sampling of the data indicated that the system is body-centred as no reflections satisfying the condition h,k,l : h+k+l = 2n+1 were observed.

Because of the rapid decomposition of the sample data were collected as quickly as possible. Thus a variable scan rate was employed with a minimum speed of 5° in 2θ per minute. Copper radiation (λ = 1.5418Å) was used to a maximum 2θ value of 120°. A total of 1994 unique reflections were measured in a total time of 23 hours, of which 1329 were considered observed ($I/\sigma(I) \geqslant 3.0$). Three standards were used and these were remeasured after every hundred reflections; the intensity drop was used to rescale the data for decomposition. It was found that for the three standards the fall off in intensity with time showed a slight break after 7 hours, and was fitted to two straight lines.

TABLE 5.3

Data For $Sn(NC(C_6H_5)_2)_4$

CELL CONSTANTS		STANDARD DEVIATIONS
a	18.137Å	.008
b	18.146Å	.007
c	14.461Å	.0025
α	90.00°	.023
β	90.00°	.026
γ	90.00°	.033
Best value <u>a</u> = 18.141		.007
Vol 4758.2$Å^3$		1.02

Experimental Details

Radiation CuK_α: λ = 1.5418Å

Maximum $(Sin\theta/\lambda)$ = .5622

Total reflections = 1994

Observed reflections ($\geq 3\sigma$) = 1329

Z = 4

F(ooo) = 1720.0

ρ_{calc} = 1.17gcm^{-3}

Linear absorption coefficient = 53.6

Scaling Coefficients

α_1 = .0233

β_1 = .0103

α_2 = .0135

β_2 = .0309

The scaling expression is:

$$F = F_{obs}(1.0 + \alpha T)(1.0 + \beta T\frac{\sin\theta}{\lambda})$$

The coefficients α_1 and β_1 for the first set were (.023) and (.010) respectively, and for the second set α_2 and β_2 were (.014) and (.031). The maximum rescaling factor required for any of the standards was 1.72 (calculated on F).

The presence of a heavy atom (tin) and the use of a fairly large crystal necessitated corrections for absorption of radiation. The mass absorption coefficient (μ/ρ) for tin is 256* and the total linear absorption coefficient for the molecule was calculated to be 53.6. Absorption corrections were applied to observed data only using the programme ABSCOR (see Chapter 3) and only these were used in subsequent refinement; transmission factors varied from .3572[illegible] to .59525, calculated on F.

Inspection of the data showed systematic extinctions for 0,0,l : l≠4n; h,k,0 : h,(k)≠2n; and h,k,l : h+k+l≠2n. These are the conditions required by the space group $I4_1/a$. The unit cell volume is 4758Å^3 which is comparable with those found in the silicon and germanium cases. It was therefore again assumed that Z = 4; on this basis the crystal density was calculated to be 1.17 gcm^{-3}.

Solution of the Structure

The space group $I4_1/a$ has a sixteen-fold general position. As there are only four tin atoms in the unit cell these must

---

* CuK$_\alpha$ Radiation.

occupy a four-fold special position. They are most likely to be situated on the $\bar{4}$ axis, owing to the presumed tetrahedral nature of the molecule. The tin atom positions are thus completely defined by the choice of origin. Two standard choices of origin are available at $\bar{4}$ or $\bar{1}$. Selection of the origin at $\bar{1}$ defines a centrosymmetric unit cell, and this was accordingly picked. The tin atoms are thus situated at 0,1/4,1/8; 0,3/4,3/8; 1/2,3/4,5/8; and 1/2,1/4,7/8. Phasing due to the **tin** atom alone gave an R value of .37, and a fourier synthesis located the remaining non-hydrogen atoms. One cycle of refinement (CRYLSQ) improved the R value to .141. Further refinement including anisotropic thermal parameters for all atoms gave an R value of .121. For the tin atom, occupying the special position, the anisotropic coefficients are limited such that $B_{11} = B_{22}$ and B_{12}, B_{13} and B_{23} are all zero. The programme BONDAT was used to locate the phenyl hydrogens and inclusion of these improved the R value to .118. This is a comparatively high R value for diffractometer data, but this is not unexpected in view of the severe decomposition encountered during data collection.

5.2. Discussion

5.2.1. Tetrakis(diphenylketimino)silane

The asymmetric unit contains two independent molecules which are shown in Figures 5.1 and 5.2. The molecules occupy a four-fold special position. They are most likely to be situated on the $\bar{4}$ axis, owing to the presumed tetrahedral nature of the molecule. The tin atom positions are thus completely defined by the choice of origin. Two standard choices of origin are available at $\bar{4}$ or $\bar{1}$. Selection of the origin at $\bar{1}$ defines a centrosymmetric unit cell, and this was accordingly picked. The tin atoms are thus situated at 0,1/4,1/8; 0,3/4,3/8; 1/2,3/4,5/8; and 1/2,1/4,7/8. Phasing due to the **tin** atom alone gave an R value of .37, and a fourier synthesis located the remaining non-hydrogen atoms. One cycle of refinement (CRYLSQ) improved the R value to .141. Further refinement including anisotropic thermal parameters for all atoms gave an R value of .131. For the tin atom, occupying the special position, the anisotropic coefficients are limited such that $B_{11} = B_{22}$ and B_{12}, B_{13} and B_{23} are all zero. The programme BONDAT was used to locate the phenyl hydrogens and inclusion of these improved the R value to .118. This is a comparatively high R value for diffractometer data, but this is not unexpected in view of the severe decomposition encountered during data collection.

5.2. Discussion

5.2.1. Tetrakis(diphenylketimino)silane

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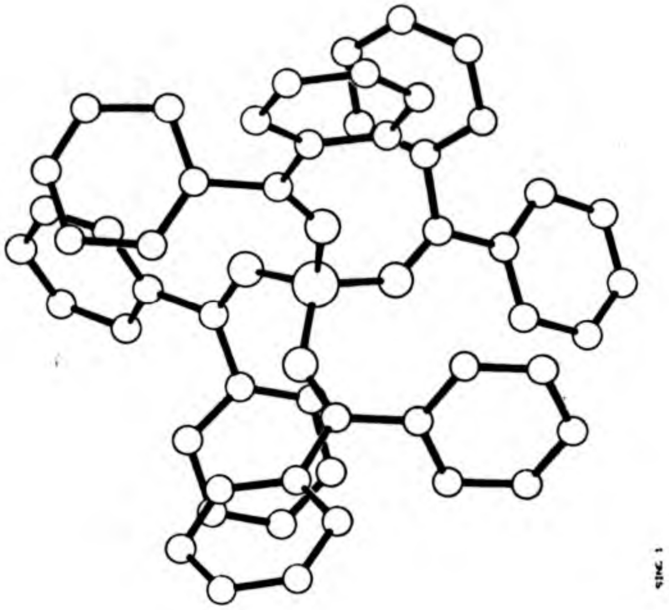
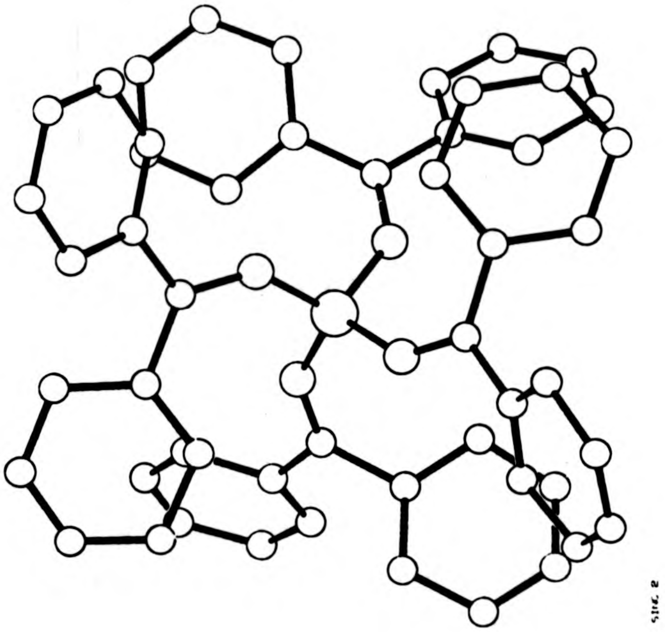
Figure 5.1



$Si(NC(C_6H_5)_2)_4$: Molecule 1.

Figure 5.2



$Si(NC(C_6H_5)_2)_4$: Molecule 2.

are monomeric with approximately tetrahedral geometry about the silicon atom. The variations in internuclear angles are significantly larger for molecule 1 than for molecule 2. The N-Si1-N angles vary from 101.8° (7) to 116.2° (7) and the N-Si2-N angles fall in the range 103.0° (7) to 114.9° (8).

The most notable feature of the structure involves the wide angle at nitrogen. In the absence of delocalisation of charge from the nitrogen lone pair into the silicon d orbitals this is expected to be 120° (i.e. pure sp^2 nitrogen). However in the ketiminosilane the angle has widened to an average value of 134.5° (13) for molecule 1 and 139.1° (15) for molecule 2. The values are all within three standard deviations of this average for molecule 2 but not for molecule 1 in which the individual angles vary from 128.2° (11) to 139.0°(13)

The substantial deviation from 120° is indicative of multiple bonding between the silicon d orbitals and the nitrogen p_π orbital. The reasons for the variations in the individual angles must lie in the fact that M-N=C angles are somewhat sensitive to their local environment. Thus although the widening of the angle is caused by the effect of multiple bonding on the hybridisation of the nitrogen, precise values will be dependent on packing effects, minimising the interactions between the bulky phenyl groups. The silicon atom does not require complete donation of four electron pairs. A suitable total overlap of electron density donation $(d_\pi - p_\pi)$ can be obtained by contributions from the four nitrogens in different ways to give different bond angles.

The silicon-nitrogen bond length is a reliable judge of the extent of d_{π}-p_{π} interaction. A pure Si-N single bond length does not in reality occur. An often quoted value for this, 1.79Å, is calculated from atomic radii with the application of the Schomaker- Stevenson electronegativity correction[143]. The equation used is purely empirical, has no theoretical basis and frequently gives erroneous results.[144] For Group IV(b) elements the exact electronegativities are questionable; thus some measurements indicate that the order is Si > Ge > Sn, whereas others give the reverse order.[145-148] A more reliable single bond length can be determined from known interatomic distances[149]. Atomic radii are estimated from interatomic distances in the diamond form of carbon and silicon. The difference in the radii is then calculated and this value added to the C-N= bond length (which is not significantly different from C-N<). The figures are tabulated (Table 5.4). On this basis a pure Si-N single bond length is determined to be 1.879Å. In the molecule trisilylamine, $(SiH_3)_3N$, the Si-N bond length is 1.738Å (2)[24]. This short distance and the planarity of the nitrogen support substantial multiple bonding. Apart from trisilylamine the structures of various other silylamine compounds have been determined, and these include $(Me_2SiNH)_3$ (Si-N = 1.78Å)[38]; $(SiH_3)_2NH$ (Si-N = 1.725 Å)[150], $ClSi(NMe_2)_3$ (Si-N = 1.715 Å)[151], and $Si(NCO)_4$ (Si-N = 1.688 Å)[152]. The Si-N distance in the ketiminosilane is comparable with these at 1.707 Å (15) (averaged), indicating a considerable amount of π orbital

TABLE 5.4

Calculations Of Group(IV) M-N Bond Distances.

M	M-M(Å)(diamond form)	RADIUS_M(Å)	RADIUS_M-RADIUS_C(Å)	C=N=(Å)	M-N(Å)
C	1.544	0.772			
Si	2.352	1.176	0.404	1.475	1.879
Ge	2.450	1.225	0.453	1.475	1.928
Sn	2.310	1.405	0.633	1.475	2.108

interaction. All values are within the standard deviation of the mean.

It is possible that the π-system of the C=N group can also interact with the vacant silicon d orbitals, and if this occurs the C=N bond should lengthen. Little structural data is available for analagous ketimine systems, but the normal bond length may be estimated as 1.265 Å from the atomic radii[149]. This value is supported by the structural analyses of $(CO)_3Fe(N=CR_2)$, in which the average C=N bond distance is 1.265 Å (16)[153], and $\pi-(C_5H_5)Mo(CO)_2N=CBu^t{}_2$, with a C=N bond length of 1.27 Å [153]. The ketiminosilane exhibits a mean C=N bond distance of 1.27 Å (2) which compares well with these, and therefore implies little involvement of the C=N π system with the silicon d orbitals.

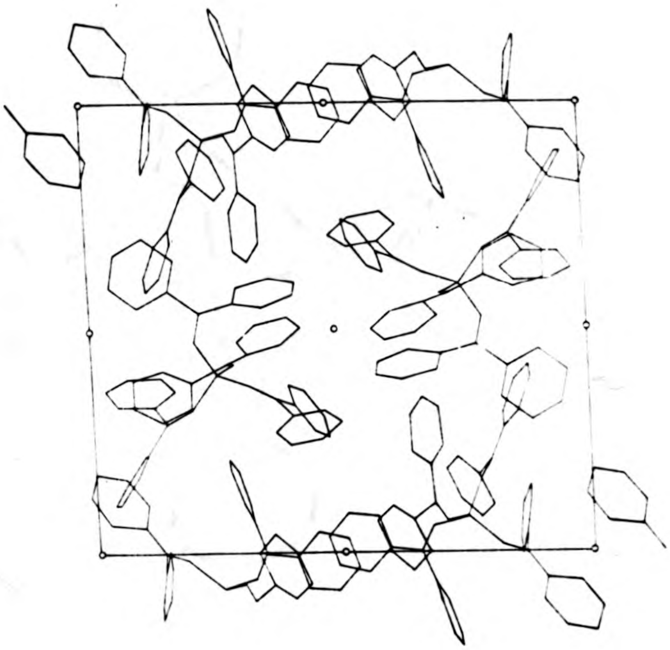
In the final stages of refinement the phenyl rings were treated as rigid bodies, with C-C bond distances of 1.395 Å and C-H distances of 0.95 Å. The rings subtend an angle of 117.2° (13) at the cyanide carbon, the deviation from 120° being probably due to steric interference between the ketimine groups.

The packing diagram, shown in Figure 5.3, presents the unit cell contents projected along **a**. The molecules are monomeric, approximately spherical in shape, with little or no interaction between them.

5.2.2. Tetrakis(diphenylketimino)germane

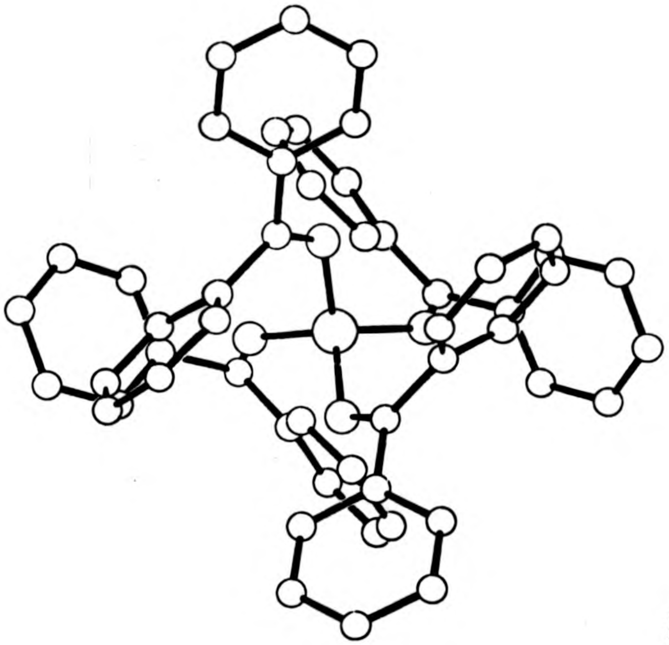
The molecule is shown in Figure 5.4. They are monomeric

Figure 5.3



Packing diagram for $Si(NC(C_6H_5)_2)_4$ showing the unit cell contents projected along <u>a</u> .

Figure 5.4



$Ge(NC(C_6H_5)_2)_4$: Viewed along the two-fold axis.

and the geometry about the germanium is approximately tetrahedral with angles varying from 111.2° (3) to 106.8° (3). The two unique angles about the nitrogen (Ge-N=C) are 123.8° (5) and 130.1° (5), and as with the silicon analogue, the widening of this angle is indicative of some interaction between the p_π orbitals on nitrogen with the empty d orbitals on germanium, although the effect is much smaller than for the silicon case.

Any shortening of the germanium-nitrogen bond length from the hypothetical single bond distance would confirm the presence of any multiple bonding. Unfortunately, the structural aspects of germanium chemistry have received little attention in the literature. Electron diffraction studies on trigermylamine, $(GeH_3)_3N$, indicate a planar structure with a Ge-N distance of 1.836 Å [155]. The Ge-N single bond length may be estimated to be 1.928 Å from consideration of the atomic radii of germanium and nitrogen as described in the previous section on the silicon analogue. The ketiminogermane compound has a Ge-N distance of 1.871 Å (5) (average), which implies some degree of π orbital interaction, although rather less than in the trigermylamine molecule.

In this compound the C=N distance is 1.26 Å (1), which is comparable to the silicon analogue and is also very similar to the estimated value (1.265 Å). Thus there is no evidence for any involvement of the C=N π system with the d orbitals on germanium.

The bond distances in the phenyl rings are normal, averaging to 1.39 Å (1). As with the silicon compound the angle subtended by the phenyl rings at the cyanide carbon shows a slight deviation from 120°, at 116.2° (7), and again this is ascribed to packing effects.

Figure 5.5 shows the molecular arrangement within the unit cell, projected along the unique axis b. The germanium atoms are situated on the two-fold axis, which relates the two halves of each molecule. The packing is again of independent, approximately spherical molecules with little intermolecular interaction.

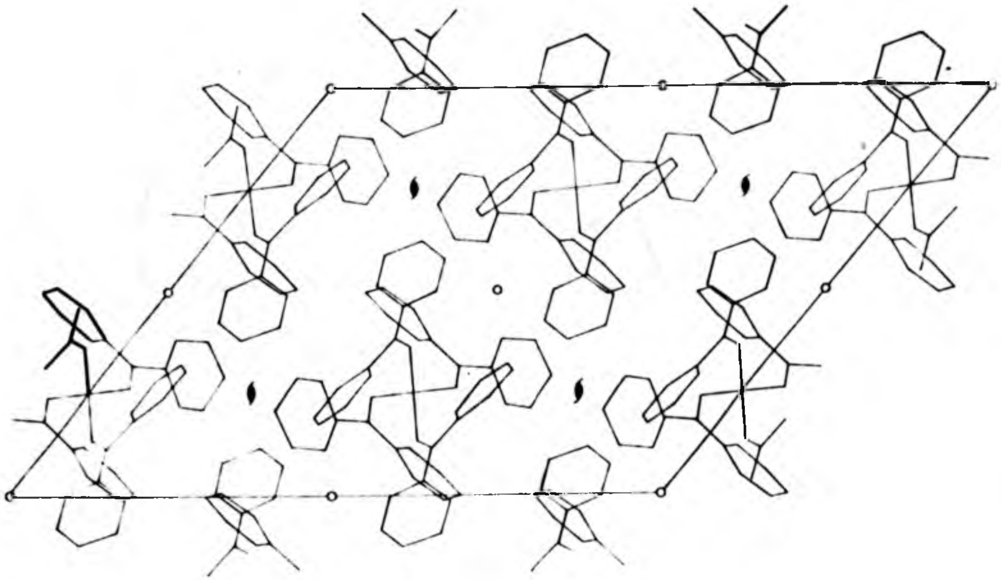
5.2.3. Tetrakis(diphenylketimino)stannane

Despite the tendency of tin(IV) to increase its coordination number via intermolecular association, in this instance the molecules are monomeric and closely tetrahedral, as shown in Figure 5.6. Both the independent angles at tin are within the standard deviation of the tetrahedral angle (109.5°), being 107.7° (7) and 110.4° (6).

The angle at nitrogen of 121.5° (13) agrees with the value of 120° expected for sp^2 hybridised nitrogen within the standard deviation. This points to a complete lack of π-bonding involving the tin d orbitals.

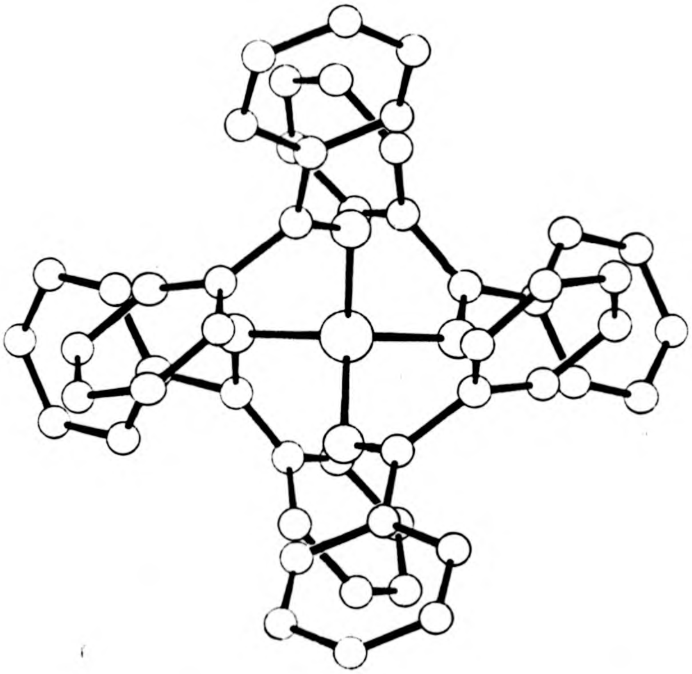
Few tin-nitrogen compounds have been structurally analysed. Those for which structural data is known include cyanamide and isothiocyanate groups. The difficulty of direct comparison with the ketimino compound lies in the tendency of tin to increase its coordination sphere by

Figure 5.5



Packing diagram for $Ge(NC(C_6H_5)_2)_4$: Projected along the unique axis b

Figure 5.6



$Sn(NC(C_6H_5)_2)_4$: Viewed along the $\bar{4}$ axis.

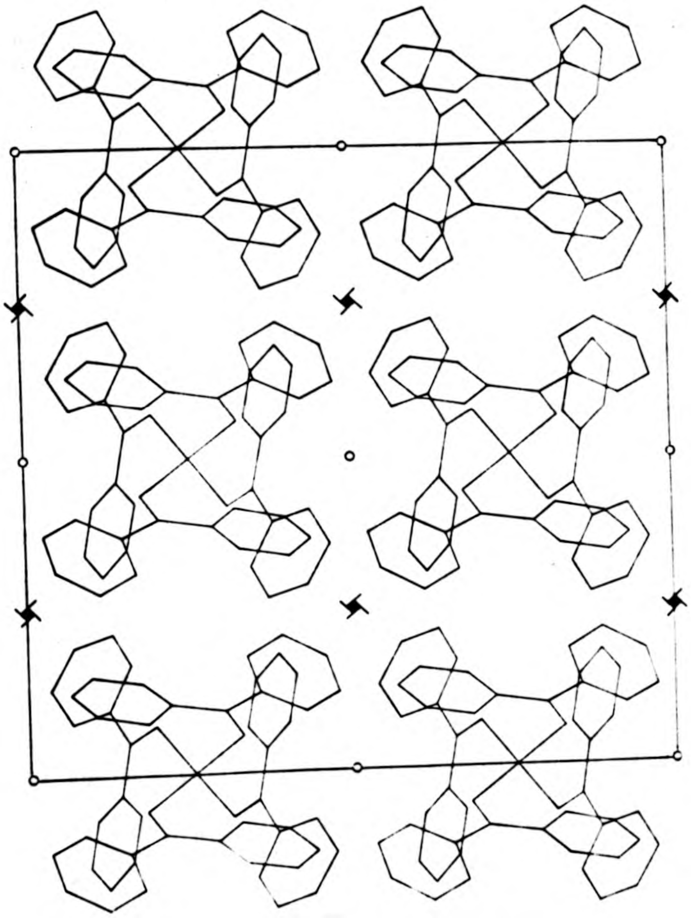
polymerisation. The necessary change in hybridisation at tin affects the covalent radius. Also, in many tin compounds there exists some ionic character in the bonds, causing bond lengthening. Thus bis(trimethyltin)cyanamide is a dimeric structure with five-coordinate tin and a Sn-N bond length of 2.47 Å [156]. Trimethyltin isothiocyanate and dimethyltin-diisothiocyanate are also approximately trigonal bipyramidal structures with Sn-N bond distances of 2.15 Å and 2.10 Å respectively[157,158]. The Sn-N pure single bond length may be estimated as for the silicon and germanium systems (see Table 5.4) and is calculated as 2.108 Å. The Sn-N bond distance in the ketiminotin compound is 2.068 Å (37), which is in close agreement with this.

The C=N linkage is 1.33 Å (36), and is rather longer than for the other ketimines; however the standard deviations are such that this difference is probably not significant.

The phenyl rings are normal, with bond distances (C-C) averaging to 1.37 Å (6) and angles within the standard deviation of 120°. The angle subtended by the phenyl groups at the cyanide carbon is 115.7° (18). The deviation from 120° is thought to be due to packing effects, as with the analagous silicon and germanium species.

Figure 5.7 shows the molecular arrangement within the unit cell, viewed along c. The molecules are centred around $\bar{4}$ axes. The unit cell is shown with the origin at $\bar{1}$ (and is therefore centrosymmetric). As with the silicon and germanium analogues, the molecules are approximately spherical and show little intermolecular interaction.

Figure 5.7



Packing diagram for $Sn(NC(C_6H_5)_2)_4$ showing the unit cell contents projected along **c** .

5.3. Conclusion

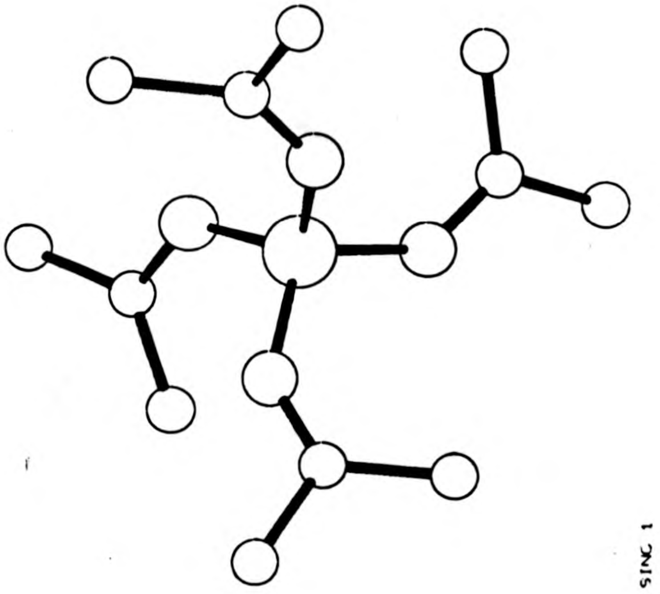
π-Bonding in the GroupIV(b) Ketimines

The π-acceptor ability of the GroupIV(b) elements (excluding carbon) is known to decrease as the atomic number increases. The structural analyses of the series of diphenylketimino compounds $M(NC(C_6H_5)_2)_4$ (M = Si,Ge and Sn) indicate that the variations in the angles at nitrogen may be a sensitive probe to the extent of M-N (d_π-p_π) interaction.

In the three cases studied the central atom is tetrahedral or nearly so. The only major difference between the structures is in the angle at nitrogen. This is sufficient to cause all three compounds to crystallise in differnt space groups with increasing site symmetry as the normal sp^2 angle of 120° is approached. Thus the silicon compound adopts triclinic symmetry ($P\bar{1}$), the germanium compound belongs to the monoclinic system (C2/c) with molecular symmetry 2, and for the tin analogue tetragonal symmetry is found, the space group is $I4_1/a$ and the molecular symmetry is $\bar{4}$.

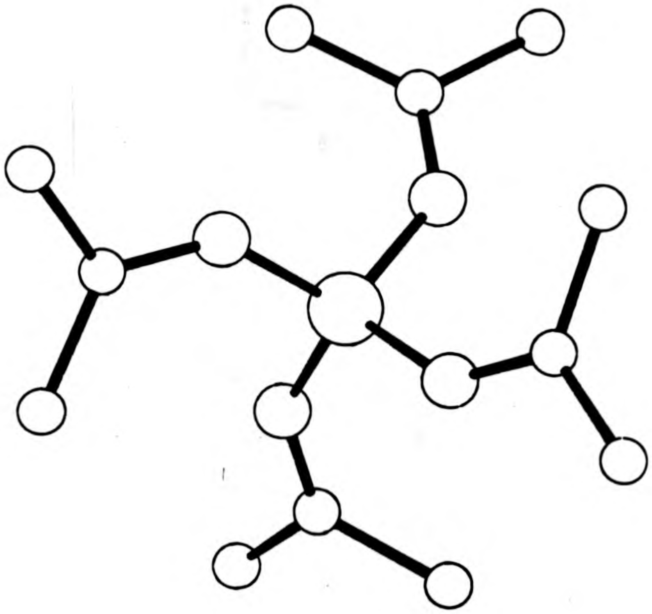
Multiple bonding in the silicon compound has a substantial effect on the nitrogen angle, increasing it from 120° to 134.7° and 139.5° (averaged) in the two independent examples. The angle widening found in the germanium analogue is very much smaller (123.8° and 130.1°) although still significant, and in the tin compound the nitrogen angle is not significantly different from 120°. Figures 5.8, 5.9, 5.10 and 5.11 show the core atoms for silicon (molecules 1 and 2), germanium and tin derivatives respectively, viewed along equivalent

Figure 5.8



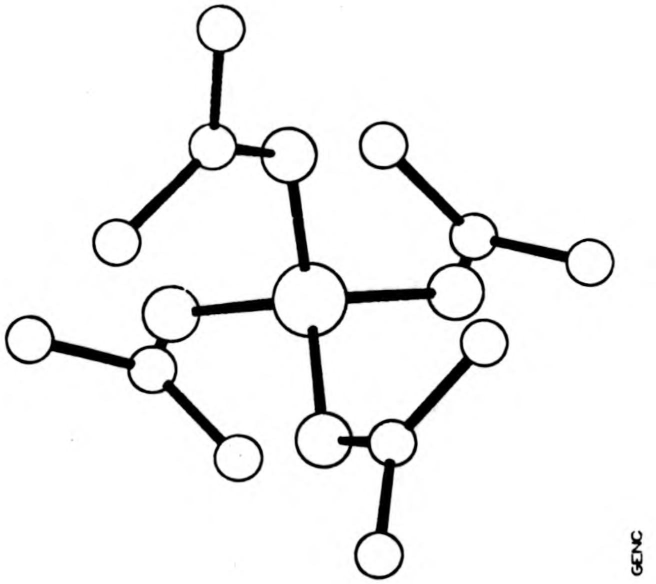
Core Atoms for $Si(NC(C_6H_5)_2)_4$: Molecule 1

Figure 5.9



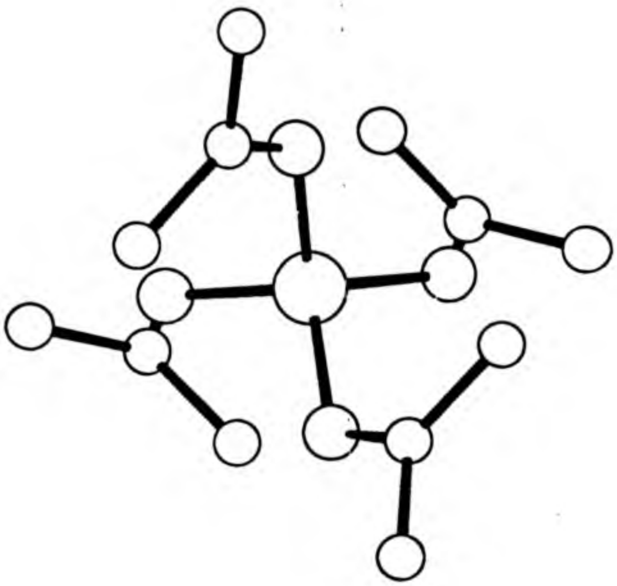
Core Atoms for $Si(NC(C_6H_5)_2)_4$: Molecule 2

Figure 5.10



Core Atoms for $Ge(NC(C_6H_5)_2)_4$

Figure 5.11



Core Atoms for $Sn(NC(C_6H_5)_2)_4$

directions.

The presence of multiple bonding is confirmed by the M-N bond length contractions from the predicted single bond lengths, as given in Table 5.5. The contraction is greatest for silicon, rather less for germanium and insignificant for tin. The calculations for the M-N single bond lengths have not accounted for electronegativity effects because of the unreliability of the Schomaker-Stevenson equation. Perhaps a more reliable guide to the difference in π-bonding effects between silicon and germanium is found by comparison of the atomic radii differences ($R_{Ge} - R_{Si}$) calculated from a) M-C distances, which are accurately known[149], and b) from the compounds under examination.

$R_{Ge} - R_{Si}$ is detrmined by a) to be .075 Å and by b) to be .155 Å, thus indicating that bond contraction is considerably more (.08 Å) for silicon than for germanium. Such comparisons for R_{Sn} are less useful because of the poorer quality of the data for this system.

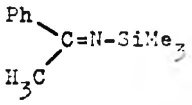
The three structures are essentially similar and so any steric effects due to the bulky phenyl groups will be similar in all cases. The angle between the two phenyl rings of each ketimine is approximately 116.4°, and the distance between the cyanide carbon and 'C1' of the phenyl rings is approximately 1.50 Å. Any steric effect of the rings on the angle at nitrogen would be expected to be similar for the three structures. As the M-N=C angle in the tin compound is not significantly different from 120° it must

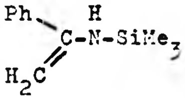
TABLE 5.5

M	M-N (calc.)Å	M-N (obs.)Å	Contraction (σ) Å
Si	1.879	1.707	.172 (15)
Ge	1.928	1.871	.057 (5)
Sn	2.108	2.068	.040 (37)

be assumed that the steric effect in all cases is only small.

In order to confirm this it would be valuable to determine the structure of the aliphatic ketimino derivatives, in which steric hindrance would be minimal. However, silyl derivatives of aliphatic ketimines cannot be prepared in a pure form as the hydrogen in the α-position enters into enamine tautomerism.[140]:

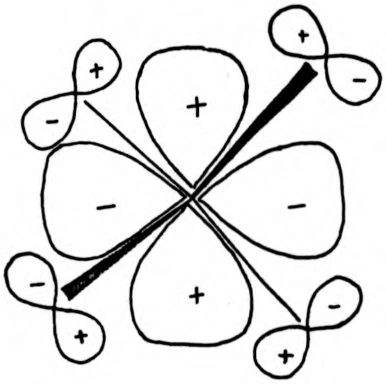


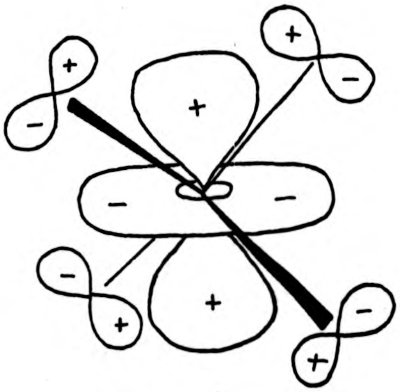


Tetrahedral molecules in which the central atom contains vacant d orbitals can form d_{π}-p_{π} bonds, and the d orbitals most suitable for π-interaction are the $d_{x^2-y^2}$ and the d_{z^2}, as illustrated in Figure 5.12. The tetrakis(diphenylketimines) of silicon, germanium and tin contain tetrahedral central atoms and can therefore invoke this type of π-bonding. There are two models for the π-interaction in this situation. The first involves donation of charge from the nitrogen lone pair into the empty M d orbitals, and in the second there is interaction between the ketimine (N=C) π-system and the d orbitals on M.

In the first case no significant change in the C=N group is expected. The nitrogen lone pair initially occupies an sp^2 hybrid orbital, which is directed away from the d orbitals, and is therefore not very favourable for interaction. Increase in the p character of this lobe would enhance effective overlap, and linearity of the M-N=C fragment

Figure 5.12





would result as the nitrogen is rehybridised to sp. The two extremes are schematically illustrated in Figure 5.13. This model explains the approach to linearity of silicon isocyanates and isothiocyanates (see Table 5.6).

Alternatively, if the C=N π-system of the ketimine is involved in d-π bonding no rehybridisation of the nitrogen is required. Overlap will depend on the orientations of the d orbitals on M and the nodal plane of the substituents, relative to one another. The orientation required for maximum overlap (as illustrated in Figure 5.14) is orthogonal to that required for interaction involving the non-bonding electrons.

(d-π) Interactions are known to exist for silicon-olefin systems. The silicon-vinyl π-bond must be interpreted in terms of both (d-π) and (d-π*) interactions, but the latter effect is much larger due to better energy matching with the d orbitals.[162] Involvement of the bonding π-orbitals in (d-π) bonding would lead to delocalisation of the π-bonding electrons, weakening and hence lengthening the π-bond of the substituent. Interaction with the π* orbital however would not seriously effect the ground state properties of the molecule, but would be significant in relation to electronic spectra or reaction mechanisms.

For effective interaction the energies of the orbitals involved should be similar. Antibonding (π*) and non-bonding orbitals will be higher in energy than the bonding (π) orbitals, and so more favourable for overlap with the d orbitals on M.

Figure 5.13

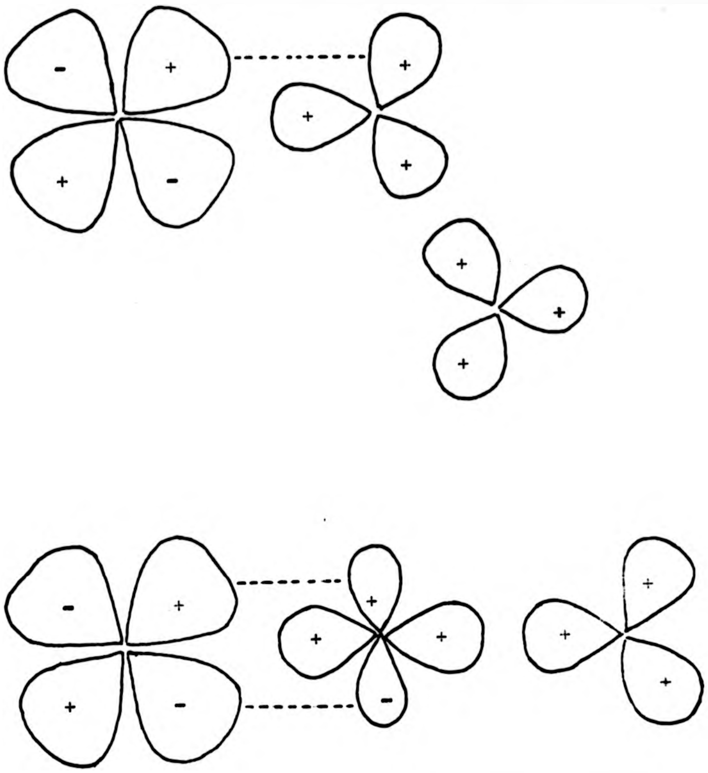


Figure 5.14

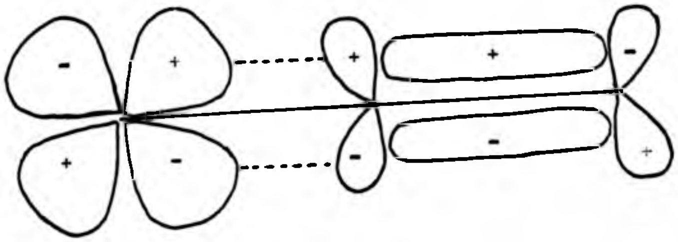


TABLE 5.6 (Measurements by electron diffraction)

COMPOUND	ANGLE
$(H_3Si)_3N$[24]	119.7
$(H_3Ge)_3N$[155]	120
$(H_3C)_3N$[25]	110.6
$H_3Si\text{-}O\text{-}SiH_3$[168]	144.1
$H_3C\text{-}O\text{-}SiH_3$[167]	120.6
$H_3C\text{-}O\text{-}CH_3$[149]	111.5
$H_3Ge\text{-}O\text{-}GeH_3$[169]	126.5
H_3SiNCO[164]	151.7
F_3SiNCO[164]	160.7
Cl_2SiNCO[165]	138
Me_3SiNCO[44]	150
$Si(NCO)_4$[152]	146.4
H_3SiNCS[166]	163.8
Me_3SiNCS[44]	154
$Si(NCS)_4$[166]	172.5 (X-ray)

This is borne out by experimental results.

Studies of the electronic spectra of the GroupIV(b) ketimines show considerable stabilisation of the antibonding (π^*) orbital by interaction with a Group IV(b) element, as discussed in Chapter 1[42]. There is also much evidence for the involvement of lone pair electrons in d_π-p_π bonding, frequently causing rehybridisation to produce lone pair orbitals of high p character. Unusual bond angles are found mainly for Si-N= and Si-O- species. The angle variations in various GroupIV(b) amines, oxides, isocyanates and isothiocyanates are tabulated in Table 5.6. Cruickshank[15] was the first to correlate the variations in bond angles and bond lengths in X-O-X systems, where X contains an vacant 3d orbital. His results show the X-O-X angle decreasing from 180° as the length X-O increases (i.e. a decrease in π interaction).

A similar correlation may be applied to the GroupIV(b) ketimines. As the angle at nitrogen increases from 120° the contraction of the M-N bond length from the hypothetical single bond length increases (see Table 5.5), implying increasing π interaction from the lone pair orbitals.

The C=N bond length in the silicon and germanium ketimines is very close to the estimated C=N double bond length, suggesting little or no interaction with the bonding π orbital. The C=N bond length in the tin analogue is apparently lengthened, but does not differ from the calculated value by more than 3σ. A slight lengthening of this bond is possible without implying d-π interaction, as the σ inductive effect will be greater for tin[163] and the subsequent increase in the electron density of the nitrogen will affect the C=N bond.

Summarising the results, the GroupIV(b) ketimines show interaction between the d orbitals on M with the antibonding (π^*) orbital and with the orbital containing the nitrogen lone pair. The extent of the latter interaction is demonstrated by the variations in the nitrogen angle. The π-acceptor ability of the GroupIV(b) elements is confirmed as Si > Ge > Sn.

APPENDIX A.

Experimental Techniques

Owing to the air/moisture sensitivity of many of the compounds handled during this work, special techniques were necessary.

a) The Dry Box

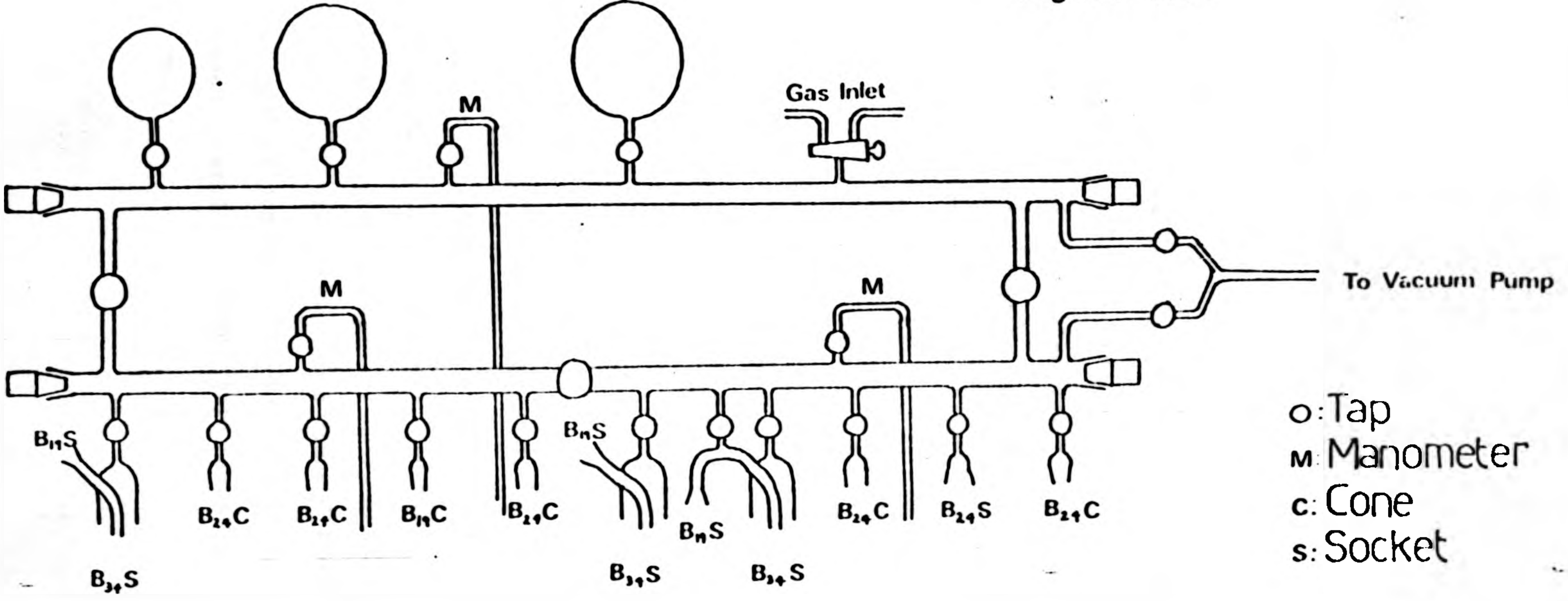
Manipulations under an inert atmosphere were carried out in a steel glove box which was continually flushed with a supply of dry, oxygen-free nitrogen. Two dishes of P_2O_5 were kept in the dry box to remove residual traces of moisture; these were regularly replaced. Entry was provided via an 'air lock' type entrance port which was continually flushed with a rapid, independent supply of nitrogen.

For the handling and mounting of air/moisture sensitive crystals a dry box was modified by insertion of a binocular stereoscopic microscope (magnification x20) sealed into the perspex window, to allow inspection of the crystals. A heating wire, operated by a foot switch, was available for cutting and sealing the capillaries. The inlet nitrogen passed through a copper coil which could be immersed in liquid nitrogen to cool the dry box.

b). The Vacuum Line

Many of the manipulations required use of a standard, all glass, high vacuum system, as illustrated in Figure A.1.

Figure A.1



The Vacuum Line

The vacuum was produced and maintained by use of a Genevac double stage rotary piston vacuum pump (type GRD2), and an electrically heated mercury diffusion pump.

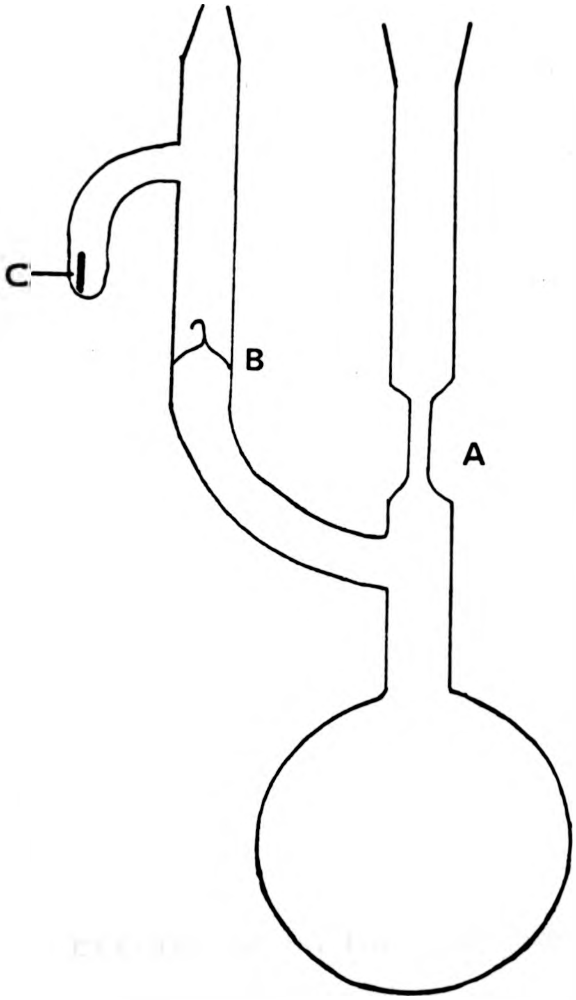
c) Reaction Vessel

Reactions were carried out in a glass ampoule as shown in Figure A.2. Reactants and solvents were loaded into the reaction vessel and sealed under vacuum at point A. On completion of the reaction the ampoule was opened under vacuum via the breakseal (B), which was broken by impact from the magnet C.

Product Isolation

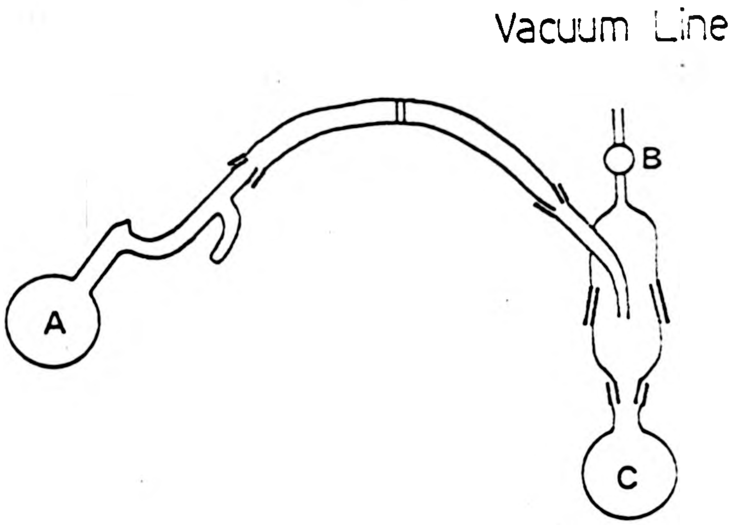
The reaction vessel was placed on the extraction system of the vacuum line (see Figure A.3), and the system was evacuated. The reaction vessel was opened (at the breakseal), the solvent distilled out, and a suitable solvent, for the extraction of either the product or excess starting material, was distilled into flask A. The system was closed at tap B, and the solution decanted through the glass sinter into flask C. The solvent was then distilled back into flask A and the process repeated until complete extraction was achieved. The solvent was removed from the system and the product pumped in vacuo for about a day. The product was stored by sealing samples into glass vials under dry nitrogen.

Figure A.2



Reaction Vessel

Figure A.3



Extraction on the Vacuum Line

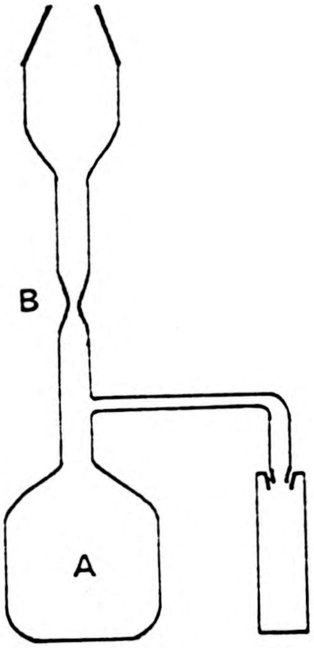
Electronic Spectra

Solution spectra were recorded using sealed 1 cm silica cells, as shown in Figure A.4. The sample was loaded into flask A in the dry box. Solvent was distilled into the flask in vacuo and the system sealed, under vacuum, at point B. This system allows ready dilution of solutions to be carried out in situ. Half the solution from the cell is tipped back to the reservoir A and pure solvent is then distilled back into the cell, thus diluting the solution.

Solvent Drying

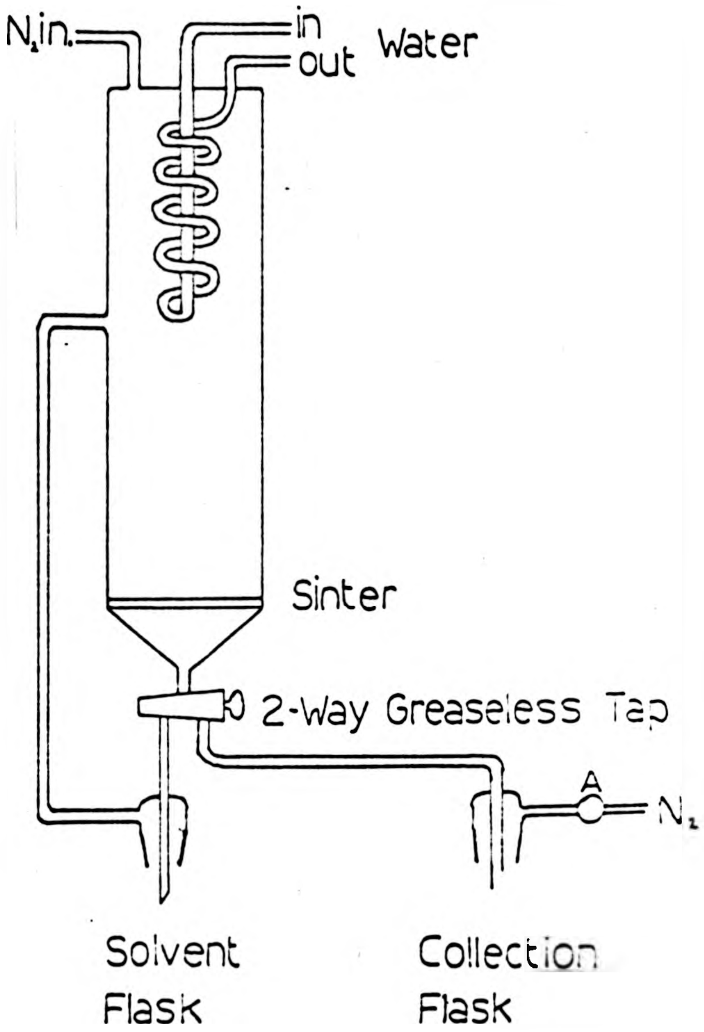
All solvents were rigorously dried by heating under reflux with CaH_2, $LiAlH_4$, or P_2O_5 under nitrogen. The use of specially designed solvent stills (see Figure A.5) readily allowed rapid reflux, collection and removal of solvents to be achieved. The incorporation of a glass sinter also allowed for efficient deoxygenation of solvents by passing dry nitrogen, via tap A, through the solvent during collection.

Figure A . 4



A uv Cell

Figure A.5



Solvent Still

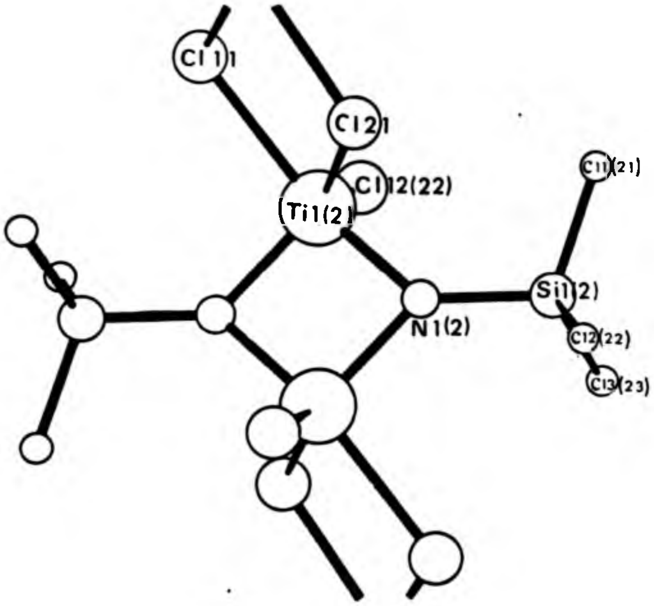
APPENDIX B

Crystallographic Results

The full results of the crystal structure analyses are presented here as atomic positions, temperature factors, interatomic distances, interatomic angles, and comparison of observed and calculated structure factors, for each structure in the order that they appear in the text; i.e. Tables B1-B5 contain all the relevant data for the cyclotitanazane, $(Cl_2TiNSiMe_3)_2$; Tables B6-B10 contain the data for the silicon diphenylketimine, $Si(NC(C_6H_5)_2)_4$; Tables B11-B15 contain the data for the germanium diphenylketimine, $Ge(NC(C_6H_5)_2)_4$; and finally, Tables B16-B20 contain all the data for the tin diphenylketimine, $Sn(NC(C_6H_5)_2)_4$.

Figures B1-B6 show the numbering scheme for each molecule. In the phenyl rings only 'C1' has been given an individual number (taking its first number(s) from the non-phenyl carbon attached to it); the remaining carbon atoms are labelled systematically (as 'C1') with the final figure changing (2-6 or 8-12).

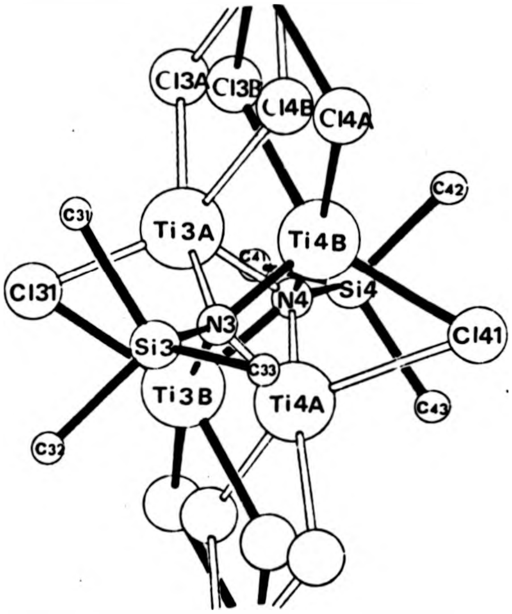
Figure B.1



$(Cl_2TiNSiMe_3)_2$: Ordered molecule.

This shows the labelling of the unique atoms of one molecule; names of equivalent atoms of the adjacent molecule in the chain follow in parentheses.

Figure B.2



$(Cl_2TiNSiMe_3)_2$: Disordered molecule.

Molecule 'A' is linked by white bonds and molecule 'B' by black bonds.

TABLE B.1

Final Atomic Positions For $(Cl_2TiNSiMe_3)_2$

ATOM	x	y	z
Ti1	-0.03817	0.02767	0.39290
Ti2	0.03846	0.03095	-0.07713
Ti3A	0.47151	0.28296	0.07228
Ti3B	0.47166	0.27243	-0.11357
Ti4A	0.55015	0.22041	-0.08466
Ti4B	0.55171	0.21882	0.10151
Cl11	-0.13115	-0.00726	0.20322
Cl12	-0.11[illegible]64	0.12026	0.41418
Cl21	-0.050[illegible]2	0.00388	-0.26695
Cl22	0.11020	0.12330	0.00372
Cl31	0.38976	0.36688	-0.05255
Cl3A	0.37784	0.25586	0.20099
Cl3B	0.46311	0.24810	-0.27273
Cl41	0.62750	0.13310	0.04574
Cl4A	0.63928	0.24880	0.28796
Cl4B	0.55815	0.25681	0.26246
Si1	0.11381	0.12120	0.52044
Si2	-0.12112	0.12094	-0.04845
Si3	0.39520	0.12534	-0.04541
Si4	0.61631	0.38013	0.03476
N1	0.06026	0.04428	0.50166
N2	-0.05628	0.04159	-0.01519
N3	0.4562[illegible]	0.19854	-0.02296
N4	0.55285	0.30211	0.01749
C11	0.21707	0.06963	0.53744
C12	0.10123	0.18071	0.65406
C13	0.10234	0.17006	0.38285
C21	-0.21391	0.06500	-0.10688
C22	-0.09749	0.17450	-0.17873
C23	-0.11672	0.17306	0.08354
C31	0.43[illegible]92	0.06070	-0.14702
C32	0.41877	0.07058	0.10554
C33	0.28692	0.15856	-0.08637
C41	0.58637	0.44001	0.13905
C42	0.71947	0.34681	0.07599
C43	0.58749	0.43312	-0.11744

TABLE B.2

Anisotropic Temperature Factors For $(Cl_2TiNSiMe_3)_2$

ATOM	B11	B22	B33	B23	B13	B12
Ti1	2.30586	1.44557	0.[illegible]6275	0.08487	0.19187	0.14560
Ti2	3.57795	1.84979	0.43900	0.29712	0.40573	-0.13582
Ti3A	3.13204	3.65687	5.68244	-0.44226	1.28672	0.13561
Ti3B	6.39529	7.43527	6.64471	0.62507	1.95734	0.12216
Ti4A	3.87807	3.65393	4.30030	0.10678	1.84457	0.73303
Ti4B	5.21633	5.04823	7.49475	0.23168	1.63854	-0.26023
Cl11	3.34168	4.49041	1.95713	0.02031	0.17973	-0.55026
Cl12	4.80036	3.46623	5.61379	0.18353	2.01141	1.35441
Cl21	2.84928	3.96721	0.82784	-0.50014	0.54571	[illegible].43292
Cl22	4.64259	3.07371	5.09114	-1.21362	0.41665	-1.45571
Cl31	8.10659	6.53103	12.05634	2.64995	2.32113	3.24261
Cl3A	3.21439	6.69321	3.54101	1.26648	0.44591	1.02689
Cl3B	3.42023	8.59392	5.37334	1.48435	1.04672	1.77770
Cl41	5.94369	6.32426	14.64266	-1.36812	2.01665	2.34073
Cl4A	3.21149	6.16062	4.05711	-1.12480	1.37249	[illegible].22091
Cl4B	4.55332	8.89584	6.71233	0.80074	1.96549	-0.33160
Si3	5.31454	7.10835	8.18364	-1.54814	2.35321	-1.25516
Si4	8.22118	4.26413	7.17694	0.63296	1.23873	-2.24067
N1	7.84964	5.57020	4.68503	-0.01078	1.51757	2.01003
N2	9.29307	6.07373	6.22180	2.54470	1.63013	-2.06737

Isotropic Temperature Factors For $(Cl_2TiNSiMe_3)_2$

ATOM	B
Si1	2.06603
Si2	3.07715
N3	0.18210
N4	1.29538
C11	6.00107
C12	3.52850
C13	4.16039
C21	8.59986
C22	1.47634
C23	3.94993
C31	9.09801
C32	6.74023
C33	5.73052
C41	7.59691
C42	2.16482
C43	5.81488

TABLE B.3

Internuclear Distances In $(Cl_2TiNSiMe_3)_2$

Ordered chain		Disordered chain	
	Distance(Å)(σ)		Distance(Å)(σ)
Ti1-Cl11	2.501(10)	Ti3A-Cl31	2.365(18)
Ti1-Cl12	2.209(10)	Ti3A-Cl3A	2.531(23)
Ti1-Cl21	2.427(9)	Ti3A-Cl4B	2.432(29)
Ti1-N1	1.942(32)	Ti3A-N3	1.895(23)
Ti1-N'1	1.834(33)	Ti3A-N4	1.736(24)
Ti2-Cl11	2.452(11)	Ti3B-Cl31	2.468(21)
Ti2-Cl21	2.449(10)	Ti4A-Cl41	2.414(19)
Ti2-Cl22	2.217(10)	Ti4A-Cl3B	2.411(25)
Ti2-N2	1.986(36)	Ti4A-N3	1.978(22)
Ti2-N'2	1.686(31)	Ti4A-N4	1.914(25)
Si1-N1	1.782(34)	Ti4B-Cl41	2.287(20)
Si2-N2	1.861(38)	Ti4B-Cl4A	2.419(27)
Si1-C11	1.930(46)	Ti4B-N3	1.976(24)
Si1-C12	1.960(40)	Ti4B-N4	1.844(27)
Si1-C13	1.861(39)	Si3-N3	1.712(32)
Si2-C21	1.893(57)	Si4-N4	1.809(33)
Si2-C22	1.926(32)	Si3-C31	1.812(72
Si2-C23	1.806(42)	Si3-C32	1.897(50)
		Si3-C33	1.999(45)
		Si4-C41	1.777(55)
		Si4-C42	1.900(31)
		Si4-C43	1.903(43)

TABLE B .4

Bond Angles In $(Cl_2TiNSiMe_3)_2$

Ordered chain.	Angle°(σ)	Disordered chain.	Angle°(σ)
Cl11-Ti1-Cl12	90.38(38)	Cl3A-Ti3A-Cl31	95.22(80)
Cl12-Ti1-Cl21	137.32(41)	Cl31-Ti3A-Cl4B	143.61(98)
Cl11-Ti1-Cl21	79.21(32)	Cl3A-Ti3A-Cl4B	73.17(78)
Cl12-Ti1-N1	106.26(104)	Cl31-Ti3A-N3	102.98(94)
Cl11-Ti1-N1	159.18(101)	Cl31-Ti3A-N4	95.03(100)
Cl21-Ti1-N1	80.06(99)	Cl3A-Ti3A-N3	98.34(91)
N1-Ti1-N'1	87.6 (20)	Cl3A-Ti3A-N4	165.37(113)
Cl11-Ti2-Cl22	89.56(37)	Cl4B-Ti3A-N3	108.32(101)
Cl21-Ti2-Cl22	137.33(41)	Cl4B-Ti3A-N4	87.65(100)
Cl11-Ti2-Cl21	78.75(31)	N3-Ti3A-N4	89.43(108)
Cl22-Ti2-N2	103.81(106)	Cl41-Ti4A-Cl3B	149.61(93)
Cl11-Ti2-N2	163.66(103)	Cl41-Ti4A-N3	92.48(81)
Cl21-Ti2-N2	84.02(100)	Cl41-Ti4A-N4	103.38(97)
N2-Ti2-N'2	84.9 (25)	Cl3B-Ti4A-N3	87.09(84)
Ti1-N1-Si1	126.9 (19)	Cl3B-Ti4A-N4	105.64(101)
Ti'1-N1-Ti1	92.5 (18)	N3-Ti4A-N4	82.10(96)
Ti2-N2-Si2	122.3 (15)	Cl31-Ti3B-N3	102.38(99)
Ti'2-N2-Si2	141.3 (22)	Cl31-Ti3B-N4	87.54(98)
Ti2-N2-Ti'2	95.1 (18)	N3-Ti3B-N4	87.35(115)
N1-Si1-C11	97.2 (18)	Cl41-Ti4B-Cl4A	95.50(82)
N1-Si1-C12	109.8 (15)	Cl41-Ti4B-N3	96.48(97)
N1-Si1-C13	108.6 (16)	Cl41-Ti4B-N4	110.83(114)
N2-Si2-C21	94.6 (21)	Cl4A-Ti4B-N3	163.92(113)
N2-Si2-C22	109.6 (13)	Cl4A-Ti4B-N4	101.70(106)
N2-Si2-C23	110.7 (17)	N3-Ti4B-N4	83.98(110)
C11-Si1-C12	120.1 (18)	Ti3A-N3-Ti4A	90.62(90)
C11-Si1-C13	107.0 (19)	Ti3B-N3-Ti4B	93.39(105)
C12-Si1-C13	112.7 (16)	Ti3A-N3-Si3	137.9 (13)
C21-Si2-C22	107.1 (20)	Ti3B-N3-Si3	133.2 (14)
C21-Si2-C23	118.4 (22)	Ti4A-N3-Si3	131.5 (12)
C22-Si2-C23	114.6 (16)	Ti4B-N3-Si3	132.5 (13)
		Ti3A-N4-Ti4A	97.84(113)
		Ti3B-N4-Ti4B	93.95(117)
		Ti3A-N4-Si4	132.6 (14)
		Ti3B-N4-Si4	132.2 (14)
		Ti4A-N4-Si4	129.4 (14)
		Ti4B-N4-Si4	133.3 (14)
		N3-Si3-C31	110.0 (24)
		N3-Si3-C32	107.1 (17)
		N3-Si3-C33	108.8 (16)
		N4-Si4-C41	108.0 (19)
		N4-Si4-C42	108.4 (13)
		N4-Si4-C43	106.1 (17)
		C31-Si3-C32	102.0 (28)
		C31-Si3-C33	117.1 (27)
		C32-Si3-C33	111.4 (20)
		C41-Si4-C42	114.2(20)
		C41-Si4-C43	104.1 (22)
		C42-Si4-C43	115.5 (18)

TABLE B.5

Comparison of observed and calculated Fs for $(Cl_2TiNSiMe_3)_2$

* H= 0	K= 1		
6	190	131	7
7	279	288	8
8	131	170	9
* H= 0	K= 2		
5	490	407	6
* H= 0	K= 3		
2	655	646	3
4	382	337	5
* H= 0	K= 4		
2	1894	1935	3
4	494	363	5
6	615	614	7
* H= 0	K= 5		
2	367	358	3
4	271	212	5
6	149	169	7
* H= 0	K= 6		
1	296	270	2
5	185	258	6
* H= 0	K= 7		
2	391	393	3
4	199	150	5
5	272	301	6
* H= 0	K= 8		
0	1338	1423	1
2	237	214	3
4	729	709	5
6	240	237	7
* H= 0	K= 9		
2	711	684	3
4	510	482	5
* H= 0	K= 10		
5	510	508	6
7	341	304	8
* H= 0	K= 11		
2	435	439	3
3	138	163	4
4	398	318	5
* H= 0	K= 12		
0	854	845	1
2	1272	1245	3
* H= 0	K= 13		
2	239	233	3
* H= 0	K= 14		
3	150	171	4
* H= 0	K= 16		
0	272	248	1
4	524	557	5
6	368	353	7
* H= 0	K= 20		
0	413	406	1
2	304	308	3
* H= 1	K= 1		
3	371	405	4
5	242	232	6
6	194	171	7
7	180	198	8
8	221	222	9
* H= 1	K= 2		
-7	110	138	8
2	123	131	3
4	232	279	5
6	391	397	7
* H= 1	K= 3		
-4	696	705	5
-2	629	648	3
2	445	439	3
6	290	288	7
* H= 1	K= 4		
-5	293	323	6
-3	118	143	4
-1	152	171	2
1	154	152	2
3	633	561	4
5	643	649	6
7	226	201	8
* H= 1	K= 5		
-4	263	303	5
-2	448	424	3
-1	128	139	2
1	196	131	2
2	355	359	3
4	334	269	5
* H= 1	K= 6		
-6	686	716	7
-4	279	247	5
-2	1299	1109	3
0	1445	1404	1
2	233	160	3
* H= 1	K= 7		
-6	374	336	7
-5	142	166	6
-2	389	353	3
-1	142	66	2
2	576	476	3
3	121	146	4
4	369	346	5
* H= 1	K= 8		
-5	298	296	6
-1	212	201	2
5	591	589	6
7	435	446	8
* H= 1	K= 9		
-5	255	263	6
-4	395	364	5
-2	540	518	3
2	464	471	3
4	278	226	5
5	142	64	6
6	163	164	7
* H= 1	K= 10		
-6	216	199	7
-4	440	435	5
-2	478	524	3
0	166	164	1
2	586	613	3
4	190	152	5
* H= 1	K= 11		
-4	548	558	5
-2	489	491	3
2	558	521	3
3	122	119	4
4	230	209	5
6	245	239	7
8	339	296	9
* H= 1	K= 12		
-3	172	161	4
-1	176	208	2
1	153	158	2
3	154	223	4
7	247	207	8
* H= 1	K= 13		
-2	246	132	3
2	253	255	3
3	298	297	4
7	250	260	8
* H= 1	K= 14		
-4	456	472	5
-2	626	641	3
0	558	556	1
2	344	372	3
4	337	321	5
6	298	328	7
* H= 1	K= 15		
-6	172	152	7
7	206	255	8
* H= 1	K= 18		
-6	284	271	7
-4	474	461	5
0	147	88	1
* H= 2	K= 0		
2	395	327	3
4	1172	1317	5
6	575	611	7
8	391	436	9
* H= 2	K= 1		
3	689	722	4
4	176	154	5
6	299	306	7
7	160	162	8
8	250	273	9
* H= 2	K= 2		
3	252	144	4
5	379	354	6
7	373	365	8
* H= 2	K= 3		
-4	647	661	5
-2	573	535	3
-1	280	222	2
1	294	256	2
2	156	135	3
3	294	306	4
5	193	131	6
6	321	290	7
8	230	205	9
* H= 2	K= 4		
-4	751	709	5
-2	1041	1120	3
0	1338	1314	1

TABLE B.5 (continued)

```
   2  1038  1007  3     -6   254   254  7      5   769   812  6
   4   276   257  5     -3   169   125  4      7   417   449  8
   6   387   396  7      2   272   303  3   * H=   3   K=  5
 * H=   2   K=  5        3   170   162  4     -5   116    84  6
  -2   275   246  3      4   211   193  5     -4   259   265  5
  -1   193   161  2      7   231   255  8     -2   274   227  3
   2   445   441  3   * H=   2   K= 14         0   131   125  1
   3   212   198  4     -1   159   188  2      2   453   458  3
   4   459   425  5      1   232   259  2      3   571   544  4
   5   117   139  6      3   180   161  4      4   398   408  5
   6   172   179  7   * H=   2   K= 15         5   133   116  6
 * H=   2   K=  6       -6   187   223  7      7   201   157  8
  -5   238   209  6      3   139   168  4   * H=   3   K=  6
   3   198   179  4      7   269   321  8     -2   176   173  3
   5   479   518  6   * H=   2   K= 16         0   477   487  1
   7   506   486  8     -6   377   379  7      2   415   419  3
 * H=   2   K=  7       -4   680   670  5      4   157   208  5
  -2   340   308  3      0   205   217  1   * H=   3   K=  7
  -1   223   200  2      2   323   289  3     -6   487   465  7
   1   133   106  2   * H=   2   K= 19        -4   339   353  5
   2   537   481  3      3   165   177  4     -2   567   496  3
   3   162   193  4   * H=   2   K= 20        -1   118    94  2
   4   510   505  5     -4   229   209  5      2   532   514  3
   6   150   165  7     -2   209   224  3      3   343   310  4
 * H=   2   K=  8        0   190   206  1      4   540   568  5
  -6   150   205  7      4   231   220  5      5   176   167  6
  -4  1139  1151  5   * H=   3   K=  0      * H=   3   K=  8
  -2   125   147  3      4   117    61  5     -4   158   122  5
   0   229   269  1   * H=   3   K=  1        -3   174   151  4
   2   595   495  3     -3   257   264  4      1   277   214  2
   4   656   864  5     -2   117    62  3      3   291   324  4
   6   323   276  7      1   246   214  2      5   614   602  6
 * H=   2   K=  9        2   120   157  3      7   393   372  8
  -4   711   726  5      3   893   696  4   * H=   3   K=  9
  -2   621   577  3      4   186   180  5     -4   376   387  5
  -1   184   171  2      5   295   273  6     -2   444   411  3
   2   454   419  3      6   190   199  7      0   135   134  1
   6   297   296  7      7   163   145  8      5   341   327  6
   8   217   207  9   * H=   3   K=  2         6   176   199  7
 * H=   2   K= 10       -4   160   102  5   * H=   3   K= 10
  -4   169   203  5     -2   244   264  3     -6   176   177  7
  -3   324   301  4      0  1039  1016  1     -4   212   227  5
  -1   525   542  2      2   717   689  3     -2   348   321  3
   1   553   516  2      3    98    64  4      0   512   522  1
   3   389   413  4      4   647   644  5      2   373   278  3
   5   625   645  6   * H=   3   K=  3         4   219   216  5
   7   398   309  8     -4   348   357  5      6   197   148  7
 * H=   2   K= 11       -2   236   233  3   * H=   3   K= 11
  -4   449   430  5     -1   291   239  2     -4   435   472  5
  -2   444   411  3      0   138   139  1     -3   135   130  4
   2   167   193  3      3   680   659  4     -2   192   246  3
   6   269   315  7      4   146   134  5      1   241   236  2
   7   239   253  8      5   183   199  6      5   169   170  6
 * H=   2   K= 12        6   216   212  7      6   201   350  7
  -6   278   279  7   * H=   3   K=  4         7   241   259  8
  -2   983   974  3     -5   409   426  6   * H=   3   K= 12
   0   476   487  1     -3   731   667  4     -1   391   348  2
   4   392   383  5     -1   877   792  2      1   422   425  2
   6   446   470  7      1  1011   905  2      4   196   144  5
 * H=   2   K= 13        3   594   600  4      5   282   310  6
```

TABLE B.5 (continued)

7	277	241	8	3	731	656	4	-3	194	125	4
* H=	3	K= 13		4	312	291	5	-2	245	259	3
-3	239	256	4	* H=	4	K= 6		1	344	354	2
1	167	181	2	-5	169	219	6	7	252	254	8
2	144	220	3	-3	237	190	4	* H=	4	K= 14	
7	397	384	8	-2	177	112	3	-1	218	224	2
* H=	3	K= 14		1	367	405	2	1	397	349	2
-4	333	364	5	3	356	354	4	5	299	224	6
-2	194	186	3	5	885	906	6	* H=	4	K= 15	
0	239	239	1	7	642	664	8	1	151	234	2
* H=	3	K= 15		* H=	4	K= 7		3	174	177	4
4	215	217	5	-5	176	171	6	5	194	220	6
* H=	3	K= 16		-4	377	376	5	* H=	4	K= 16	
-3	144	171	4	-3	195	217	4	-6	249	257	7
1	238	213	2	-2	511	474	3	-2	313	322	3
* H=	3	K= 17		1	260	197	2	0	749	759	1
3	188	185	4	2	253	247	3	2	441	445	3
5	222	203	6	3	436	437	4	* H=	4	K= 20	
* H=	3	K= 18		4	287	340	5	-4	246	224	5
-6	325	293	7	5	311	289	6	2	277	232	3
-4	360	357	5	* H=	4	K= 8		* H=	5	K= 0	
-2	153	127	3	-6	240	243	7	-4	161	145	5
0	395	361	1	-4	358	313	5	* H=	5	K= 1	
* H=	4	K= 0		-2	692	659	3	-5	220	199	6
-4	752	827	5	0	1169	1139	1	-3	624	633	4
-2	446	512	3	2	590	608	3	1	370	217	2
0	1548	1593	1	4	751	767	5	2	178	165	3
2	568	681	3	8	173	138	9	3	619	767	4
4	573	588	5	* H=	4	K= 9		5	248	283	6
6	237	314	7	-4	300	310	5	* H=	5	K= 2	
* H=	4	K= 1		-2	227	202	3	-4	759	775	5
-5	252	232	6	0	151	163	1	-3	279	112	4
-4	136	146	5	1	227	218	2	-2	621	576	3
-3	694	727	4	3	187	218	4	0	653	545	1
-1	145	129	2	5	167	185	6	3	161	114	4
2	121	123	3	6	154	169	7	4	151	180	5
3	902	865	4	* H=	4	K= 10		* H=	5	K= 3	
5	368	339	6	-7	297	279	8	-5	258	265	6
6	120	100	7	-5	497	505	6	-4	164	130	5
* H=	4	K= 2		-3	272	304	4	-3	577	525	4
-5	337	339	6	-1	571	536	2	-2	207	244	3
-3	456	394	4	1	706	676	2	2	165	177	3
-1	360	275	2	3	165	155	4	3	1096	976	4
3	351	379	4	5	348	353	6	8	223	215	9
5	332	366	6	* H=	4	K= 11		* H=	5	K= 4	
* H=	4	K= 3		-3	126	155	4	-5	691	564	6
-3	195	213	4	-2	146	162	3	-3	368	361	4
0	130	149	1	-1	238	267	2	-2	155	147	3
3	982	932	4	1	247	225	2	-1	270	314	2
5	222	197	6	5	222	236	6	3	443	495	4
* H=	4	K= 4		7	243	287	8	5	593	696	6
-2	1579	1626	3	* H=	4	K= 12		6	294	73	7
0	1839	1868	1	-6	169	80	7	7	346	365	8
2	1512	1536	3	-4	319	306	5	* H=	5	K= 5	
4	275	254	5	-2	426	404	3	-4	248	276	5
* H=	4	K= 5		0	263	274	1	-3	459	457	4
-4	343	319	5	2	672	633	3	-2	215	215	3
-2	694	637	3	4	389	365	5	-1	292	266	2
1	199	245	2	* H=	4	K= 13		0	197	112	1
2	281	289	3	-4	271	315	5	1	181	91	2

TABLE B.5 (continued)

2	158	117	3	* H=	5	K= 15		2	264	263	3
3	810	777	4	-4	227	246	5	3	172	191	4
5	148	133	6	-2	161	180	3	4	236	225	5
* H=	5	K= 6		1	237	275	2	6	199	213	7
-6	179	174	7	3	146	186	4	8	207	247	9
-2	434	413	3	6	177	160	7	* H=	6	K= 5	
0	452	402	1	* H=	5	K= 16		-6	174	227	7
3	119	117	4	-5	181	77	6	-5	372	398	6
* H=	5	K= 7		1	246	246	2	-4	391	420	5
-5	175	144	6	3	132	140	4	-3	556	525	4
-4	430	433	5	* H=	5	K= 17		-2	467	513	3
-3	185	239	4	-3	179	127	4	1	204	204	2
-2	483	465	3	-1	286	232	2	3	541	426	4
-1	151	106	2	1	283	279	2	4	213	204	5
0	166	190	1	3	192	213	4	* H=	6	K= 6	
1	347	348	2	* H=	5	K= 18		-5	814	820	6
2	143	124	3	-6	216	219	7	-4	172	132	5
3	321	306	4	0	241	254	1	-3	407	401	4
5	173	192	6	* H=	6	K= 0		-2	192	197	3
* H=	5	K= 8		-8	287	315	9	-1	443	433	2
-5	700	692	6	-6	714	782	7	1	504	562	2
-3	274	232	4	-4	979	1023	5	3	352	395	4
-1	518	551	2	-2	554	625	3	5	723	822	6
0	131	135	1	0	1103	1101	1	7	335	346	8
1	788	796	2	2	336	313	3	* H=	6	K= 7	
3	171	172	4	4	526	585	5	-6	154	146	7
5	617	663	6	6	434	432	7	-4	523	505	5
7	298	327	8	* H=	6	K= 1		-3	474	506	4
* H=	5	K= 9		-7	154	95	8	-2	349	350	3
-6	140	89	7	-6	381	436	7	-1	375	373	2
-4	196	206	5	-4	366	386	5	1	125	93	2
-3	197	238	4	-3	657	630	4	2	164	163	3
-2	245	210	3	-1	391	268	2	3	271	262	4
-1	318	352	2	3	704	643	4	5	146	208	6
1	276	244	2	6	179	196	7	* H=	6	K= 8	
3	138	131	4	7	192	247	8	-6	200	269	7
5	294	266	6	8	228	256	9	-4	944	986	5
* H=	5	K= 10		* H=	6	K= 2		-3	158	149	4
-4	160	126	5	-6	165	172	7	-2	585	586	3
0	279	291	1	-5	199	165	6	-1	142	41	2
4	172	122	5	-4	136	165	5	4	399	400	5
* H=	5	K= 11		-3	137	108	4	6	378	351	7
-6	154	163	7	3	164	166	4	8	173	167	9
-5	147	199	6	5	156	125	6	* H=	6	K= 9	
-2	179	160	3	* H=	6	K= 3		-6	235	247	7
1	375	335	2	-6	286	269	7	-5	394	304	6
7	199	211	8	-5	190	167	6	-4	192	200	5
8	269	262	9	-4	142	110	5	-1	159	116	2
* H=	5	K= 12		-3	932	908	4	1	351	343	2
-1	309	309	2	3	767	761	4	7	294	44	8
1	450	415	2	6	273	250	7	8	233	254	9
5	409	358	6	7	307	252	8	* H=	6	K= 10	
* H=	5	K= 13		8	244	241	9	-7	146	184	8
-5	186	173	6	* H=	6	K= 4		-6	170	67	7
-3	169	187	4	-6	318	316	7	-5	442	445	6
-1	335	342	2	-5	116	68	6	-1	628	582	2
1	262	264	2	-4	334	322	5	1	539	535	2
* H=	5	K= 14		-3	267	181	4	5	294	339	6
-6	272	304	7	-2	1086	1142	3	7	191	217	8
-2	149	155	3	0	635	609	1	* H=	6	K= 11	

TABLE B.5 (continued)

```
   -6   296   280  7      -6   157   159  7       0   276   276  1
   -1   492   401  2      -5   350   408  6       2   192   188  3
    0   144   156  1      -4   174   187  5       4   179   160  5
    1   284   216  2      -3   754   761  4       6   185   164  7
    6   215   201  7       3   466   491  4   * H=   7    K= 11
* H=    6    K= 12         4   183   195  5      -5   242   257  6
   -6   461   461  7       6   234   234  7      -1   137   131  2
   -4   595   590  5       7   286   262  8       1   149   168  2
   -2   636   617  3       8   274   252  9       6   213   217  7
    0   188   171  1   * H=   7    K=  4          8   294   299  9
    4   213   216  5      -5   655   664  6   * H=   7    K= 12
    6   299   212  7      -3   311   299  4      -5   340   328  6
* H=    6    K= 13         1   183   167  2      -3   148   150  4
   -6   196   188  7       5   310   262  6      -1   380   363  2
   -5   273   184  6       7   271   241  8       1   364   406  2
   -4   246   266  5   * H=   7    K=  5          5   241   233  6
   -2   259   250  3      -6   125   131  7   * H=   7    K= 13
   -1   155   149  2      -3   806   819  4      -7   237   199  8
    1   256   258  2      -2   142   130  3      -1   273   294  2
* H=    6    K= 14        -1   170   209  2       2   164   164  3
   -5   241   223  6       2   289   294  3       3   140   163  4
   -1   298   196  2       3   257   291  4       4   299   226  5
    1   242   262  2       4   254   272  5   * H=   7    K= 14
    5   218   189  6       7   297   238  8      -6   194   216  7
* H=    6    K= 15    * H=   7    K=  6         -1   158    91  2
   -2   154   170  3      -3   262   201  4       2   184   190  3
   -1   341   340  2      -2   125   132  3       4   240   210  5
    1   258   273  2       2   220   239  3   * H=   7    K= 15
    3   190   221  4       6   295   220  7      -6   256   246  7
* H=    6    K= 16    * H=   7    K=  7         -3   141   155  4
   -2   324   287  3      -6   165   149  7       1   218   224  2
    0   274   242  1      -5   434   372  6       3   196   219  4
* H=    6    K= 17        -3   311   324  4       4   292   216  5
   -3   144   177  4       1   219   237  2   * H=   7    K= 17
    1   165   201  2       2   365   322  3      -3   210   242  4
    3   156   218  4       3   133    47  4      -1   230   268  2
* H=    6    K= 19         4   413   445  5       3   146   222  4
    3   138   124  4       8   388   152  9   * H=   7    K= 18
* H=    7    K=  0    * H=   7    K=  8          0   148   140  1
   -4   113    91  5      -7   381   384  8   * H=   7    K= 20
* H=    7    K=  1        -5   659   667  6       1   197   146  2
   -5   232   252  6      -3   156   106  4   * H=   8    K=  0
   -3   868   816  4      -1   726   724  2      -8   235   286  9
    3   409   470  4       1   598   550  2      -6   352   404  7
    4   248   212  5       2   132    70  3       0   551   514  1
    5   149   137  6       3   226   278  4       2   749   725  3
    6   259   270  7       4   199    66  5       4   435   463  5
    7   261   278  8       5   499   527  6       6   715   779  7
* H=    7    K=  2         7   184   195  8       8   310   293  9
   -5   129   223  6   * H=   7    K=  9      * H=   8    K=  1
   -4   420   450  5      -7   393   325  8      -8   190   274  9
   -3   396   114  4      -6   148   108  7      -6   198   201  7
   -2   296   217  3      -3   197   207  4      -5   377   389  6
    0   158    68  1      -1   386   419  2      -3   574   523  4
    2   381   368  3       0   163   169  1      -1   164   164  2
    3   152   138  4       6   219   266  7       1   231   203  2
    4   166   163  5       8   191   206  9       3   274   252  4
    6   363   368  7   * H=   7    K= 10          5   224   166  6
    8   242   263  9      -2   142   140  3       7   235   261  8
* H=    7    K=  3        -1   165    94  2   * H=   8    K=  2
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TABLE B.5 (continued)

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  -8   153   145  9     -5   275   291  6     -2   152    68  3
  -5   228   269  6     -1   306   290  2     -1   327   317  2
  -3   305   325  4      1   251   224  2      1   290   256  2
  -1   333   371  2      5   293   329  6      5   152   139  6
   1   388   468  2      7   264   277  8   * H=   9   K=  5
   3   113   103  4   * H=   8   K= 11        -7   243   247  8
   5   244   294  6     -7   279   319  8     -5   175   194  6
   7   243   275  8     -4   163   131  5     -3   379   400  4
 * H=   8   K=  3       -1   210   210  2      0   308   306  1
  -3   667   886  4      3   154   144  4      1   344   337  2
  -2   163   125  3   * H=   8   K= 12         2   321   276  3
   0   149   129  1     -2   174   175  3      4   250   234  5
   1   205   285  2      0   252   231  1      6   196   176  7
   3   200   242  4      2   373   330  3   * H=   9   K=  6
   6   217   213  7      4   499   484  5     -7   151   213  8
   7   238   206  8   * H=   8   K= 13        -3   170   217  4
 * H=   8   K=  4       -5   180   212  6     -2   156   139  3
  -3   374   188  4      3   143   181  4      0   376   322  1
  -2   686   669  3      4   255   228  5      6   588   590  7
   0  1174  1174  1   * H=   8   K= 14      * H=   9   K=  7
   2  1031  1027  3     -5   242   268  6     -5   357   373  6
   4   521   495  5     -1   253   317  2     -4   161   162  5
   6   309   329  7      1   227   264  2     -2   166   205  3
   8   284   297  9      2   141    30  3     -1   177   176  2
 * H=   8   K=  5    * H=   8   K= 15         2   450   380  3
  -6   142   112  7     -7   291   276  8      4   344   317  5
  -5   311   293  6     -5   181   165  6      6   308   365  7
  -3   462   483  4     -3   179   220  4   * H=   9   K=  8
  -2   154   186  3     -1   273   262  2     -7   284   263  8
  -1   178   204  2      3   274   252  4     -5   573   546  6
   2   218   195  3   * H=   8   K= 16        -3   274   251  4
   4   303   264  5     -2   163   194  3     -1   378   357  2
   8   214   177  9      0   417   411  1      1   344   342  2
 * H=   8   K=  6        2   352   342  3   * H=   9   K=  9
  -7   564   560  8   * H=   8   K= 20        -4   214   157  5
  -5   848   857  6     -2   172   143  3     -2   242   221  3
  -3   307   325  4   * H=   9   K=  1         1   139   144  2
  -1   619   591  2     -7   133   120  8      4   216   188  5
   1   513   504  2     -5   145   105  6      6   170   110  7
   5   196   199  6     -3   499   523  4   * H=   9   K= 10
 * H=   8   K=  7       -1   270   251  2     -4   237   244  5
  -7   296   311  8      1   445   424  2     -2   378   343  3
  -3   287   300  4      2   174   141  3      0   187   246  1
  -2   163   139  3      3   152   174  4      2   282   200  3
  -1   204   230  2   * H=   9   K=  2         4   279   276  5
   1   227   198  2     -6   143    99  7   * H=   9   K= 11
   2   230   225  3     -3   278   240  4     -5   207   173  6
   4   291   358  5     -2   196   200  3      1   135    73  2
 * H=   8   K=  8        0   728   718  1   * H=   9   K= 12
  -2   521   507  3      1   133   182  2     -7   196   105  8
   0   821   826  1      6   579   605  7     -5   341   329  6
   2   701   705  3      8   313   316  9     -1   337   362  2
   4   383   375  5   * H=   9   K=  3         1   353   324  2
   6   452   445  7     -3   446   477  4   * H=   9   K= 13
 * H=   8   K=  9       -2   125   143  3     -7   342   332  8
  -5   367   331  6     -1   341   308  2      3   213   243  4
   2   178   163  3      0   268   311  1      4   254   241  5
   6   194   131  7   * H=   9   K=  4      * H=   9   K= 14
   8   210   235  9     -7   374   437  8     -7   207   201  8
 * H=   8   K= 10       -5   426   427  6     -3   133    87  4
```

TABLE B.5 (continued)

```
   2   165   170  3      -5   440   454  6      -3   160   213  4
   4   198   192  5      -4   245   128  5      -1   190   192  2
* H=  9   K= 15          -2   161    98  3       0   392   417  1
  -5   187   108  6      -1   406   401  2       1   193   231  2
* H=  9   K= 16           1   380   365  2       4   291   230  5
  -3   195    81  4    * H= 10   K=  7         * H= 11   K=  2
* H=  9   K= 17          -4   424   396  5      -7   192   160  8
  -5   222   196  6      -2   461   458  3      -6   241   226  7
  -3   204   233  4       1   226   274  2      -5   167   243  6
* H= 10   K=  0           6   240   233  7       0  1213  1223  1
  -6   345   366  7    * H= 10   K=  8           6   395   412  7
  -4   619   604  5      -6   278   269  7    * H= 11   K=  3
  -2   668   670  3      -4   518   616  5      -6   297   244  7
   0   382   348  1      -2   805   634  3      -2   144   133  3
   4   435   475  5       2   410   398  3      -1   197   191  2
   6   393   443  7       4   275   258  5       0   345   336  1
   8   256   260  9    * H= 10   K=  9           2   390   319  3
* H= 10   K=  1          -6   228   190  7       4   337   327  5
  -7   187   232  8      -5   184   209  6       6   192   181  7
  -6   247   274  7       2   284   267  3    * H= 11   K=  4
  -4   281   313  5    * H= 10   K= 10          -7   190   262  8
  -3   238   245  4      -7   215   241  8      -5   255   278  6
  -2   148   155  3      -5   326   411  6      -4   156    74  5
  -1   399   399  2      -1   182   158  2      -2   139    79  3
   0   215   265  1       1   236   263  2       1   273   272  2
   1   220   228  2       3   147   168  4       2   146    56  3
   6   175   186  7    * H= 10   K= 11           5   179   190  6
* H= 10   K=  2          -7   232   267  8    * H= 11   K=  5
  -6   133    57  7      -6   209   220  7      -5   241   272  6
  -5   254   254  6      -5   172   115  6      -2   321   315  3
  -3   208   222  4       2   157   139  3       0   193   166  1
* H= 10   K=  3           3   137   144  4       1   160   145  2
  -6   209   175  7       4   306   283  5       6   262   243  7
  -5   244   304  6    * H= 10   K= 12        * H= 11   K=  6
  -4   196   205  5      -7   229   173  8      -6   162   170  7
  -3   230   258  4      -6   243   216  7      -2   231   203  3
  -1   154   149  2      -4   374   347  5       0   377   286  1
   0   387   377  1       0   138    90  1       2   395   405  3
   1   390   304  2       2   219   229  3       6   277   293  7
   2   152   140  3       4   257   242  5    * H= 11   K=  7
   4   247   231  5    * H= 10   K= 13          -7   172   219  8
* H= 10   K=  4          -4   216   203  5      -4   270   235  5
  -6   262   255  7      -3   132   183  4      -1   155   163  2
  -5   144    87  6      -2   173   208  3       2   264   226  3
  -4   514   510  5       2   161   166  3       6   215   196  7
  -2   717   720  3    * H= 10   K= 14        * H= 11   K=  8
   0  1309  1279  1      -1   142   145  2      -7   148   183  8
   2   179   137  3    * H= 10   K= 15          -5   375   340  6
   6   719   701  7      -3   285   282  4      -1   167   154  2
* H= 10   K=  5          -2   218   206  3       1   291   208  2
  -6   164   157  7    * H= 10   K= 16        * H= 11   K=  9
  -5   146    76  6      -2   435   363  3      -5   285   202  6
  -4   352   312  5       0   365   310  1      -2   352   362  3
  -2   495   422  3       2   253   232  3       0   136   112  1
  -1   261   255  2       4   361   323  5       1   141   161  2
   0   208   236  1    * H= 10   K= 19           2   297   262  3
   2   350   337  3      -3   136   129  4       4   282   339  5
   8   260   290  9    * H= 11   K=  1        * H= 11   K= 10
* H= 10   K=  6          -7   248   336  8      -5   176   293  6
  -7   332   356  8      -5   194   161  6      -2   344   357  3
```

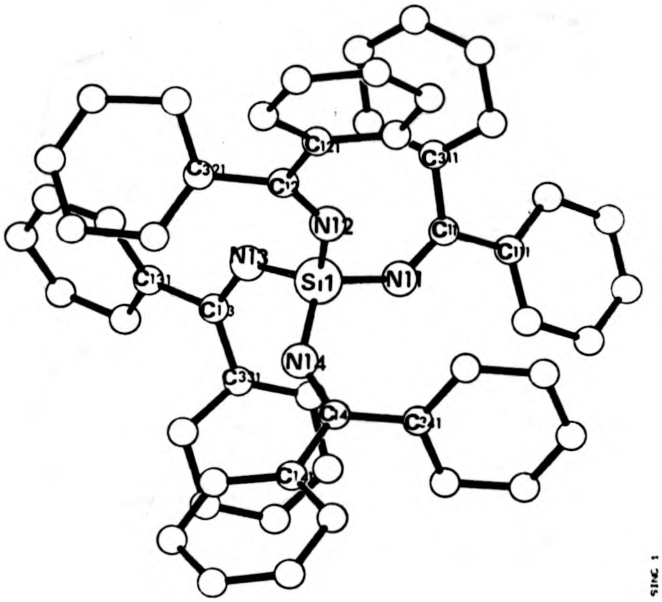
TABLE B.5 (continued)

```
    0   198   183  1     -4   184   217  5     -6   492   448  7
    4   310   285  5     -2   349   363  3     -2   399   309  3
 * H= 11    K= 11         0   157   121  1      0   291   271  1
   -6   167   176  7      2   173   138  3   * H= 13    K=  7
   -2   158   163  3   * H= 12    K=  8        -6   214   219  7
    2   392   366  3     -6   338   308  7     -4   218   176  5
    4   210   254  5     -5   173   111  6      0   146   176  1
 * H= 11    K= 12        -2   261   238  3   * H= 13    K=  8
   -5   265   248  6      0   585   605  1     -5   187   174  6
   -2   142    42  3      2   214   185  3   * H= 13    K=  9
 * H= 11    K= 13         4   269   274  5     -8   173   213  9
   -3   217   236  4   * H= 12    K=  9        -5   292   191  6
   -2   262   256  3     -6   232   257  7     -2   189   248  3
 * H= 11    K= 14         2   293   314  3      2   248   391  3
   -3   161   113  4   * H= 12    K= 10     * H= 13    K= 10
   -2   349   326  3     -5   383   347  6     -4   297   262  5
    0   219   178  1     -2   299    39  3     -2   175   156  3
    2   335   385  3      2   182    50  3      6   187   116  7
 * H= 11    K= 18      * H= 12    K= 11     * H= 13    K= 11
   -4   216   198  5     -2   326   314  3     -4   243   295  5
 * H= 12    K=  0         4   220   232  5      2   391   326  3
   -6   610   672  7   * H= 12    K= 12         4   295   186  5
   -4   197   219  5     -4   272   253  5   * H= 13    K= 13
   -2   215   234  3     -3   129    65  4     -2   291   255  3
    0  1595  1466  1     -2   402   423  3      0   185   133  1
    2   519   546  3      0   333   331  1   * H= 13    K= 14
    6   164   163  7      2   442   469  3     -2   293   395  3
 * H= 12    K=  1      * H= 12    K= 13         0   276   272  1
   -7   236   325  8     -4   259   199  5   * H= 14    K=  0
   -6   382   427  7      2   214   210  3     -6   342   279  7
    0   461   432  1   * H= 12    K= 15        -4   371   339  5
 * H= 12    K=  2        -2   211   186  3     -2   598   486  3
   -7   191   224  8   * H= 12    K= 16         0   697   710  1
   -6   158   206  7     -4   213   236  5      2   313   338  3
   -5   281   319  6     -2   194   139  3      4   399   392  5
    3   131   147  4   * H= 13    K=  1     * H= 14    K=  1
 * H= 12    K=  3        -6   256   254  7     -4   246   255  5
   -5   299   238  6      0   405   398  1     -2   290   224  3
   -2   263   282  3      2   298   226  3      0   194   196  1
    0   262   271  1   * H= 13    K=  2         3   177   245  4
    2   159   185  3     -6   464   459  7   * H= 14    K=  2
 * H= 12    K=  4         0   660   653  1     -4   292    92  5
   -6   173   199  7      4   291   261  5     -3   194   238  4
   -2   415   434  3      6   168   124  7     -2   150    51  3
    0   290   256  1   * H= 13    K=  3         5   192   147  6
    2   531   513  3     -7   186   194  8   * H= 14    K=  3
    4   415   373  5     -6   264   256  7     -6   342   313  7
    6   299   238  7     -4   182   175  5     -4   373   319  5
 * H= 12    K=  5         2   226   223  3     -2   251   265  3
   -7   168   174  8      4   265   232  5      3   172   175  4
   -4   283   276  5   * H= 13    K=  4     * H= 14    K=  4
    2   336   290  3     -4   197   129  5     -6   546   590  7
 * H= 12    K=  6        -2   156   157  3     -4   347   323  5
   -4   191   115  5     -1   152   138  2     -2   341   341  3
   -3   118   114  4      1   135   150  2      4   212   223  5
   -2   169    48  3   * H= 13    K=  5     * H= 14    K=  5
    6   261    95  7     -6   240   194  7     -6   385   309  7
 * H= 12    K=  7        -4   194   156  5   * H= 14    K=  7
   -6   272   215  7     -2   419   402  3      0   140    93  1
   -5   258   266  6   * H= 13    K=  6         2   234   274  3
```

TABLE B.5 (continued)

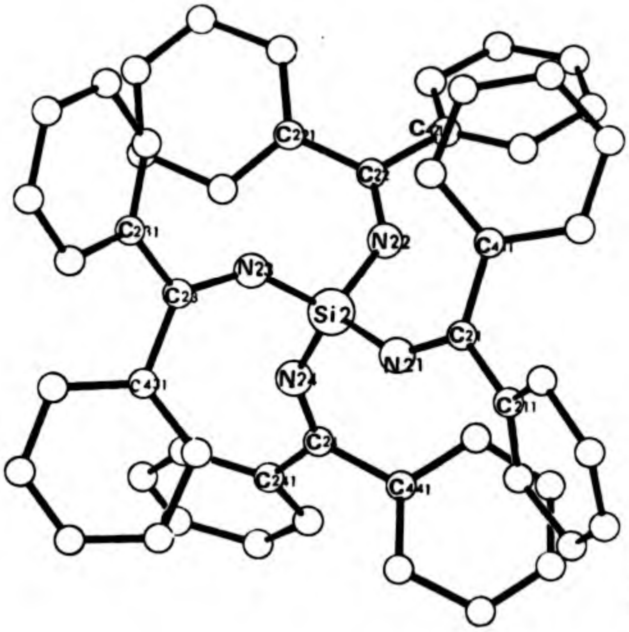
```
* H= 14   K=  8
 -4   363   312  5
 -2   288   278  3
  0   256   239  1
  2   198   185  3
* H= 14   K=  9
 -4   352   363  5
 -2   254   291  3
  2   274   200  3
* H= 14   K= 10
 -4   255   170  5
 -2   184   114  3
* H= 14   K= 11
 -2   262   310  3
  0   178   132  1
* H= 14   K= 12
 -2   413   433  3
  0   415   385  1
* H= 14   K= 14
  1   152   176  2
* H= 14   K= 16
 -4   354   319  5
* H= 15   K=  1
 -6   213   237  7
  3   257   305  4
* H= 15   K=  2
 -6   325   340  7
 -2   170   196  3
  2   203   205  3
  3   196    84  4
  4   283   235  5
* H= 15   K=  3
 -6   189   169  7
  3   195   277  4
* H= 15   K=  4
  1   139    87  2
* H= 15   K=  5
 -6   199   220  7
 -4   211   164  5
  2   243   237  3
* H= 15   K=  6
 -6   193   198  7
 -2   170   117  3
  2   178   175  3
  3   134    69  4
* H= 15   K=  7
 -6   320   241  7
 -2   310   242  3
  3   158   238  4
  4   233   219  5
* H= 15   K=  8
 -4   235   154  5
 -2   253   169  3

* H= 15   K= 10
  0   224   212  1
* H= 15   K= 11
 -4   226   247  5
  0   152   111  1
  1   172   169  2
* H= 15   K= 14
  0   157   175  1
* H= 16   K=  0
 -4   250   230  5
 -2   181   190  3
  4   366   336  5
* H= 16   K=  1
 -3   182   184  4
  3   236   340  4
* H= 16   K=  3
 -6   178   172  7
 -4   258   287  5
  3   185   192  4
* H= 16   K=  4
 -6   243   232  7
 -4   297   253  5
 -2   293   231  3
  0   163   178  1
  2   296   318  3
  3   217    58  4
* H= 16   K=  5
 -6   337   263  7
 -2   210   198  3
  3   194   214  4
* H= 16   K=  6
 -2   169    61  3
* H= 16   K=  8
  0   224   257  1
* H= 16   K=  9
 -4   193   169  5
 -2   161   191  3
* H= 16   K= 11
 -1   167   151  2
* H= 16   K= 12
  2   197   158  3
* H= 16   K= 13
  1   197   179  2
* H= 17   K=  1
 -4   229   178  5
 -3   210   274  4
  3   171   233  4
* H= 17   K=  2
 -4   265   202  5
 -3   241   124  4
  3   162   160  4
* H= 17   K=  3
 -3   162   177  4

 -2   141   147  3
  3   191   239  4
* H= 17   K=  5
 -7   184    71  8
 -4   217   164  5
 -3   172   162  4
* H= 17   K=  6
 -4   278   163  5
 -3   131    16  4
* H= 17   K=  8
  1   192   168  2
* H= 18   K=  0
 -4   378   338  5
 -2   177   136  3
  0   143   121  1
  2   146   199  3
* H= 18   K=  1
 -4   293   197  5
 -3   232   240  4
* H= 18   K=  3
 -3   175   228  4
* H= 18   K=  4
 -3   162    29  4
 -2   379   280  3
  0   274   233  1
* H= 18   K=  5
 -5   219   224  6
 -2   191   151  3
* H= 18   K=  6
 -2   148   115  3
* H= 18   K=  7
 -3   156   169  4
 -1   153   137  2
* H= 18   K=  8
 -3   206    32  4
  0   153   122  1
* H= 18   K= 10
 -1   156   186  2
* H= 19   K=  1
 -3   168   235  4
* H= 19   K=  2
 -3   214   187  4
  3   136    21  4
* H= 19   K=  3
 -5   207   210  6
* H= 19   K=  4
 -5   215   148  6
* H= 19   K=  5
 -3   178   181  4
* H= 19   K=  6
 -3   172   142  4
```

Figure B.3



$Si(NC(C_6H_5)_2)_4$: Molecule 1.

Figure B.4



Si(NC(C_6H_5)$_2$)$_4$: Molecule 2.

TABLE B.6

Final Atomic Positions For $Si(NC(C_6H_5)_2)_4$

ATOM	X	Y	Z
Si1	0.03798	0.92426	0.75150
Si2	0.46133	0.60513	0.25705
N11	-0.00677	0.93902	0.68368
N12	0.04987	0.83758	0.78711
N13	0.19807	0.93580	0.71245
N14	0.03413	0.98479	0.81804
N21	0.46275	0.68160	0.20189
N22	0.44553	0.52911	0.21423
N23	0.58085	0.58084	0.29157
N24	0.35433	0.62909	0.31873
C11	0.05814	0.00511	0.34364
C12	0.02917	0.20209	0.20223
C13	0.28131	0.89693	0.68536
C14	0.09509	1.00279	0.86163
C21	0.41834	0.70704	0.14978
C22	0.40057	0.46900	0.22352
C23	0.31649	0.41895	0.72537
C24	0.33628	0.66509	0.37566
C111	0.10850	0.01468	0.40858
C112	0.12506	0.08631	0.42582
C113	0.16593	0.09740	0.48754
C114	0.19023	0.03685	0.53202
C115	0.17366	-0.03478	0.51478
C116	0.13280	-0.04587	0.45306
H112	0.10851	0.12755	0.39553
H113	0.17721	0.14628	0.49923
H114	0.21006	0.04440	0.57405
H115	0.19021	-0.07602	0.54507
H116	0.12151	-0.09465	0.44132
C311	0.06894	0.92804	0.31735
C312	0.17216	0.88976	0.30065
C313	0.18107	0.81746	0.27719
C314	0.08678	0.78343	0.27044
C315	-0.01644	0.82170	0.28714
C316	-0.02535	0.89401	0.31060
H312	0.23638	0.91294	0.30524
H313	0.25137	0.79139	0.26531
H314	0.09285	0.73419	0.25446
H315	-0.08066	0.79853	0.28255
H316	-0.09565	0.92007	0.32198
C121	0.01282	0.27988	0.17275
C122	0.10135	0.31803	0.14411
C123	0.08311	0.39019	0.11630
C124	-0.02366	0.42420	0.11714
C125	-0.11219	0.38605	0.14573
C126	-0.09395	0.31389	0.17358
H122	0.17407	0.29487	0.14354
H123	0.14340	0.41616	0.09630
H124	-0.03609	0.47334	0.09820
H125	-0.18491	0.40921	0.14635
H126	-0.15424	0.28792	0.19309

(continued)

TABLE B.6 (continued)

ATOM	x	y	z
C321	0.14254	0.17554	0.22195
C322	0.19112	0.21594	0.26679
C323	0.29127	0.18821	0.28856
C324	0.34284	0.12008	0.26550
C325	0.29427	0.07967	0.22057
C326	0.19412	0.10740	0.19889
H322	0.15599	0.26235	0.28249
H323	0.32435	0.21573	0.31910
H324	0.41105	0.10120	0.28033
H325	0.32940	0.03327	0.20496
H326	0.16104	0.07988	0.16835
C131	0.28832	0.81423	0.68200
C132	0.37208	0.76841	0.70873
C133	0.37516	0.69124	0.70574
C134	0.29447	0.65988	0.67602
C135	0.21070	0.70570	0.64928
C136	0.20762	0.78287	0.65227
H132	0.42704	0.78976	0.72897
H133	0.43221	0.66004	0.72395
H134	0.29657	0.60733	0.67399
H135	0.15575	0.68435	0.62904
H136	0.15057	0.81407	0.63406
C331	0.37837	0.93449	0.65471
C332	0.45018	0.90094	0.60171
C333	0.53962	0.93689	0.57085
C334	0.55724	1.00640	0.59299
C335	0.48542	1.03995	0.64600
C336	0.39599	1.00400	0.67686
H332	0.43818	0.85361	0.58662
H333	0.58852	0.91404	0.53475
H334	0.61814	1.03089	0.57198
H335	0.49742	1.08729	0.66108
H336	0.34708	1.02685	0.71296
C141	0.20834	0.96575	0.86857
C142	0.22724	0.88882	0.87896
C143	0.33424	0.85532	0.87856
C144	0.42234	0.89876	0.86776
C145	0.40345	0.97569	0.85736
C146	0.29645	1.00919	0.85776
H142	0.16724	0.85924	0.88632
H143	0.34710	0.80292	0.88564
H144	0.49521	0.87594	0.86748
H145	0.46345	1.00528	0.85000
H146	0.28358	1.06159	0.85068
C341	0.05475	0.06346	0.91089
C342	-0.02889	0.11556	0.89232
C343	-0.06656	0.17534	0.93436
C344	-0.02057	0.18303	0.99499
C345	0.06308	0.13093	1.01356
C346	0.10074	0.07115	0.97151
H342	-0.06021	0.11033	0.85103
H343	-0.12352	0.21082	0.92172
H344	-0.04622	0.22374	1.02362
H345	0.09439	0.13617	1.05484
H346	0.15771	0.03567	0.98416

(continued)

TABLE B.6(continued)

ATOM	x	y	z
C211	0.45291	0.77488	0.11252
C212	0.38047	0.82848	0.08388
C213	0.42049	0.88880	0.04487
C214	0.53295	0.89551	0.03450
C215	0.60538	0.84191	0.06315
C216	0.56536	0.78160	0.10216
H212	0.30389	0.82391	0.09094
H213	0.37116	0.92530	0.02536
H214	0.56020	0.93659	0.00794
H215	0.68197	0.84648	0.05609
H216	0.61469	0.74509	0.12166
C411	0.32546	0.67199	0.12263
C412	0.24685	0.63850	0.16805
C413	0.16504	0.60412	0.14238
C414	0.16182	0.60323	0.07128
C415	0.24043	0.63672	0.02586
C416	0.32224	0.67110	0.05153
H412	0.24904	0.63910	0.21645
H413	0.11151	0.58131	0.17331
H414	0.10611	0.57982	0.05380
H415	0.23824	0.63612	-0.02255
H416	0.37577	0.69391	0.02060
C221	0.34720	0.44386	0.30368
C222	0.39887	0.45279	0.35184
C223	0.35143	0.42975	0.41701
C224	0.25231	0.39779	0.42402
C225	0.20064	0.38886	0.36586
C226	0.24808	0.41190	0.30069
H222	0.46636	0.47455	0.34707
H223	0.38662	0.43583	0.45662
H224	0.22001	0.38210	0.46841
H225	0.13314	0.36710	0.37063
H226	0.21289	0.40582	0.26108
C421	0.40261	0.41790	0.16553
C422	0.41184	0.44966	0.09874
C423	0.41675	0.40478	0.04212
C424	0.41242	0.32813	0.05229
C425	0.40319	0.29637	0.11909
C426	0.39828	0.34125	0.17570
H422	0.41479	0.50186	0.09181
H423	0.42304	0.42641	-0.00337
H424	0.41576	0.29757	0.01374
H425	0.40024	0.24417	0.12602
H426	0.39199	0.31962	0.22119
C231	0.26691	0.38460	0.79337
C232	0.28045	0.41610	0.85514
C233	0.22813	0.38925	0.91756
C234	0.16228	0.33090	0.91821
C235	0.14874	0.29940	0.85644
C236	0.20105	0.32625	0.79403
H232	0.32529	0.45584	0.85470
H233	0.23735	0.41071	0.95963
H234	0.12665	0.31261	0.96072
H235	0.10389	0.25966	0.85689
H236	0.19183	0.30480	0.75196

(continued)

TABLE B.6(continued)

ATOM	x	y	z
C431	0.23734	0.45342	0.68002
C432	0.12957	0.47654	0.70642
C433	0.05967	0.51663	0.66408
C434	0.09754	0.53360	0.59533
C435	0.20532	0.51048	0.56193
C436	0.27521	0.47039	0.61127
H432	0.10377	0.46499	0.75324
H433	-0.01372	0.53237	0.68206
H434	0.04995	0.56090	0.56650
H435	0.23111	0.52204	0.52211
H436	0.34861	0.45465	0.59329
C241	0.22190	0.67438	0.41050
C242	0.18904	0.73544	0.45178
C243	0.07971	0.74386	0.48014
C244	0.00323	0.70122	0.46722
C245	0.03609	0.64016	0.42594
C246	0.14542	0.62673	0.39758
H242	0.24112	0.76789	0.46059
H243	0.05734	0.79045	0.50826
H244	-0.07123	0.71037	0.49653
H245	-0.01600	0.60771	0.41713
H246	0.16779	0.58515	0.36946
C441	0.42589	0.69632	0.40581
C442	0.42904	0.68744	0.47638
C 443	0.51206	0.71536	0.50722
C444	0.59192	0.75267	0.41648
C 445	0.53876	0.76206	0.39541
C446	0.50575	0.73413	0.36508
H442	0.37466	0.66203	0.50463
H443	0.51421	0.70397	0.55562
H444	0.64845	0.77169	0.47714
H445	0.64315	0.78747	0.36767
H446	0.50360	0.74053	0.31668

TABLE B.7(a)

Anisotropic Temprature Factors For Si(NC(C_6H_5)$_2$)$_4$

ATOM	U11	U22	U33	U12	U13	U23
Si1	4.30398	4.49074	5.51038	0.13131	-1.42509	-0.19054
Si2	6.70881	5.28719	4.83650	-1.45017	-0.91704	-0.65334
N11	4.44884	4.35970	5.75003	0.64582	-2.41790	1.19254
N12	3.86199	5.59439	3.59327	-1.39129	0.09420	0.97551
N13	2.86960	5.25281	4.97640	-0.39959	-0.98500	0.76105
N14	3.92187	5.00226	3.41132	-0.69772	-0.92663	-1.03938
N21	8.22780	6.03577	5.35542	- 1.38328	-2.00749	0.09678
N22	3.69824	4.72443	8.04625	-2.12792	-1.86364	-1.09662
N23	5.12663	6.22301	5.49135	-0.41305	-1.09891	-0.57966
N24	3.97279	3.61179	4.74787	-0.01900	-0.31054	-0.87558
C11	6.19995	5.45786	3.07220	-2.88275	1.12325	0.32690
C12	3.83545	5.56402	4.76136	-0.12931	-0.22093	-0.05645
C13	2.98419	6.70614	4.78362	-0.12189	-2.14597	1.13332
C14	4.89004	4.51392	3.09939	-0.13610	0.69242	0.23277
C21	9.63646	6.13664	3.43538	-3.08798	0.37752	-2.11613
C22	5.53951	5.41929	3.65069	0.62926	-0.54753	-3.46467
C23	6.44092	3.52217	6.77169	0.04934	-1.91614	0.35723
C24	6.91284	3.33562	7.05372	-0.13932	-1.80236	0.63915

TABLE B.7(b)

Isotropic Temprature Factors For $Si(NC(C_6H_5)_2)_4$

ATOM	U	ATOM	U
C111	5.10857	C131	6.72295
C112	5.23369	C132	6.63912
C113	7.55447	C133	8.40911
C114	7.09679	C134	8.88311
C115	7.97024	C135	7.78465
C116	7.21013	C136	6.19403
H112	11.17755	H132	10.53753
H113	7.25891	H133	18.47073
H114	21.83110	H134	23.04120
H115	27.70377	H135	13.92941
H116	11.36079	H136	6.61864
C311	6.22747	C331	5.84836
C312	10.49810	C332	7.76630
C313	10.22219	C333	9.48805
C314	7.82174	C334	8.99835
C315	12.25310	C335	8.13562
C316	8.66624	C336	6.80201
H312	-8.85602	H332	2.58852
H313	19.69711	H333	19.04161
H314	51.75836	H334	35.29706
H315	10.37518	H335	13.79684
H316	9.65749	H336	2.49883
C121	4.92038	C141	4.46353
C122	7.36917	C142	7.36674
C123	8.75434	C143	8.50181
C124	8.57965	C144	8.78341
C125	8.68236	C145	8.43971
C125	6.24304	C146	7.45910
H122	3.98615	H142	3.39869
H123	19.39386	H143	8.34387
H124	27.55536	H144	34.91826
H125	12.25631	H145	20.33018
H126	9.57347	H146	7.93003
C321	5.52014	C341	4.77698
C322	7.09607	C342	5.65093
C323	8.44586	C343	7.80962
C324	8.61473	C344	8.51150
C325	9.73643	C345	8.58388
C326	7.00350	C346	7.79590
H322	3.48287	H342	12.08772
H323	25.66925	H343	15.91397
H324	31.18138	H344	18.93839
H325	17.48927	H345	30.36359
H326	8.84866	H346	9.96090

(continued)

TABLE B .7(continued)

ATOM	U	ATOM	U
C211	6.56423	C231	6.76496
C212	9.27930	C232	8.39222
C213	10.95880	C233	9.51833
C214	10.24064	C234	10.21896
C215	10.87485	C235	11.18754
C216	7.92683	C236	10.33736
H212	6.51806	H232	6.51550
H213	22.69795	H233	23.61024
H214	35.95767	H234	37.55408
H215	11.24011	H235	24.73267
H216	6.06765	H236	7.65374
C411	5.09898	C431	7.18697
C412	7.33456	C432	8.38574
C413	9.00419	C433	11.41795
C414	8.85070	C434	8.57106
C415	8.69436	C435	8.11037
C416	7.58582	C436	7.20286
H412	9.37308	H432	12.44474
H413	13.15472	H433	22.41644
H414	21.82314	H434	29.96104
H415	21.17442	H435	15.09078
H416	9.01319	H436	12.11945
C221	5.50861	C241	5.92806
C222	6.58486	C242	7.39501
C223	9.02406	C243	8.43797
C224	8.44899	C244	9.70644
C225	8.38709	C245	10.07555
C226	7.51262	C246	7.58776
H222	6.54407	H242	7.66886
H223	20.51543	H243	12.42915
H224	21.59433	H244	16.49500
H225	13.23580	H245	23.76347
H226	[illegible].95781	H246	12.42145
C421	5.33940	C441	6.08371
C422	6.87008	C442	8.52035
C423	10.36354	C443	11.30488
C424	9.02714	C444	10.74839
C425	9.48489	C445	11.22202
C426	7.39478	C446	8.06411
H422	3.65077	H442	0.82692
H423	20.03676	H43	29.80275
H424	41.17239	H444	44.94501
H425	16.47289	H445	14.40911
H426	7.02787	H446	4.97115

TABLE B.3

Internuclear Distances in $Si(NC(C_6H_5)_2)_4$

Molecule 1		Molecule 2	
	Distance Å (σ)		Distance Å (σ)
Si1-N11	1.703(15)	Si2-N21	1.710(15)
Si1-N12	1.707(15)	Si2-N22	1.684(15)
Si1-N13	1.718(14)	Si2-N23	1.707(18)
Si1-N14	1.723(14)	Si2-N24	1.708(14)
N11-C11	1.268(21)	N21-C21	1.261(24)
N12-C12	1.260(24)	N22-C22	1.265(22)
N13-C13	1.258(21)	N23-C23	1.271(23)
N14-C14	1.279(22)	N24-C24	1.299(21)
C11-C111	1.506(17)*	C21-C211	1.468(18)*
C11-C311	1.496(17)*	C21-C411	1.528(20)*
C12-C121	1.497(18)*	C22-C221	1.513(15)*
C12-C321	1.522(18)*	C22-C421	1.493(17)*
C13-C131	1.492(18)*	C23-C231	1.514(17)*
C13-C331	1.484(18)*	C23-C431	1.479(20)*
C14-C141	1.506(16)*	C24-C241	1.486(16)*
C14-C341	1.499(15)*	C24-C441	1.493(18)*

*The standard deviation is based solely on the contribution from the non-phenyl carbon atom

TABLE B.9

Bond Angles In $Si(NC(C_6H_5)_2)_4$

Molecule 1	ANGLE°(σ)	Molecule 2	ANGLE°(σ)
N11-Si1-N12	108.49(72)	N21-Si2-N22	110.12(73)
N11-Si1-N13	101.77(64)	N21-Si2-N23	114.87(79)
N11-Si1-N14	116.18(66)	N21-Si2-N24	103.2 (67)
N12-Si1-N13	115.26(66)	N22-Si2-N23	103.03(71)
N12-Si1-N14	105.99(63)	N22-Si2-N24	113.73(70)
N13-Si1-N14	109.48(68)	N23-Si2-N24	112.23(71)
Si1-N11-C11	135.6 (13)	Si2-N21-C21	138.8 (15)
Si1-N12-C12	135.2 (13)	Si2-N22-C22	140.2 (12)
Si1-N13-C13	139.0 (13)	Si2-N23-C23	138.9 (12)
Si1-N14-C14	128.2 (11)	Si2-N24-C24	138.4 (13)
N11-C11-C111	119.1 (14)*	N21-C21-C211	120.4 (16)*
N11-C11-C311	124.3 (14)*	N21-C21-C411	123.5 (15)*
C111-C11-C311	1 6.5 (11)*	C211-C21-C411	116.1 (12)*
N12-C12-C121	120.4 (14)*	N22-C22-C221	122.1 (13)*
N12-C12-C321	122.4 (14)*	N22-C22-C421	120.8 (12)*
C121-C12-C321	117.0 (13)*	C221-C22-C421	117.0 (11)*
N13-C13-C131	123.5 (15)*	N23-C23-C231	123.5 (15)*
N13-C13-C331	118.9 (15)*	N23-C23-C431	120.8 (13)*
C131-C13-C331	117.5 (11)*	C231-C23-C431	115.7 (14)*
N14-C14-C141	124.2 (12)*	N24-C24-C241	117.7 (14)*
N14-C14-C341	120.3 (12)*	N24-C24-C441	122.1 (13)*
C141-C14-C341	115.5 (11)*	C241-C24-C441	120.2 (11)*

*The standard deviation is based solely on the contribution from the non-phenyl carbon atom.

TABLE B.10

Comparison of observed and calculated Fs for $Si(NC(C_6H_5)_2)_4$

	0,0,L	
-18	191	-145
-15	165	151
-13	145	-115
-11	465	-469
-10	287	302
-8	124	-105
-7	910	878
-6	179	204
-5	1174	-1168
-4	927	-914
-2	1358	-1353
2	1363	-1353
4	904	-914
5	1176	-1168
6	214	204
7	896	878
8	139	-105
10	297	302
11	468	-469
13	26	-115
15	28	151
16	164	-145
	0,1,L	
-15	145	105
-12	138	161
-11	244	-252
-10	295	286
-9	326	295
-8	24	141
-7	222	212
-6	413	366
-5	1470	-1435
-4	214	213
-3	1161	-1153
-2	136	118
-1	133	149
1	180	-222
2	436	412
3	1381	1377
4	747	757
5	533	546
6	337	311
8	119	67
9	365	336
10	436	-418
15	27	70
16	290	262
18	187	-176
	0,2,L	
-18	205	-204
-17	29	116
-16	261	290
-14	301	-267
-11	337	-342
-9	430	375
-8	207	-202
-6	152	120
-5	528	532
-4	1634	-1584
-3	333	-314
-2	658	-702
-1	906	864
0	593	587
1	1924	-1900
2	216	-216
3	1439	1403
4	606	608
5	228	-237
6	221	-217
7	934	911
8	124	-104
9	186	190
10	366	-317
11	475	-469
12	395	381
14	187	226
16	252	-267
17	225	-231
	0,3,L	
-16	28	-111
-14	274	-276
-12	148	137
-10	243	-228
-8	176	-180
-7	292	-256
-6	386	393
-5	418	363
-4	2089	-2055
-3	337	-331
-2	275	297
-1	201	195
0	1363	1374
1	918	-914
2	765	791
3	2046	[illegible]
5	442	454
6	1272	[illegible]
7	745	756
8	174	167
9	600	[illegible]
10	706	-649
11	234	[illegible]
12	242	256
16	262	236
18	260	-241
	0,4,L	
-17	212	236
-16	201	-182
-11	193	-191
-10	343	-343
-9	192	194
-8	491	462
-7	433	-366
-4	140	121
-3	1245	-1165
-2	491	527
-1	1228	[illegible]
0	873	-872
1	1730	[illegible]
2	162	-175
3	327	345
4	784	-772
6	860	853
7	159	134
8	232	-226
10	282	236
11	537	536
14	215	166
15	168	196
16	245	-224
	0,5,L	
-16	160	-223
-15	174	167
-9	443	-443
-8	356	345
-6	24	-42
-3	377	352
-2	499	-467
-1	967	927
1	141	-131
2	512	-477
3	181	140
4	362	-365
5	477	-474
6	420	-429
7	522	493
8	186	-150
10	161	-142
11	533	520
13	27	-146
14	256	265
	0,6,L	
-16	179	-90
-15	229	215
-14	171	133
-12	305	-259
-10	276	238
-8	169	-156
-6	271	268
-5	508	474
-4	466	-464
-3	576	-506
-1	186	196
0	301	-257
1	644	621
2	381	374
4	338	-343
5	879	928
6	162	168
7	727	-723
8	369	-372
11	194	-197
12	167	157
13	231	199
14	261	232
15	231	207
	0,7,L	
-11	145	-164
-9	195	-175
-8	25	64
-7	367	328
-6	232	228
-4	270	-247

TABLE B.10 (continued)

0,7,L

-3	945	-907
-2	247	230
-1	577	594
0	147	-123
2	290	284
3	290	-279
4	600	-596
6	479	450
8	243	223
9	236	-232
12	161	-140
13	27	-71
15	159	108

0,8,L

-11	272	281
-10	190	177
-9	257	-255
-8	275	233
-7	26	90
-6	246	241
-5	154	-133
-4	370	-389
-3	168	114
-2	724	686
-1	190	-164
0	522	-525
3	503	-486
4	273	-280
5	582	595
8	26	67
9	290	270
10	345	-322
11	443	-428
14	28	-189
16	167	187

0,9,L

-14	28	-174
-13	202	-176
-10	167	190
-4	228	-228
-2	290	295
-1	233	-215
0	25	78
1	404	384
2	366	-345
4	564	-523
6	239	228
7	197	188
8	[illegible]	-183
10	342	350
11	168	-173
12	225	-189

0,10,L

[illegible]	239	-237
-8	291	309
-7	474	470
-5	203	-181
-2	198	-188
-1	158	138
0	684	684
1	186	190
2	454	-501
3	254	-250
4	235	-226
13	167	-161

0,11,L

[illegible]	185	-109
-6	27	205
-3	522	516
-1	293	-320
3	199	-194
5	390	408
7	252	-238
11	220	-225
13	217	185

0,12,L

-10	153	-107
-9	28	-208
-8	156	-192
0	181	178
2	278	-334
4	349	315
6	202	-228
11	28	-220

0,13,L

-6	163	-159
-4	213	[illegible]
-2	160	[illegible]
-1	28	[illegible]
0	348	[illegible]
2	263	[illegible]
4	190	[illegible]
5	192	[illegible]
6	236	[illegible]
7	224	[illegible]
8	28	[illegible]
9	28	[illegible]
10	237	[illegible]
12	240	216

0,14,L

0	200	[illegible]
7	295	[illegible]

0,15,L

-5	175	192
-2	211	-177
-1	28	157
0	166	184
4	190	191

1,-14,L

-6	237	[illegible]
-4	32	174
5	199	213

1,-13,L

-1	251	[illegible]
5	221	226
6	211	[illegible]

1,-12,L

-6	31	-175
-2	250	-265
1	208	-255
4	223	[illegible]

1,-11,L

-11	31	232
-9	30	-34
-6	429	-403
-5	272	251
-4	307	346
-3	191	-195
-2	219	-222
0	253	264
1	29	-86
3	186	214

1,-10,L

-7	206	-157
-6	185	179
-5	212	206
-3	257	-254
-2	237	-196
0	251	242
1	29	-134
3	362	326
5	260	-266
7	273	274
11	297	291

1,-9,L

-12	255	319
-10	227	-289
-8	212	175
-7	[illegible]	-425
-5	288	319
-4	282	-269
0	584	-614
1	350	-346
2	322	-335
3	527	531
4	276	288
5	[illegible]	-281
9	161	-170

1,-8,L

-8	336	-276
-7	300	315
-6	284	308
-5	[illegible]	170
-4	416	-416
-3	252	225
-1	561	-583
0	[illegible]	174

TABLE B.10 (continued)

1,-8,L

1	161	164
2	291	305
4	470	-435
9	216	-226
13	197	-241

1,-7,L

-13	203	217
-11	29	-140
-9	300	361
-7	325	-309
-5	540	532
-4	232	218
-3	260	-277
-2	370	-360
-1	328	352
0	671	-694
1	556	542
2	308	327
3	204	-198
4	805	-783
5	453	-420
6	559	513
12	370	-340

1,-6,L

-14	31	166
-13	223	-221
-11	154	194
-8	455	455
-7	185	151
-6	397	368
-5	734	722
-4	235	-241
-3	168	164
-2	329	317
-1	549	-549
0	228	-226
1	221	213
3	241	-246
5	332	310
6	740	-746
8	467	-469
10	30	211

1,-5,L

-14	266	301
-11	328	-317
-10	263	274
-8	272	240
-5	754	710
-4	220	-205
-1	219	257
0	874	878
1	216	190
2	562	588
4	846	-839
5	158	171
10	254	267
11	220	-247
12	372	-359

1,-4,L

-15	203	218
-13	291	-288
-12	315	351
-11	366	385
-9	415	-409
-8	374	-372
-7	666	-654
-6	27	-140
-5	601	594
-4	559	557
-3	475	-460
-2	872	916
-1	267	-269
0	1229	-1288
1	1303	1335
2	278	-298
3	367	-403
4	570	540
6	288	294
8	495	487
10	578	-615
14	183	-130

1,-3,L

-15	269	-278
-14	208	157
-11	333	299
-10	299	251
-9	418	-400
-6	266	277
-5	644	-612
-4	794	-794
-3	1499	1571
-2	167	-166
-1	239	-221
0	313	310
1	163	-191
2	857	849
3	2364	-2385
4	240	228
5	919	920
6	500	-505
7	244	-224
8	378	-419
9	435	401
10	308	-272
12	174	106

1,-2,L

-14	247	-251
-12	319	347
-11	29	-128
-9	335	-317
-7	319	-317
-5	515	-504
-3	510	-516
-2	403	389
-1	429	-434
1	379	-395
2	1438	1460
3	414	404
4	323	-314
5	865	845
6	293	280
8	271	261
11	203	-227
14	306	-323

1,-1,L

-14	29	100
-11	167	204
-9	632	-624
-7	27	-166
-6	675	-672
-5	993	973
-4	1956	1948
-3	1002	-1008
-2	1763	-1847
-1	547	-544
0	667	677
1	1354	1345
4	1363	1364
5	561	-577
6	192	180
7	541	-522
8	225	-183
9	647	617
10	467	462
11	268	251
15	215	-239

1,0,L

-12	275	310
-6	816	826
-5	1049	1061
-4	201	-210
-3	297	-279
-2	229	-270
-1	116	89
0	111	97
1	21	-19
2	113	99
3	602	-595
4	968	1008
5	1099	-1075
6	223	-208
7	413	435
8	513	-451
9	463	501
10	269	255
11	189	146
16	239	219

1,1,L

-16	216	240
-14	275	-272
-12	257	284
-8	331	-338
-7	189	-170
-6	1244	1201
-5	364	-357
-3	128	-99
-2	926	-918
-1	245	-279
0	1796	1811

TABLE B.10 (continued)

	1,1,L	
1	302	-275
2	619	-615
3	1262	1264
4	1527	1526
5	658	-681
6	523	-522
7	232	215
8	229	212
9	403	403
14	210	-205
	1,2,L	
-11	216	-232
-10	401	378
-9	231	-212
-8	571	-571
-7	560	569
-6	1154	1136
-5	915	-890
-4	970	-962
-3	289	264
-2	252	-235
-1	998	-1005
0	920	904
1	1015	1058
4	775	-773
5	1866	-1875
6	1662	-1619
7	148	-140
8	609	623
9	616	592
11	28	173
12	227	-237
14	291	-295
16	401	427
	1,3,L	
-15	279	-301
-14	394	-394
-13	192	230
-11	209	-190
-9	303	284
-8	599	616
-6	26	-112
-4	735	-729
-3	656	-685
-2	499	-500
-1	504	482
0	1050	-1054
1	820	869
2	1078	1114
3	845	-853
4	975	-938
5	816	-825
7	326	366
8	239	-192
10	548	-523
12	182	186
15	345	337
	1,4,L	
-11	170	-157
-10	394	-367
-9	461	-494
-8	191	-191
-7	358	370
-6	355	332
-5	305	-283
-4	497	490
-2	433	-452
-1	1240	-1240
0	968	981
2	843	-831
3	1509	1493
4	348	363
5	27	-120
7	492	472
8	268	-306
9	659	-637
11	220	246
13	190	-153
	1,5,L	
-14	332	371
-8	529	511
-7	1010	-974
-5	510	496
-4	552	539
-3	678	-656
-2	410	-409
-1	771	752
0	629	-633
1	297	-312
2	1274	1241
3	655	-653
5	602	560
7	161	-150
8	278	-295
9	264	257
11	250	241
12	506	-498
13	317	-321
14	449	432
15	423	414
	1,6,L	
-10	175	-141
-7	291	[illegible]
-4	605	[illegible]
-2	295	-278
-1	261	274
0	641	644
1	402	-366
2	348	-378
3	703	[illegible]
4	413	-347
5	221	231
6	544	526
7	964	944
8	367	316
9	428	-456
13	30	[illegible]
	1,7,L	
-11	197	248
-9	311	-295
-7	29	-241
-6	511	528
-5	214	178
-4	603	-555
-3	257	-248
0	271	-284
2	652	655
3	648	-662
5	601	628
7	375	-358
9	528	509
13	31	-274
	1,8,L	
-6	28	201
-3	954	-945
-1	453	459
0	282	-312
1	517	-500
2	730	731
4	729	-708
5	301	276
7	314	-300
8	20	-121
10	298	271
11	232	238
13	235	-296
	1,9,L	
-11	30	130
-10	30	-144
-7	289	297
-6	316	330
-4	178	177
0	320	-326
2	182	215
3	564	-551
6	240	-247
	1,10,L	
-8	188	90
-7	284	-256
-6	231	207
-5	171	166
-4	340	-332
1	163	109
2	28	146
3	433	-426
4	522	-549
6	218	249
7	293	-276
9	217	247
12	220	-252
	1,11,L	
-9	188	-210
-7	336	343
-1	255	285
0	325	329
4	267	249
6	215	-201

TABLE B.10 (continued)

6	235	-210
7	211	210
9	255	-276

1,12,L

-6	207	162
-3	301	324
1	465	465
3	313	-300
5	189	142
6	291	-258
7	267	-309
8	253	198
9	312	291

1,13,L

-3	30	151

1,14,L

2	334	-323
4	377	393
5	205	138
7	196	-129

2,-14,L

0	202	208

2,-13,L

-7	224	253
-4	183	176
-2	284	-320
-1	219	-244
0	311	311
6	203	-201

2,-12,L

-4	234	223
-2	301	-279
4	259	-239
5	262	283
7	279	-295

2,-11,L

-5	30	266
0	293	320
1	337	-344
4	315	261

2,-10,L

-9	234	-271
-6	196	-142
-4	327	322
-3	282	-267
-1	332	296
0	186	200
1	201	-180
5	195	196
8	371	388
11	31	-183

2,-9,L

-7	204	-172
-6	260	-274
-3	28	-66
-1	214	206
0	202	-174
1	340	343
2	29	-196
3	211	251
7	471	461
11	206	185

2,-8,L

-10	243	-258
-9	218	176
-8	399	390
-7	244	-233
-5	190	180
-4	29	-191
-3	680	684
-2	519	-498
0	301	-309
1	548	-568
2	161	132
6	434	-383
7	434	437
8	232	193
9	186	-215
12	204	228
13	31	-173

2,-7,L

-6	313	295
-5	282	278
-4	222	235
-3	525	-557
-2	392	393
-1	281	-249
0	445	443
1	341	370
4	326	-332
6	255	231
9	192	-199
13	207	216

2,-6,L

-14	31	215
-13	199	135
-11	207	-204
-10	276	279
-9	480	446
-7	746	-762
-5	28	197
-4	525	510
-2	616	-627
-1	369	-392
0	229	-243
3	466	485
4	468	-441
5	145	140
7	193	234
8	563	-569
11	538	552
13	228	-264

2,-5,L

-13	394	-407
-11	266	275
-7	261	-208
-6	197	224
-5	633	579
-4	196	203
-2	217	175
-1	1236	1250
0	1411	-1378
1	272	-292
2	459	-451
4	224	-225
5	149	167
6	640	-612
7	399	369
10	179	138
11	29	-78

2,-4,L

-14	219	253
-10	190	197
-8	508	-526
-6	636	602
-4	785	-785
-3	219	-198
0	1935	1937
1	255	266
3	253	223
4	1071	-1080
6	339	366
7	451	-457
9	381	-367
10	456	483
11	177	-165
12	29	-100
14	334	282

2,-3,L

-13	307	-321
-12	346	345
-9	304	-285
-7	233	-225
-6	27	94
-3	624	-596
-2	412	-451
-1	1460	-1448
0	708	-686
1	606	-636
2	1426	1421
3	672	668
4	259	-264
5	226	-198
6	475	470
7	317	-310
9	401	436
10	284	-292
11	183	163
14	289	-343

TABLE B.10 (continued)

	2,-2,L		-11	252	268	-7	368	-361	0	439	-453
			-9	321	322	-5	861	-848	1	263	-261
-8	287	-301	-7	170	-187	-4	476	-470	2	397	-418
-7	331	323	-6	579	-613	-3	817	812	5	561	-566
-6	237	180	-5	216	219	-2	2104	-2141	6	557	503
-5	620	+603	-4	371	384	-1	1299	-1359	7	470	-487
-3	1543	1552	-3	26	-111	0	507	-529	8	552	-571
-2	1465	1495	-2	617	-633	1	1057	1092	9	175	164
-1	515	520	0	750	737	2	289	-279	10	474	480
0	229	209	1	930	912	3	1488	1467	11	536	558
2	1457	-1512	2	1253	1276	4	943	972	13	207	-297
3	472	-469	3	352	-354	6	648	-643	14	31	-260
4	1559	-1550	5	618	598	7	294	-289	16	210	174
5	1577	1617	6	454	435	9	270	268			
7	341	-333	7	401	-385	10	404	-398		2,5,L	
8	258	-264	9	287	281	11	510	498			
9	248	217	12	331	347	12	176	131	-9	307	291
10	293	-279	14	263	-215				-8	230	247
11	193	-156					2,3,L		-7	209	-152
12	310	276		2,1,L					-6	335	-311
16	213	-208				-9	387	-378	-4	27	166
			-10	221	164	-8	402	-377	-2	234	-274
	2,-1,L		-9	455	-432	-7	460	478	-1	421	407
			-8	355	-342	-6	212	-241	0	623	600
-12	156	174	-7	454	395	-5	715	-698	1	1145	-1146
-11	286	-279	-6	300	258	-2	1933	-1977	2	26	-93
-10	473	455	-4	965	-966	-1	595	-590	4	230	-254
-8	549	-523	-3	1241	1259	0	426	385	5	426	-421
-7	285	292	-2	1025	975	1	549	-556	7	189	183
-6	177	-179	-1	325	340	2	151	-152	8	326	306
-3	1147	1196	0	1157	1192	3	449	-471	9	267	266
-2	1175	-1169	1	862	-855	5	276	272	11	332	290
-1	1678	1721	2	199	-203	7	935	907	15	219	218
0	829	824	3	263	258	9	507	-502			
1	1144	-1180	4	377	382	10	393	-387		2,6,L	
2	1252	1252	5	1059	1066	12	190	195			
3	608	606	6	696	-702	15	308	-280	-14	343	353
4	1445	-1482	7	404	-383				-12	236	-235
5	693	661	9	536	-515		2,4,L		-10	318	380
6	545	548	10	457	-468				-8	310	-325
7	269	-261	11	341	340	-15	264	-314	-7	220	207
9	351	350	12	404	435	-13	227	243	-6	648	623
11	266	-275				-11	328	-255	-5	607	597
12	29	115		2,2,L		-9	300	311	-4	172	133
						-8	190	229	-3	865	-806
	2,0,L		-14	262	-278	-7	494	-498	-2	484	472
			-12	158	169	-5	708	712	-1	333	-274
-14	293	-280	-11	292	-271	-4	388	366	1	507	493
-13	275	-298	-10	353	-335	-3	983	-924	2	414	-420
-12	202	179	-9	431	442	-2	936	-874			

TABLE B.10 (continued)

	2,6,L	
3	231	-206
4	308	288
5	265	222
8	312	-339
9	289	-315
10	177	-144
14	312	343

	2,7,L	
-7	233	-200
-6	360	324
-5	479	456
-4	422	400
-1	279	275
0	150	133
1	564	-586
2	227	251
3	317	302
4	346	-297
6	251	201
9	274	-283
11	191	214
13	322	-308

	2,8,L	
-9	302	-299
-8	307	-327
-7	128	232
-6	162	173
-5	198	-205
-4	210	-214
-3	560	549
-2	508	508
-1	307	262
1	382	-360
2	540	-536
3	253	-252
4	228	221
5	349	-336
6	251	246
11	313	-327
12	308	-313
13	241	-181

	2,9,L	
-5	321	292
-3	230	-200
-2	166	171
1	332	-352
2	951	937
4	554	-553
5	195	205
6	230	211
7	301	-335
8	305	-303
9	250	233
12	51	-113
13	220	-271

	2,10,L	
-11	51	165
-9	276	-297
-7	30	182
-5	174	-132
-4	205	193
-1	217	169

	2,11,L	
-5	231	178
-4	401	-470
-3	221	266
-2	266	286
-1	226	-230
1	339	297
2	198	202
5	220	190
6	29	-181
7	401	-409
9	259	234

	2,12,L	
-5	194	-199
-2	271	-264
5	30	-82
6	230	249

	2,13,L	
-5	212	-234
-3	198	259
-1	31	-198
1	245	243
3	407	[illegible]
5	239	[illegible]

	2,14,L	
-1	31	[illegible]
4	267	[illegible]

	2,15,L	
-2	226	[illegible]
2	278	-229

	3,-14,L	
-2	219	-235
-1	31	-264
2	32	[illegible]

	3,-13,L	
-3	260	[illegible]
-1	229	-231

	3,-12,L	
-8	198	148
-1	261	-279
0	477	438
2	402	-377

	3,-11,L	
-8	31	-149
-7	30	-46
-5	208	[illegible]
-3	219	191
-2	409	-550
7	230	-187
9	452	475

	3,-10,L	
-9	385	340
-7	266	-252
-5	181	144
6	30	-152
9	31	-167

	3,-9,L	
-8	192	215
-4	255	258
-2	[illegible]	-187
0	466	455
1	[illegible]	-193
6	280	-283
7	203	217
8	353	385
9	206	-93
10	438	-447

	3,-8,L	
-7	279	-302
-5	331	359
-4	322	345
-3	455	-455
-1	154	-201
0	473	-457
3	330	343
4	190	-263
5	270	-280
7	200	205
9	29	145

	3,-7,L	
-9	504	512
-8	355	411
-6	221	-233
-3	222	230
-1	266	233
0	342	348
1	178	183
2	423	-430
3	501	-509
4	230	-270
5	393	-410
6	506	-498
7	791	775
9	652	-672
11	366	367
13	454	-444

	3,-6,L	
-12	206	-197
-10	211	193

TABLE F. 10 (continued)

3,-6,L

-7	212	-226
-6	418	403
-5	309	319
-4	237	-248
-1	361	380
0	157	170
2	656	671
3	150	151
4	349	-317
14	226	-147

3,-5,L

-14	31	151
-10	287	293
-8	251	-271
-7	387	-394
-6	317	328
-5	525	537
-3	443	-462
-2	402	402
-1	503	-518
0	155	167
5	160	-128
7	407	428
8	672	-662
10	572	574
11	289	276
12	276	-256
13	397	-392
14	568	557

3,-4,L

-13	31	-165
-11	207	189
-9	313	-321
-7	28	-176
-6	192	-215
-4	416	-408
-3	278	284
-1	528	514
1	478	504
2	363	326
7	444	412
8	211	-199
9	356	-354
11	241	-222
14	201	184

3,-3,L

-13	248	-229
-11	248	260
-9	378	-388
-8	159	-220
-7	165	164
-6	174	152
-5	367	-417
-4	290	-314
-3	660	694
-1	317	295
0	826	-817
1	285	292
2	243	251
4	767	709
6	698	687
7	430	419
8	551	-600
9	28	190
10	277	262
11	221	-230
14	186	165
15	419	-409

3,-2,L

-9	248	-257
-7	376	-325
-5	425	421
-4	680	-670
-3	657	658
-2	505	-512
-1	205	-195
1	542	-501
2	532	-525
3	284	-300
4	177	155
5	552	-547
6	26	106
7	275	308
9	663	664
10	248	254

3,-1,L

-11	173	105
-9	165	180
-8	28	102
-5	28	-170
-4	319	-315
-3	1138	1141
-2	1071	-1096
-1	345	-363
1	2279	2313
2	804	822
3	293	-269
4	515	-532
6	705	675
7	288	-269
8	434	-413
9	347	356
12	205	209
13	253	228
15	211	-200
16	31	216

3,0,L

-14	280	-337
-10	342	362
-9	179	123
-8	713	-691
-7	301	301
-6	440	438
-5	368	-394
-4	209	-220
-3	1248	1239
-2	424	-437
-1	1174	1198
0	220	-238
2	966	-961
5	432	-449
6	308	309
9	285	294

3,1,L

-12	287	275
-11	232	233
-9	436	-427
-8	394	425
-6	790	-785
-4	438	453
-3	186	-160
-2	1652	-1681
-1	252	252
0	138	127
1	640	615
2	575	-600
3	176	-160
4	231	249
6	167	164
7	577	-526
8	343	-346
9	423	416
12	201	204
13	181	212
15	200	157
16	31	200

3,2,L

-13	31	-204
-10	29	-238
-9	173	154
-8	221	232
-4	430	-415
-3	151	-172
-2	1299	-1309
-1	405	382
0	156	-157
1	916	953
2	367	327
3	139	-121
4	327	-324
6	203	163
7	585	-555
8	233	227
10	537	-527
11	141	-86
14	253	-227

3,3,L

-14	368	-414
-11	269	-268
-10	344	-320
-9	377	383
-7	296	-331
-5	586	588
-3	341	-302
-2	1086	-1080
-1	161	-180
0	216	-196
1	761	-758
2	201	-203

TABLE B.10 (continued)

	3,3,L	
4	462	-455
6	161	-129
7	227	-222
10	406	-401
12	215	226
	3,4,L	
-7	236	-202
-6	712	710
-5	368	353
-3	680	-711
-2	750	-775
0	336	-329
3	244	-253
4	605	622
5	512	481
6	411	-407
7	335	-377
8	197	186
9	304	-395
10	153	-132
11	242	272
12	183	184
14	250	-223
	3,5,L	
-11	379	-374
-8	518	-519
-7	159	160
-6	791	779
-5	338	352
-4	399	356
-2	228	-210
-1	345	325
0	228	203
1	291	-320
3	28	-118
5	246	256
6	182	181
7	296	271
9	250	-260
13	31	-185
15	308	243
	3,6,L	

-11	211	212
-10	282	-320
-9	169	-107
-7	161	-170
-6	253	213
-3	547	536
-1	27	120
0	626	584
2	347	294
4	315	370
5	718	-693
6	316	-280
7	292	296
8	536	511
10	259	-270
11	222	203
13	234	-202
	3,7,L	
-10	157	170
-8	306	-302
-7	229	287
-6	263	221
-3	295	-293
-2	236	254
-1	365	393
1	287	-277
2	215	235
3	165	-156
4	160	152
5	358	340
7	250	238
9	255	-225
10	29	136
12	186	-198
13	293	-322
	3,8,L	
-12	259	245
-9	239	237
-7	354	-364
-6	233	231
-5	271	259
-3	216	-204
-2	191	-139
0	167	-157
2	150	113
3	409	-397

6	181	156
7	464	455
8	322	-302
13	31	-2[illegible]
	3,9,L	
-7	247	236
-6	177	190
-5	242	-207
-4	29	-115
-1	216	-205
1	317	-264
2	244	246
4	326	-307
9	30	-205
12	340	-370
	3,10,L	
-9	30	-50
-8	215	-207
-6	364	355
-2	234	237
0	566	-552
3	453	-471
4	277	264
5	310	-2[illegible]1
6	225	165
8	238	-2[illegible]
9	203	193
11	31	245
12	279	-2[illegible]5
	3,11,L	
-9	331	-397
-4	180	143
-2	179	-176
0	409	434
4	261	-305
7	195	144
8	236	-260
	3,12,L	
-8	207	273
-7	228	220
-5	247	-245
-4	261	-226

-3	228	178
-2	227	233
-1	194	-186
1	561	561
2	329	352
7	324	-271
	3,13,L	
-3	217	-240
2	204	211
7	217	-252
9	31	183
	3,14,L	
-2	312	-287
0	367	396
1	227	231
3	338	-346
4	31	229
5	252	243
	3,15,L	
2	32	-252
	4,-13,L	
-3	31	-153
0	244	-230
	4,-12,L	
-3	322	294
-2	277	-276
-1	216	-247
	4,-11,L	
-5	187	203
0	390	392
	4,-10,L	
-4	221	205
-3	194	194
-1	365	-345
0	180	161

TABLE B.10 (continued)

4,-10,L		
7	200	-177
9	289	309
4,-9,L		
-9	315	316
-7	324	-293
-1	533	538
0	297	-241
7	256	265
4,-8,L		
-10	252	-222
-7	206	-172
-6	29	-149
0	452	449
1	218	261
3	28	-129
5	183	-165
6	192	-231
7	290	287
8	383	380
9	308	-326
10	324	-348
11	266	248
12	203	145
4,-7,L		
-6	389	406
-4	225	168
-3	227	-232
-2	219	-234
-1	451	-468
0	251	-261
1	428	-415
2	482	452
3	28	-7
8	177	131
9	29	-167
13	212	-230
4,-6,L		
-11	275	-303
-9	454	459
-8	184	161
-7	225	-185
-5	223	210
-3	204	-178
-2	514	523
0	182	-186
1	270	231
2	426	-400
3	231	-241
5	223	-230
7	202	195
9	445	-430
10	188	190
11	494	498
13	289	-248
4,-5,L		
-12	268	-282
-9	189	-195
-8	472	-468
-6	191	180
-4	226	172
-2	694	-675
-1	398	380
0	306	345
1	521	529
2	508	488
3	314	-316
4	440	-466
5	158	170
6	261	-204
8	364	308
9	319	332
13	31	-147
14	256	239
4,-4,L		
-8	177	-162
-6	301	312
-5	161	172
-4	376	-379
-3	264	-309
-2	163	180
-1	261	263
1	159	-156
2	602	615
3	244	214
4	502	-488
6	249	250
7	491	-512
10	278	323
14	329	316
4,-3,L		
-8	216	-255
-6	250	-240
-5	218	-225
-4	287	271
-3	169	-177
-1	526	492
1	302	-314
4	436	433
5	250	242
6	765	-730
7	27	146
8	634	628
9	503	-544
11	232	224
14	275	275
4,-2,L		
-12	288	-274
-11	186	144
-10	246	279
-9	275	-237
-8	29	-166
-6	384	-361
-5	500	-520
-4	263	-285
-3	279	324
-2	585	-619
-1	150	-166
1	1154	1132
2	791	770
3	457	470
4	796	-808
5	350	-306
6	776	737
7	151	136
8	204	-174
9	174	-116
12	192	-213
13	217	224
15	195	-152
4,-1,L		
-9	233	226
-7	252	268
-6	273	288
-5	27	-169
-4	424	-448
-3	159	162
-2	285	-297
-1	713	694
1	695	-667
2	705	-73
3	161	16
4	26	-181
5	176	16
7	561	533
9	570	-546
10	222	229
12	261	-217
14	286	259
4,0,L		
-14	180	-137
-13	219	-277
-11	212	294
-10	186	200
-9	28	161
-8	202	-172
-4	681	645
-3	606	640
-2	632	-638
-1	882	-863
0	392	-392
1	457	473
3	294	-277
4	263	-240
5	550	527
6	567	531
7	438	-419
9	421	393
10	241	195
4,1,L		
-9	200	165
-8	277	-346
-6	361	353
-5	572	-556
-3	383	409
-2	440	-420

TABLE B.10 (continued)

4,1,L

-1	670	613
0	370	371
1	312	343
3	287	-256
4	527	-497
7	398	-403
9	198	-173
10	295	281
15	266	-247

4,2,L

-9	29	-200
-8	306	334
-7	421	404
-6	494	-505
-3	695	-661
-2	196	-187
0	194	-194
2	500	-473
3	406	-394
4	415	438
5	28	-119
7	575	-563
9	169	173
10	226	-183
11	175	-172
12	239	207

4,3,L

-13	285	-323
-11	482	491
-8	662	-601
-7	398	-403
-6	218	-219
-5	179	167
-4	699	660
-3	265	-308
-2	472	-442
-1	489	-460
0	306	-304
1	320	-318
2	290	272
3	375	355
4	391	-391
5	473	485
6	223	232
7	276	-761
9	591	360
10	570	-409
11	236	-212
12	358	346
13	221	196

4,4,L

-10	269	-284
-9	29	82
-5	182	168
-3	406	-412
-2	361	-377
-1	205	179
0	315	-318
1	236	-260
2	220	219
3	265	255
7	559	-545
9	459	-483
10	354	-352
11	267	251
12	254	245
13	275	-270

4,5,L

-12	213	159
-11	273	294
-9	266	-248
-8	178	166
-7	670	636
-6	207	-190
-5	295	326
-4	213	235
-3	26	-57
0	163	-109
2	193	-209
3	292	287
4	897	867
5	164	-174
7	223	-251
8	470	479
10	180	-200
12	275	222
13	214	-257
14	178	-131

4,6,L

-8	267	-249
-5	283	298
-4	658	670
-3	294	276
-1	174	-200
0	234	-220
1	785	-725
2	544	499
5	232	232
6	225	203
7	345	341
9	186	-207
11	263	256
15	230	213

4,7,L

-10	274	-221
-9	284	226
-6	28	-97
-5	320	322
-4	303	[illegible]
-3	156	-165
1	416	[illegible]
2	26	-94
3	415	415
4	468	-451
5	314	-342
7	159	[illegible]
8	28	135
11	355	361
13	240	-211
14	231	-248

4,8,L

-7	198	-215
-5	467	471
-4	276	[illegible]
-2	206	197
-1	348	342
0	232	-220
1	162	168
3	410	-398
5	175	186
7	252	-254
11	210	207
12	219	-270
13	348	-301

4,9,L

-11	194	-120
-9	275	310
-8	163	-177
-7	266	-296
-5	253	211
-4	306	-280
0	206	-205
5	248	-191

4,10,L

-10	263	255
-8	427	-421
-7	260	-292
-1	171	-166
0	216	192
1	254	299
6	337	-359
8	177	204
11	342	339
12	362	-411

4,11,L

-9	[illegible]	-264
-7	224	198
-6	[illegible]	310
-5	182	-226
0	361	-426
1	167	167
2	[illegible]	232
6	267	250
8	297	-279
10	275	173
11	372	418

4,12,L

10	232	201

4,13,L

-4	401	434
-1	291	-275
0	28	-135
1	272	281

TABLE B.10 (continued)

4,13,L

2	172	190
4	182	-158
5	306	301
6	227	235
7	487	-538

4,14,L

-3	233	-328
2	203	197
3	30	-49
6	306	-295

5,-12,L

-2	452	-492
0	245	-276
2	312	340
3	29	120

5,-11,L

-3	227	197
1	358	340
2	184	-136
3	331	-313
5	260	291
7	265	-230

5,-10,L

-4	203	214
-2	333	-327
2	244	286
3	29	182
4	163	196

5,-9,L

-1	322	-307
0	171	168
2	182	-207
6	323	-316
8	407	436
9	262	196

5,-8,L

-9	208	189
-8	29	-178
-5	237	244
-4	28	120
-3	168	-141
-2	28	171
0	177	140
5	293	-295
7	168	189

5,-7,L

-10	287	-304
-8	267	283
2	208	221
5	284	-344
6	234	-207
7	187	183
8	216	218
9	28	-128
11	214	174

5,-6,L

-10	29	171
-8	29	-183
-7	321	-348
-5	252	226
-2	240	211
-1	106	-190
0	212	234
3	489	-500
4	216	195
6	328	-328
9	157	215

5,-5,L

-9	174	202
-7	468	-487
-6	219	172
-5	602	623
-1	407	-408
1	414	465
2	466	522
3	236	262
4	303	293
5	271	-291
8	242	-251
9	236	-230
11	299	302

5,-4,L

-12	241	-235
-9	184	223
-8	222	-152
-7	200	-215
-4	162	-144
-2	233	-196
1	375	-392
3	271	240
4	771	751
5	231	-204
6	142	-136
7	207	165
8	159	157
9	312	326
10	218	-212
12	207	163

5,-3,L

-13	238	246
-10	203	214
-9	173	-201
-8	311	-289
-7	28	-165
-6	330	369
-4	184	-163
1	266	-277
2	874	876
3	483	450
4	332	-346
5	417	-421
6	360	374
8	415	-391
9	209	213

5,-2,L

-8	206	-221
-7	186	-214
-6	402	508
-4	431	459
-3	317	-327
-2	205	-208
0	550	-513
2	235	302
3	319	292
5	562	-560
6	26	-5
7	192	189
11	292	290

5,-1,L

-12	445	-491
-10	382	408
-9	368	-409
-8	28	-186
-7	270	271
-5	652	-641
-3	716	760
-2	432	-411
-1	486	-464
0	421	-395
1	437	415
2	518	505
3	343	-342
4	480	-444
5	366	-373
6	651	673

5,0,L

-4	157	-148
-3	26	-102
-2	251	272
-1	212	-194
0	863	865
1	268	286
5	422	-424
6	224	227
7	254	-263
8	421	-463
10	232	219
11	180	194
12	285	-243

5,1,L

-13	224	-270
-12	186	154
-8	27	107
-7	234	222
-6	352	327
-5	692	-713
-4	710	696

TABLE B.10 (continued)

5,1,L

-2	456	-476
-1	308	-337
0	143	156
1	26	140
2	26	-158
3	645	-610
4	269	-268
5	624	604
6	254	-237
7	27	-129
8	413	417
9	279	-259
11	155	-167
15	243	244

5,2,L

-12	180	-142
-11	216	-231
-10	277	266
-8	223	-203
-7	181	-152
-6	27	228
-5	551	-565
-2	431	-414
-1	356	-360
0	142	165
1	534	504
5	244	-249
6	330	339
7	510	-523
11	450	-414
13	201	210
15	291	-288

5,3,L

-8	174	155
-7	252	262
-6	282	-284
-4	249	195
-2	551	-536
-1	26	99
1	834	-792
3	136	-170
4	701	737
9	446	-426
12	190	178
14	171	-191

5,4,L

-11	227	236
-7	407	421
-5	282	-272
-4	507	513
-3	233	-237
-2	373	-388
-1	300	271
0	320	282
1	330	-345
2	201	-190
3	304	-260
4	683	-645
5	361	381
9	410	390
10	176	-185
11	416	-469
12	366	395
13	331	291

5,5,L

-6	238	244
-5	171	-162
-4	556	585
-3	267	240
-2	345	-340
-1	702	709
0	27	-69
1	594	-544
2	240	197
3	468	474
4	498	-440
6	299	358
9	468	-475

5,6,L

-10	201	-195
-8	255	251
-7	266	-280
-5	340	347
-4	628	636
-3	303	271
-1	368	377
0	514	-474
2	163	184
4	675	685
5	162	169
7	28	-116
10	222	-187
11	201	[illegible]
12	463	[illegible]

5,7,L

-11	214	-207
-10	177	176
-9	233	275
-8	430	[illegible]
-7	202	-278
-5	159	[illegible]
-4	243	241
-3	150	156
-1	327	302
0	318	324
1	149	126
2	152	-147
3	394	-353
4	281	[illegible]
5	222	231
6	223	[illegible]
7	160	[illegible]
8	302	-257
13	183	176

5,8,L

-7	314	-316
-5	186	194
-1	244	214
0	364	-376
2	27	-126
3	185	164
5	242	267
7	169	132
9	298	-277
10	230	-221
11	257	231

5,9,L

-10	180	146
-8	372	-369
-7	198	-244
-1	192	174
1	154	132
2	223	-223
4	297	266

5,10,L

-9	29	96
-7	224	-191
-4	303	-313
-3	207	-189
-2	293	325
-1	177	165
1	316	-317
2	29	120
4	335	-307
9	182	-206
10	246	199
11	251	269

5,11,L

-6	292	251
-4	206	-237
1	278	317
8	228	192

5,12,L

-4	207	-235
-3	195	203
-2	362	414
-1	29	-146
0	175	-149
1	30	269
2	222	179
3	175	-177
5	225	242
8	261	-187

5,13,L

-3	235	278
-1	[illegible]	-149
3	184	150
7	247	-253

5,14,L

0	192	177
3	186	-99

TABLE B.10 (continued)

6,-11,L

-2	195	-171
1	210	-224

6,-10,L

-4	352	342
-2	244	280
2	249	-296
4	334	352
5	349	315
7	424	-396

6,-9,L

-6	29	-157
-2	225	-193
-1	236	209
4	180	182
6	280	-194
9	29	67

6,-8,L

-6	259	-280
3	169	213
4	162	115
8	28	152
9	29	-210
10	198	-244

6,-7,L

-9	343	361
-7	237	-227
-4	29	108
-2	28	158
3	262	-271
4	309	319
11	199	191

6,-6,L

-8	334	330
-6	345	-379
-4	28	227
2	215	256
5	398	-363
7	283	264
8	205	176
11	360	423

6,-5,L

-9	255	314
-3	28	-87
0	209	-202
1	159	166
4	233	276
6	370	-340
8	342	328
11	210	250

6,-4,L

-9	212	211
-8	251	-349
-7	444	-503
-6	29	145
-5	321	326
-4	200	169
-3	337	-335
-2	471	473
-1	364	398
0	455	-360
1	211	219
2	154	-114
4	120	150
5	27	-87
6	154	161
7	371	343
9	306	-381
10	176	172
11	339	344
12	167	-133
13	228	267

6,-3,L

-9	29	160
-7	455	-496
-5	216	-213
-3	346	331
-2	239	223
-1	219	-189
1	357	-407
3	270	228
4	169	181
7	319	-320
9	314	-254
11	359	365
13	29	[illegible]

6,-2,L

-10	223	[illegible]
-6	257	243
-5	302	-301
-3	450	-427
-2	255	245
-1	533	-539
0	796	-815
2	803	834
3	396	390
6	217	213
7	235	216
8	347	-337
9	211	-207
11	190	-172
13	184	165

6,-1,L

-10	273	293
-9	29	63
-8	198	-237
-7	257	-237
-6	322	326
-4	437	442
-3	202	-230
-1	210	-222
1	26	105
2	427	-416
3	308	-290
4	238	-227
5	307	296
6	171	142
9	274	-305
11	261	215
14	219	-161

6,0,L

-12	204	-219
-11	249	236
-8	173	174
-7	180	198
-5	580	-589
-4	363	379
-3	261	257
-1	620	-620
0	500	-473
5	166	177
7	341	-360
8	274	-232
10	163	149
11	212	218

6,1,L

-8	200	-180
-6	313	333
-4	270	237
-3	212	-190
-2	203	206
-1	622	-612
0	297	329
1	263	240
3	218	244
5	212	-243
10	221	196
14	304	339

6,2,L

-11	29	190
-5	245	-233
-4	555	597
-2	27	145
-1	215	227
0	205	210
2	252	-266
3	487	-481
4	212	-209
5	260	257
6	319	-315
7	163	-133
9	208	-220
12	29	156

6,3,L

-5	249	-217
-1	341	-366
1	420	447
2	26	151
3	142	123
4	211	-217

TABLE B. 10 (continued)

6,3,L

5	236	229
6	198	-195
7	602	-586
9	284	252
10	172	-187
12	203	-155
13	169	179

6,4,L

-10	222	-296
-7	28	104
-5	247	262
-4	192	174
-3	196	-188
-1	282	-328
0	178	158
1	421	418
3	399	381
4	259	237
7	338	313
10	207	-214
13	207	-207

6,5,L

-9	206	-232
-8	29	185
-7	331	343
-4	182	157
-3	163	170
-2	174	-215
-1	171	155
0	163	154
1	170	-202
2	207	-188
3	165	178
5	304	298
6	184	175
7	169	-167
8	290	253
10	315	-296
12	200	212

6,6,L

-9	186	194
-8	179	-154
-4	437	451
-1	159	157
0	208	216
2	229	-194
4	159	-153
6	206	221
7	241	241
8	164	150
12	274	-228

6,7,L

-8	319	314
-6	375	-413
-4	245	225
-2	225	-215
-1	178	182
0	213	231
2	300	298
8	328	297
10	229	-234
11	323	312
12	152	151

6,8,L

-8	221	-223
-7	192	-195
-3	209	-165
-1	344	327
2	437	-404
7	174	-154

6,9,L

-7	234	-214
-5	227	293
-3	313	-280
-1	413	393
1	255	-150
2	174	-175
5	279	-268
7	193	156
9	312	-292
10	188	196

6,10,L

0	241	-283
3	28	-72

6,11,L

-6	252	278
-4	248	-208
-2	330	310
0	233	-280
2	184	159
9	225	-254

6,12,L

-2	221	213
-1	30	174
1	326	379
3	213	-266
5	178	173

6,13,L

-1	185	-266
0	321	-326
1	521	566
2	191	174
3	222	-226

7,-10,L

0	29	177
1	244	-253
2	243	-252

7,-9,L

1	171	148

7,-8,L

-6	276	-307
-3	196	132
5	29	173

7,-7,L

-7	279	297
-6	306	-303
-2	29	-173

7,-6,L

-7	295	-283
-2	162	-152
-1	186	-185

7,-5,L

-9	161	105
-8	194	189
-7	174	-172
-4	185	194
-2	217	-258
-1	253	293
1	172	-168
7	306	321
9	[illegible]	-131
11	254	276

7,-4,L

-9	31	218
-8	197	-175

8,-4,L

5	244	-190
9	313	-258

8,-3,L

2	325	-327
4	229	250

8,-2,L

-7	199	-168
-4	213	-224
-2	276	252
0	304	-298
1	323	-346
2	[illegible]	118
3	196	122
5	408	-440
7	224	235
9	30	-69

8,-1,L

-7	270	-211
-3	214	-223

TABLE B.10 (continued)

8,-1,L

3	272	245
4	247	-252
7	171	87

8,0,L

-8	219	-238
-6	317	336
-4	207	-232
-3	252	275
-2	301	310
0	392	-387
4	181	-178
6	239	-176

8,1,L

-9	197	211
-2	257	324
0	569	-598
1	191	-190
2	234	239
3	252	233
4	184	-209
6	248	260
8	201	-185
11	199	-210

8,2,L

-8	245	-258
-4	196	147
-3	387	377
-1	224	-230
0	188	209
1	420	371
4	222	-262
10	210	-231

8,3,L

-1	231	-199
1	191	231
2	224	219
4	349	-307
5	30	150
6	291	-296
11	31	154

8,4,L

-4	290	305
-2	249	-250
5	224	243
9	31	237

8,5,L

1	206	232
3	194	-163
5	351	368
7	234	-182
9	247	243
11	214	-243

8,6,L

-4	263	-317
2	206	156
9	251	223

8,7,L

-5	214	-293
-4	202	235
-1	142	-137
2	307	-286
3	212	-207
4	265	254
6	253	-221
8	330	301

8,8,L

8	31	-151

8,9,L

-3	213	-245
-1	190	-168
2	274	-251
4	255	237
5	256	-213
6	228	-264

8,10,L

[illegible]	32	-236

8,11,L

2	31	36

9,-6,L

1	30	96

9,-5,L

1	206	-135
2	218	-172
3	31	165

9,-4,L

1	281	249
3	259	-261
6	31	-2[illegible]

9,-3,L

1	214	-22[illegible]
3	401	485
6	224	-214

9,-2,L

-2	30	-24[illegible]
2	30	-146
4	216	240
5	188	-204
7	226	234
8	193	-260
9	282	-330

9,-1,L

-5	230	203
-4	237	-195
-2	330	329
0	249	-254
1	242	-182
4	262	-203
9	214	-206

9,0,L

-6	240	-231
-5	242	199
-4	31	-218
1	239	-203
2	226	210
7	347	375

9,1,L

-6	32	-189
-3	247	241
-2	355	355
-1	30	20
0	30	-191
1	206	279
3	343	-387
5	252	287
7	247	241

9,2,L

-6	322	-344
0	276	-325
2	272	351
3	30	-187
5	30	-107
6	316	310
7	295	248
8	433	-427
10	227	277

9,3,L

0	31	258
3	245	-235
5	246	227
6	311	278

9,4,L

-3	197	-38
-2	31	161
3	25[illegible]	-199
5	45[illegible]	419
7	317	-257
9	210	192

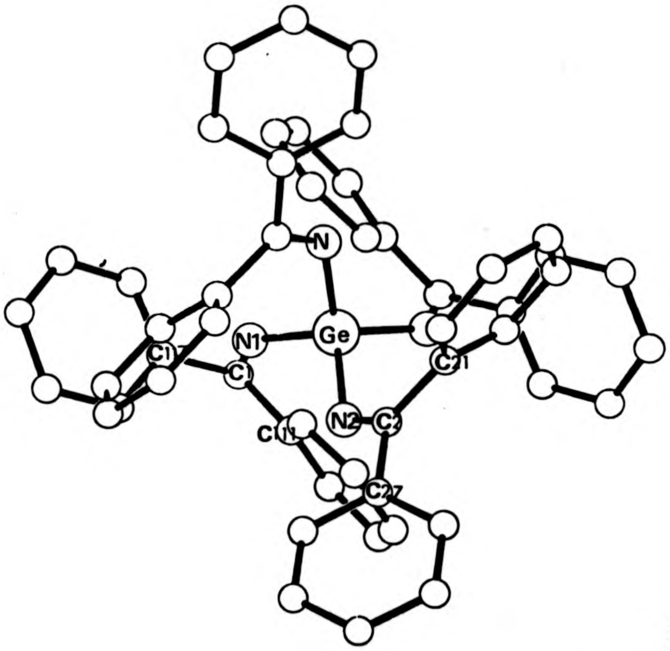
9,6,L

-1	32	-198

TABLE B.10 (continued)

9,6,L		
3	204	-201
5	274	262
8	363	376
9,7,L		
-1	249	-249
9,8,L		
2	268	-242
6	32	-152
9,9,L		
3	202	-190
10,-1,L		
-2	415	-422
3	300	309
5	456	-500
10,1,L		
-1	292	254
1	283	-247
4	309	-292
6	297	214
10,2,L		
1	361	411
2	260	240
4	244	-144
10,3,L		
-1	243	385
3	452	-492
4	218	-219
6	281	259
10,4,L		
0	300	376

Figure B.5



Ge(NC(C_6H_5)$_2$)$_4$.

TABLE B.11

Final Atomic Positions For $Ge(NC(C_6H_5)_2)_4$

ATOM	x	y	z
Ge	0.00000	0.13104	0.25000
N1	0.05733	0.22155	0.23767
N2	0.05828	0.04332	0.35682
C1	0.03727	0.30756	0.18538
C2	0.09038	0.95300	0.37069
C21	0.09836	0.89758	0.30498
C22	0.08614	0.78219	0.28799
C23	0.08939	0.73277	0.22461
C24	0.10724	0.79535	0.18049
C25	0.12214	0.90811	0.19975
C26	0.11657	0.96041	0.26068
C27	0.12117	0.89100	0.45806
C28	0.08636	0.89855	0.49488
C29	0.11245	0.84012	0.57465
C210	0.17413	0.77771	0.61985
C211	0.21159	0.77110	0.58690
C212	0.18394	0.82683	0.50528
C111	0.08765	0.37825	0.19416
C112	0.07129	0.43487	0.11769
C113	0.12318	0.49894	0.12669
C114	0.19229	0.51097	0.21247
C115	0.20908	0.45577	0.28940
C116	0.15837	0.38905	0.28026
C117	-0.04404	0.34676	0.11759
C118	-0.06390	0.45606	0.12030
C119	-0.13358	0.49411	0.06225
C120	-0.18293	0.42329	-0.00223
C121	-0.17302	0.31676	-0.01132
C122	-0.10105	0.27717	0.04912
H22	0.07119	0.73861	0.31654
H23	0.08161	0.65743	0.21414
H24	0.11332	0.75535	0.14030
H25	0.13568	0.95675	0.17201
H26	0.12473	1.04219	0.27014
H28	0.04437	0.92818	0.46139
H29	0.08428	0.84133	0.59273
H210	0.19557	0.73595	0.67974
H211	0.25595	0.72549	0.61433
H212	0.21167	0.82240	0.47881
H112	0.02643	0.42442	0.06101
H113	0.11180	0.53158	0.07231
H114	0.22919	0.55178	0.21783
H115	0.25520	0.46837	0.34437
H116	0.16902	0.34821	0.32872
H118	-0.02406	0.50526	0.16698
H119	-0.14313	0.58586	0.06305
H120	-0.23570	0.45952	-0.04248
H121	-0.21226	0.27277	-0.05405
H122	-0.08947	0.20037	0.04176

TABLE B.12

Anisotropic Temperature Factors For $Ge(NC(C_6H_5)_2)_4$

ATOM	B11	B22	B33	B23	B13	B12
Ge	2.11306	1.20436	2.11929	0.00000	1.42543	0.00000
N1	2.01502	1.19337	3.16576	-0.21905	1.96780	-0.95780
N2	3.27914	0.97818	2.58962	0.48293	1.99796	0.30102
C1	2.80852	1.19604	2.24688	-0.17947	2.05703	-0.26723
C2	1.96152	0.71394	2.21056	0.06550	1.12392	0.12456
C21	2.11574	2.29517	2.54336	0.76557	1.46345	0.96078
C22	2.80591	1.82173	3.41259	-0.30380	2.09286	0.17571
C23	4.03436	2.75858	5.04919	-1.19099	3.01007	0.08207
C24	3.86273	4.56362	4.00649	-0.25789	2.75541	1.36382
C25	4.47585	4.33894	4.89576	1.42295	3.71743	2.07175
C26	3.19382	2.98253	4.18718	0.88151	2.71549	0.95794
C27	2.85495	1.06402	2.99818	-0.12459	1.79083	0.04398
C28	4.08853	2.22246	3.94831	0.54805	2.83094	0.12850
C29	6.09057	2.36273	4.76281	-0.06595	4.17918	-0.87571
C210	4.48305	2.82694	3.05963	0.78054	1.97341	-1.29636
C211	3.48410	2.83650	3.71913	0.77250	1.73728	0.65914
C212	3.20407	2.33081	3.20146	0.31100	1.89391	0.48076
C111	3.48404	1.53768	2.77674	0.03243	2.24644	0.37143
C112	3.46838	2.04103	3.03498	0.12355	2.17754	-0.40412
C113	4.91904	2.15819	4.34101	0.31211	3.66811	-1.21063
C114	4.46774	2.25479	6.02108	-0.37341	4.36732	-0.74709
C115	3.69726	3.49904	3.92378	-0.70317	2.50015	-1.57038
C116	3.80224	2.09700	3.58993	-0.00295	2.93967	-0.32011
C117	3.30801	2.34972	2.43578	0.42394	2.14186	-0.77435
C118	3.10956	3.26584	3.01545	0.49633	2.05541	0.88260
C119	4.57367	4.63534	4.59329	1.08230	3.37102	1.31495
C120	4.20656	6.99479	4.91249	2.41208	3.12472	1.58574
C121	3.68952	6.02515	3.98414	0.60070	1.83491	-1.60764
C122	3.92144	2.67497	2.68659	0.91780	1.9[illegible]	-0.39547

Isotropic Temperature Factors For $Ge(NC(C_6H_5)_2)_4$

ATOM	B	ATOM	B
H22	-1.32587	H112	1.08046
H23	2.91434	H113	1.68423
H24	2.97645	H114	-0.71075
H25	1.29298	H115	0.37025
H26	0.00442	H116	-0.15714
H28	0.50835	H118	3.21570
H29	2.28470	H119	1.03577
H210	2.22192	H120	4.99047
H211	3.19577	H121	1.95793
H212	0.63293	H122	-0.27317

TABLE B.13

Internuclear Distances In $Ge(NC(C_6H_5)_2)_4$

	Distance (Å)(σ)		Distance (Å)(σ)
Ge-N1	1.883 (4)	C119-C120	1.365 (14)
Ge-N2	1.859 (5)	C120-C121	1.374 (15)
N1-C1	1.275 (8)	C121-C122	1.399 (13)
N2-C2	1.258 (8)	C122-C117	1.393 (110)
C1-C111	1.474 (9)	C21-C22	1.405 (10)
C1-C117	1.492 (10)	C22-C23	1.380 (8)
C2-C21	1.523 (7)	C23-C24	1.379 (11)
C2-C27	1.492 (8)	C24-C25	1.383 (12)
C111-C112	1.403 (8)	C25-C26	1.388 (9)
C112-C113	1.368 (10)	C26-C21	1.389 (9)
C113-C114	1.381 (12)	C27-C28	1.395 (8)
C114-C115	1.393 (10)	C29-C29	1.385 (9)
C115-C116	1.372 (10)	C29-C210	1.388 (13)
C116-C111	1.399 (10)	C210-C211	1.396 (11)
C117-C118	1.397 (10)	C211-C212	1.385 (9)
C118-C119	1.371 (12)	C212-C27	1.385 (10)

TABLE B.14

Bond Angles In $Ge(NC(C_6H_5)_2)_4$

	Angle° (σ)		Angle° (σ)
N1-Ge-N2	111.15 (23)	C117-C118-C119	123.17 (76)
N1-Ge-N2'	106.75 (25)	C118-C119-C120	119.34 (83)
N1-Ge-N1'	109.31 (25)	C119-C120-C121	119.38 (84)
N2-Ge-N2'	111.25 (25)	C120-C121-C122	120.70 (85)
Ge-N1-C1	123.78 (45)	C121-C122-C117	120.32 (80)
Ge-N2-C2	130.08 (48)	C2-C21-C22	119.58 (50)
N1-C1-C111	116.89 (58)	C2-C21-C26	120.56 (60)
N1-C1-C117	127.13 (53)	C22-C21-C26	119.75 (55)
C111-C1-C117	115.96 (50)	C21-C22-C23	119.83 (61)
C21-C2-C27	116.51 (51)	C22-C23-C24	120.28 (72)
C1-C111-C112	122.17 (59)	C23-C24-C25	120.07 (58)
C1-C111-C116	120.35 (50)	C24-C25-C26	120.62 (66)
C112-C111-C116	117.46 (61)	C25-C26-C27	119.36 (73)
C111-C112-C113	121.49 (67)	C2-C27-C28	119.25 (60)
C112-C113-C114	120.50 (58)	C2-C27-C212	122.52 (52)
C113-C114-C115	118.92 (65)	C28-C27-C212	118.22 (56)
C114-C115-C116	120.81 (72)	C27-C28-C29	120.80 (70)
C115-C116-C111	120.78 (58)	C28-C29-C210	119.94 (54)
C1-C117-C118	121.22 (60)	C29-C210-C211	120.91 (61)
C1-C117-C122	122.35 (63)	C210-C211-C212	118.65 (74)
C118-C117-C122	116.43 (69)	C211-C212-C27	121.40 (62)

TABLE B.15

Comparison of observed and calculated Fs for $Ge(NC(C_6H_5)_2)_4$

* H=	0	K= 0		-7	201	208	1	8	155	163	1
2	579	615	1	-6	109	112	1	9	43	22	2
4	472	475	1	-4	82	69	1	10	119	120	2
6	174	174	1	-3	120	135	1	11	53	57	2
8	301	308	1	-1	149	163	1	12	115	122	2
10	217	182	2	11	105	103	2	14	55	56	2
* H=	0	K= 2		* H=	0	K= 12		16	76	56	2
-14	73	65	2	-4	95	84	1	* H=	1	K= 5	
-13	151	162	2	-2	184	215	1	-16	95	81	2
-12	93	99	2	-1	120	127	1	-13	73	74	2
-11	289	290	2	0	185	197	1	-11	[illegible]	93	2
-10	42	41	2	3	101	93	2	-9	72	70	2
-9	261	254	2	* H=	1	K= 1		-7	173	190	1
-8	95	99	1	-17	75	66	2	-3	341	353	1
-7	329	332	1	-15	138	138	2	-2	59	60	1
-6	80	66	1	-13	86	102	2	-1	194	189	1
-5	332	316	1	-12	121	128	2	0	229	231	1
-4	242	235	1	-11	182	179	2	1	377	352	1
-3	132	119	1	-10	278	266	2	2	103	97	1
-2	55	41	1	-9	123	121	2	3	229	224	1
-1	359	338	1	-7	264	264	1	4	275	273	1
0	43	47	1	-5	340	359	1	5	340	344	1
* H=	0	K= 4		-4	419	427	1	7	172	159	1
-14	93	104	2	-3	85	88	1	10	113	116	2
-12	121	138	2	-2	320	316	1	11	72	84	2
-11	48	45	2	-1	206	190	1	12	64	63	2
-9	95	93	2	0	213	192	1	13	94	91	2
-8	84	95	1	1	519	508	1	14	97	78	2
-7	295	196	1	2	173	177	1	* H=	1	K= 7	
-5	205	199	1	4	200	286	1	-14	75	73	2
-4	377	376	1	6	100	116	1	-13	94	94	2
-1	307	302	1	7	266	273	1	-12	96	103	2
0	64	61	1	8	187	184	1	-11	104	107	2
16	101	82	2	9	176	178	2	-10	119	125	2
* H=	0	K= 6		10	99	102	2	-9	99	104	2
-13	75	79	2	11	73	78	2	-8	102	109	1
-12	60	68	2	12	139	136	2	-7	107	124	1
-11	101	113	2	13	73	77	2	-6	159	156	1
-9	112	115	2	15	95	93	2	-5	110	115	1
-7	159	159	1	* H=	1	K= 3		-4	216	217	1
-5	131	131	1	-16	62	46	2	-3	144	147	1
-3	162	161	1	-14	49	56	2	-2	71	70	1
-2	67	46	1	-13	67	77	2	1	92	85	1
-1	170	167	1	-12	65	78	2	3	210	217	1
0	79	66	1	-10	62	68	2	4	177	127	1
15	125	110	2	-9	206	199	2	5	140	154	1
* H=	0	K= 8		-8	74	66	1	6	134	134	1
-10	109	119	2	-7	259	252	1	7	151	146	1
-9	65	61	2	-6	402	395	1	9	43	57	2
-7	140	171	1	-4	212	212	1	10	95	96	2
-5	234	227	1	-3	307	323	1	11	61	73	2
-4	201	213	1	-2	143	140	1	12	103	121	2
-3	77	61	1	-1	285	274	1	14	105	85	2
-2	222	222	1	0	379	355	1	* H=	1	K= 9	
0	157	162	1	1	181	171	1	-13	58	53	2
14	81	66	2	2	257	248	1	-11	104	101	2
* H=	0	K= 10		4	244	236	1	-9	108	119	2
-10	93	77	2	5	55	46	1	-7	101	102	1
-9	113	110	2	6	125	126	1	-6	117	134	1
-8	142	155	[illegible]	7	147	141	1	-5	116	129	1

TABLE B.15 (continued)

-4	132	147	1	1	649	617	1	-6	191	201	1
-3	144	129	1	2	665	638	1	-5	76	91	1
-1	165	182	1	3	153	147	1	-4	194	212	1
0	74	89	1	4	354	344	1	-3	75	47	1
1	166	163	1	5	381	360	1	-2	93	95	1
2	93	92	1	7	198	199	1	-1	90	94	1
3	88	76	1	9	296	282	2	0	[illegible]	126	1
5	103	96	1	11	232	234	2	2	144	158	1
7	104	97	1	13	105	116	2	4	302	317	1
9	75	91	2	* H=	2	K= 4		6	[illegible]	152	1
12	49	52	2	-16	132	120	2	10	102	105	2
* H=	1	K= 11		-14	120	129	2	12	[illegible]	114	2
-11	54	56	2	-12	79	91	2	* H=	2	K= 10	
-10	125	121	2	-10	166	173	2	-13	113	109	2
-8	140	135	2	-8	155	165	1	-10	132	123	2
-5	111	127	1	-7	116	110	1	-9	104	97	2
-4	95	93	1	-6	217	208	1	-8	93	104	1
-3	100	113	1	-5	226	220	1	-5	154	139	1
-2	133	156	1	-4	213	213	1	-3	125	121	1
0	166	165	1	-3	86	83	1	-2	77	104	1
2	215	222	1	-2	258	243	1	-1	115	116	1
3	102	105	1	-1	151	154	1	0	82	86	1
6	132	128	1	0	324	314	1	1	184	195	1
10	135	125	2	1	76	73	1	3	204	217	1
* H=	1	K= 13		2	137	134	1	4	98	116	1
-1	141	163	1	3	62	72	1	5	113	116	1
0	84	79	1	5	237	238	1	6	153	168	1
1	116	123	1	7	117	112	1	7	184	190	1
2	108	143	1	8	82	63	1	8	102	131	1
* H=	2	K= 0		9	104	99	2	9	143	162	2
-16	173	164	2	10	40	6	2	11	156	171	2
-14	134	139	2	11	47	49	2	* H=	2	K= 12	
-12	103	136	2	12	89	102	2	-10	177	165	2
-10	378	356	2	14	76	73	2	-6	100	118	2
-8	99	115	1	* H=	2	K= 6		-5	117	108	1
-6	355	352	1	-16	51	44	2	-4	99	120	1
-4	242	247	1	-15	95	93	2	-2	191	200	1
-2	563	573	1	-14	53	54	2	-1	83	82	1
0	588	579	1	-13	106	111	2	0	158	179	1
2	643	631	1	-11	133	143	2	3	141	173	1
4	176	173	1	-9	217	210	2	4	109	110	1
6	137	153	1	-7	256	263	1	7	91	90	1
8	278	273	1	-5	187	150	1	8	93	81	2
10	129	131	2	-4	87	77	1	* H=	2	K= 14	
14	177	175	2	-3	123	123	1	-1	108	116	1
16	135	102	2	-1	266	258	1	* H=	3	K= 1	
* H=	2	K= 2		1	171	170	1	-18	43	35	2
-15	47	59	2	2	76	74	1	-17	95	88	2
-12	48	40	2	3	97	76	1	-15	144	149	2
-11	105	204	2	4	73	78	1	-14	63	44	2
-9	35	42	2	5	149	159	1	-13	125	128	2
-8	152	155	1	6	135	119	1	-12	77	86	2
-7	243	244	1	7	84	112	1	-11	173	130	2
-6	63	53	1	13	77	79	2	-10	250	234	2
-5	105	204	1	* H=	2	K= 8		-9	143	145	2
-4	398	394	1	-14	77	73	2	-8	93	94	1
-3	830	798	1	-12	89	94	2	-6	116	106	1
-2	139	129	1	-11	88	66	2	-4	560	560	1
-1	410	396	1	-10	47	54	2	-3	376	369	1
0	56	[illegible]	1	-9	104	106	1	-2	497	485	1

TABLE B.15 (continued)

-1	334	326	1	3	87	82	1	2	97	97	1
0	352	330	1	4	126	129	1	4	100	112	1
1	318	305	1	5	118	115	1	5	139	140	1
2	63	50	1	7	150	142	1	* H=	3	K= 13	
3	316	297	1	8	136	145	1	-7	94	92	1
4	88	98	1	12	93	101	2	-3	97	58	1
5	302	293	1	13	79	60	2	-1	102	112	1
6	144	149	1	14	69	71	2	3	120	125	1
7	109	119	1	* H=	3	K= 7		* H=	4	K= 0	
8	151	145	1	-16	118	98	2	-18	92	78	2
9	162	160	2	-15	59	55	2	-14	107	113	2
11	43	61	2	-14	87	98	2	-12	221	218	2
12	68	66	2	-13	69	70	2	-10	343	334	2
13	87	83	2	-11	101	103	2	-8	133	131	1
15	59	54	2	-10	56	59	2	-6	97	93	1
* H=	3	K= 3		-9	89	85	2	-4	190	183	1
-17	53	43	2	-7	122	130	1	-2	587	579	1
-15	106	117	2	-6	217	214	1	0	727	705	1
-14	86	99	2	-5	87	98	1	2	89	75	1
-13	108	111	2	-4	81	100	1	4	258	247	1
-12	72	89	2	-3	125	124	1	6	306	332	1
-11	102	112	2	-2	143	151	1	8	256	272	1
-10	149	143	2	-1	74	66	1	12	172	168	2
-9	127	125	2	0	253	250	1	14	115	107	2
-8	260	254	1	1	76	73	1	* H=	4	K= 2	
-7	138	137	1	2	311	318	1	-17	56	67	2
-6	439	444	1	4	74	52	1	-16	54	54	2
-4	435	426	1	5	182	168	1	-15	90	107	2
-2	98	92	1	6	95	99	1	-13	120	130	2
-1	155	154	1	8	125	126	1	-12	47	59	2
0	177	175	1	10	83	91	2	-9	229	220	2
1	592	572	1	12	52	52	2	-8	150	143	1
2	422	402	1	* H=	3	K= 9		-6	163	151	1
3	144	137	1	-13	61	52	2	-5	589	582	1
4	229	223	1	-11	120	114	2	-4	452	438	1
5	150	151	1	-9	195	190	2	-3	485	479	1
7	153	152	1	-8	126	144	1	-1	731	710	1
8	126	131	1	-7	128	143	1	0	154	154	1
9	118	120	2	-6	158	165	1	1	388	373	1
10	173	175	2	-5	96	98	1	3	353	345	1
12	136	142	2	-4	103	97	1	4	137	124	1
14	74	73	2	-3	131	147	1	5	62	82	1
15	57	44	2	-2	123	120	1	7	132	126	1
* H=	3	K= 5		-1	163	178	1	9	106	114	2
-17	107	87	2	0	135	142	1	11	106	113	2
-16	89	80	2	1	87	72	1	12	56	51	2
-15	97	107	2	2	97	93	1	14	47	20	2
-13	83	91	2	3	125	132	1	* H=	4	K= 4	
-12	87	92	2	4	104	111	1	-18	85	67	2
-11	86	97	2	7	178	197	1	-16	134	137	2
-9	243	235	2	9	117	117	2	-14	150	162	2
-7	97	93	1	10	64	59	2	-12	91	101	2
-6	187	185	1	11	85	82	2	-11	78	67	2
-5	201	209	1	* H=	3	K= 11		-10	288	278	2
-3	107	108	1	-12	145	129	2	-9	59	51	2
-2	246	229	1	-10	125	118	2	-8	290	281	1
-1	60	50	1	-8	97	94	2	-7	180	168	1
0	105	110	1	-4	200	226	1	-6	301	296	1
1	187	186	1	-2	170	195	1	-4	73	69	1
2	87	82	1	0	110	120	1	-3	98	87	1

TABLE B.15 (continued)

-1	67	67	1	-7	108	109	1	-4	611	580	1
0	190	193	1	-5	116	136	1	-3	246	240	1
1	291	203	1	-4	86	65	1	-2	309	302	1
2	364	369	1	-3	171	174	1	-1	103	115	1
3	147	139	1	-2	89	108	1	0	175	156	1
4	148	142	1	-1	158	169	1	1	90	74	1
6	187	193	1	0	142	148	1	2	252	253	1
7	117	89	1	1	208	228	1	3	106	117	1
8	230	230	1	5	182	204	1	4	79	99	1
10	144	155	2	9	96	105	2	5	236	238	1
11	112	116	2	* H=	4	K= 12		6	94	93	1
12	91	87	2	-10	105	95	2	8	144	123	1
13	50	37	2	-8	59	41	2	9	153	153	2
* H=	4	K= 6		-2	125	123	1	10	88	100	2
-17	99	85	2	2	100	87	1	11	44	47	2
-15	110	116	2	4	92	96	1	12	82	83	2
-14	79	76	2	6	131	149	1	* H=	5	K= 5	
-13	110	122	2	* H=	4	K= 14		-18	46	56	2
-11	142	150	2	-3	97	98	1	-17	59	63	2
-10	89	85	2	* H=	5	K= 1		-15	123	132	2
-9	120	125	2	-18	45	33	2	-14	112	125	2
-8	79	79	1	-17	72	70	2	-13	100	106	2
-7	191	206	1	-15	58	67	2	-12	95	99	2
-5	223	216	1	-14	132	136	2	-11	102	103	2
-4	197	200	1	-13	61	75	2	-10	186	185	2
-3	289	280	1	-12	153	157	2	-9	289	271	2
-2	154	149	1	-11	91	104	2	-8	123	126	1
-1	87	69	1	-10	137	134	2	-7	152	158	1
0	131	120	1	-8	158	156	1	-6	121	124	1
1	304	320	1	-6	437	433	1	-5	71	82	1
2	165	154	1	-5	294	277	1	-4	173	174	1
3	221	228	1	-4	137	136	1	-2	407	407	1
5	146	156	1	-3	355	350	1	2	317	320	1
9	56	69	2	-2	115	114	1	3	163	176	1
10	68	65	2	-1	593	582	1	5	139	134	1
12	50	34	2	0	332	313	1	6	92	99	1
* H=	4	K= 8		1	546	533	1	9	104	115	2
-14	74	74	2	2	113	101	1	11	71	56	2
-13	131	131	2	3	369	352	1	12	57	41	2
-12	109	114	2	4	118	100	1	13	62	73	2
-11	108	107	2	5	269	254	1	* H=	5	K= 7	
-10	97	95	2	6	107	120	1	-17	47	29	2
-9	134	133	2	7	179	161	1	-16	119	107	2
-8	220	231	1	8	99	113	1	-14	136	142	2
-7	167	178	1	9	52	53	2	-12	144	149	2
-6	194	203	1	10	127	129	2	-9	51	50	2
-5	136	197	1	12	43	53	2	-8	153	143	1
-4	133	142	1	13	90	75	2	-7	82	79	1
-2	154	165	1	14	92	72	2	-6	142	119	1
0	81	72	1	* H=	5	K= 3		-5	139	140	1
2	132	146	1	-18	83	71	2	-4	189	184	1
3	122	112	1	-15	113	116	2	-2	136	119	1
4	132	128	1	-13	71	75	2	-1	76	79	1
5	132	161	1	-12	51	55	2	0	232	221	1
6	126	121	1	-11	170	167	2	1	143	154	1
8	113	136	1	-10	121	119	2	2	307	314	1
9	96	91	2	-9	158	143	2	3	106	104	1
10	122	127	2	-8	350	357	1	4	231	223	1
* H=	4	K= 10		-6	295	292	1	9	69	75	2
-11	80	73	2	-5	287	263	1	10	79	92	2

TABLE B.15 (continued)

```
* H=   5    K=   9
-15     56     41   2
-13     69     68   2
-11    121    116   2
-10    110    109   2
 -9    234    229   2
 -8    135    141   1
 -7    181    183   1
 -6    195    191   1
 -5    183    187   1
 -3    182    195   1
 -1    167    182   1
  0    108    112   1
  5    170    123   1
  6     93     86   1
  7    149    174   1
  9     93     94   2
 10     72     66   2
* H=   5    K=  11
-12     97    104   2
-11     59     52   2
-10     88     80   2
 -4    128    152   1
 -2    118    113   1
 -1     87     63   1
  0    151    153   1
  1     95     83   1
  4    119    117   1
  6    198    120   1
* H=   5    K=  13
 -1    113     83   1
  1    139    182   1
  3     90     87   1
* H=   6    K=   0
-14     41     49   2
-12    258    253   2
-10    184    176   1
 -8    220    224   1
 -6    296    295   1
 -4    716    710   1
  0    278    256   1
  2     60     50   1
  4    172    169   1
  6    278    285   1
  8    152    164   1
 10     73     81   2
 12    147    147   2
* H=   6    K=   2
-19    116     90   2
-18     54     30   2
-17    127    132   2
-16    105    108   2
-15    176    192   2
-13    156    163   2
-11     71     81   2
-10     76     74   2
 -8    317    319   1
 -7    228    237   1
 -4    413    407   1
 -3    156    143   1

 -2    371    369   1
 -1    377    366   1
  1    394    372   1
  3    158    154   1
  4    136    139   1
  5    146    160   1
  6    122    102   1
  8    112    122   1
  9    196    169   2
 12     91     73   2
* H=   6    K=   4
-18     65     70   2
-17     53     35   2
-15     77     63   2
-14     96    110   2
-12    166    169   2
-10    237    225   2
 -8    471    459   1
 -6    418    406   1
 -5    196    190   1
 -4    219    221   1
 -2    381    376   1
 -1    133    126   1
  0    271    286   1
  2    217    225   1
  4    251    256   1
  6    155    157   1
  7     85    111   1
  8     95     94   1
 10    153    163   2
 11     40     42   2
 12     47     62   2
* H=   6    K=   6
-17     66     93   2
-16     77     61   2
-15    102    111   2
-13    175    185   2
-11    138    192   2
 -9    186    182   2
 -7    164    166   1
 -6    152    156   1
 -5    276    291   1
 -3    249    255   1
 -2    190    183   1
 -1    170    182   1
  0    243    248   1
  1     99    111   1
  3    268    272   1
  4    174    160   1
  5    132    139   1
 10     42     32   2
 11    116    111   2
* H=   6    K=   8
-16     66     73   2
-14     84     60   2
-13    124    139   2
-11     43     47   2
-10    211    202   2
 -9     79     70   2
 -8    171    169   1

 -7    145    162   1
 -6    150    155   1
 -3    147    159   1
 -2    130    164   1
  0    137    151   1
  2    271    233   1
  5     94     81   1
  6    195    224   1
  8    125    140   1
  9     71     71   2
 10     93    116   2
* H=   6    K=  10
-13     56     53   2
-12    126    130   2
-11     73     83   2
 -9 [illegible]  37   2
 -5    137    150   1
 -4    172    175   1
 -3     76     49   1
 -2     87    113   1
 -1    157    179   1
  1    170    133   1
  3    141    153   1
  4    106    113   1
* H=   6    K=  12
-10     72     63   2
 -9     57     56   2
 -8     61     45   2
 -4    115    125   1
* H=   7    K=   1
-14    229    218   2
-13     78     97   2
-11    176    177   2
-10    275    199   2
 -9    252    226   2
 -7     73     73   1
 -6    316    324   1
 -5    105    104   1
 -4    217    216   1
 -3    255    243   1
 -2    233    224   1
 -1    161    156   1
  0    272    198   1
  1     86     87   1
  2    347    326   1
  3    298    284   1
  4    192    177   1
  5    125    128   1
  6     92    106   1
  7     97     84   1
  8     97     97   1
  9     43     35   2
 10     92     88   2
* H=   7    K=   3
-19     31     71   2
-18    156    144   2
-17    137    129   2
-16    116    125   2
-14    133    111   2
-13 [illegible] 138   2
```

TABLE B.15 (continued)

-12	64	74	2	0	169	171	1	-9	74	75	2
-11	275	261	2	1	138	144	1	-8	69	82	1
-10	148	152	2	2	214	209	1	-7	449	456	1
-9	266	242	2	3	145	158	1	-6	252	236	1
-7	146	148	1	4	143	163	1	-5	194	193	1
-6	101	117	1	6	107	114	1	-4	124	128	1
-5	446	456	1	9	92	90	2	-3	66	76	1
-4	116	106	1	10	51	50	2	-1	252	244	1
-3	295	292	1	* H=	7	K= 9		0	103	114	1
-2	84	66	1	-15	71	68	2	1	77	87	1
-1	321	316	1	-14	50	44	2	3	133	142	1
0	125	116	1	-13	63	52	2	4	104	106	1
1	232	245	1	-11	102	101	2	5	73	78	1
5	89	89	1	-10	92	91	2	7	163	161	1
6	80	93	1	-9	111	104	2	9	[illegible]	85	2
8	104	93	1	-7	146	151	1	11	76	66	2
10	148	149	2	-5	146	165	1	* H=	8	K= 4	
11	64	70	2	-3	243	252	1	-19	78	66	2
12	58	53	2	-1	150	151	1	-18	105	115	2
* H=	7	K= 5		3	90	108	1	-16	51	72	2
-18	79	80	2	5	62	72	2	-14	71	77	2
-17	86	90	2	* H=	7	K= 11		-12	103	108	2
-16	83	87	2	-12	91	75	2	-11	105	98	2
-15	98	106	2	-9	67	73	2	-10	283	273	2
-14	127	132	2	-7	94	102	1	-9	117	106	2
-13	71	77	2	-6	94	70	1	-8	177	189	1
-12	127	125	2	0	103	110	1	-7	124	125	1
-11	153	162	2	2	101	119	1	-6	304	310	1
-10	253	246	2	4	122	145	1	-4	316	315	1
-9	160	153	2	6	94	75	1	-3	66	67	1
-8	161	166	1	* H=	7	K= 13		-2	405	423	1
-7	390	403	1	-9	111	98	2	0	274	272	1
-6	104	97	1	-4	90	96	1	1	71	72	1
-5	97	100	1	-3	105	101	1	2	222	225	1
-3	141	133	1	* H=	8	K= 0		4	117	132	1
-1	346	341	1	-20	67	59	2	6	147	151	1
0	246	243	1	-18	135	132	2	7	90	91	1
1	198	200	1	-16	107	110	2	8	63	69	1
2	121	135	1	-14	275	275	2	10	48	55	2
3	101	115	1	-12	235	243	2	11	54	47	2
4	96	91	1	-10	353	339	2	* H=	8	K= 6	
5	139	144	1	-8	106	114	1	-17	173	135	2
6	197	200	1	-6	357	370	1	-16	76	62	2
7	96	75	1	-4	146	146	1	-15	105	114	2
9	95	102	2	-2	313	302	1	-13	159	167	2
11	68	65	2	0	51	57	1	-12	57	65	2
* H=	7	K= 7		2	150	159	1	-11	153	157	2
-14	128	129	2	4	192	198	1	-10	93	86	2
-12	209	216	2	6	245	243	1	-9	177	171	2
-11	70	73	2	8	125	69	1	-6	103	120	1
-10	161	159	2	10	191	186	2	-5	102	135	1
-9	58	61	2	12	66	57	2	-4	112	104	1
-8	235	241	1	* H=	8	K= 2		-3	85	85	1
-7	148	140	1	-17	63	77	2	-2	74	80	1
-6	186	182	1	-16	49	44	2	-1	207	242	1
-5	203	197	1	-15	91	105	2	0	93	87	1
-4	198	204	1	-13	157	168	2	1	277	296	1
-3	82	88	1	-12	49	39	2	3	293	306	1
-2	197	190	1	-11	126	131	2	5	149	153	1
-1	160	159	1	-10	66	69	2	7	[illegible]	[illegible]	[illegible]

TABLE B.15 (continued)

```
   9   113   126  2    -14    49    54  2    -2   138   138  1
 * H=    8   K=  8     -13    93    92  2     0   142   147  1
 -16    96    94  2    -12   130   131  2     1    70    77  1
 -15   101    96  2    -11   168   161  2     2   153   149  1
 -14    64    60  2    -10    50    17  2     3    76    53  1
 -13    46    48  2     -9   113   103  2     4   105   110  1
 -12    87    76  2     -7   196   184  1     5    90    78  1
 -10   161   164  2     -6    71    84  1     6   130   150  1
  -8   292   304  1     -5   244   233  1     9    56    63  2
  -6   160   175  1     -3   460   430  1   * H=    9   K=  9
  -4   150   177  1     -2   156   168  1   -15    77    80  2
  -2   100   112  1     -1    73    75  1   -13    86    71  2
   0   225   231  1      0   318   308  1   -12    49    47  2
   1   136   151  1      2    93    84  1   -11    58    52  2
 * H=    8   K= 10       3   127   123  1    -9    47    60  2
 -15    75    54  2      4   109   108  1    -8   114   139  1
 -12    92    86  2      9    44    39  2    -6   186   220  1
 -11   116   108  2     10    69    67  2    -5   119   115  1
  -9   104   102  2     11    63    60  2    -3   148   170  1
  -7   100    70  1   * H=    9   K=  5      -2    92    94  1
  -6    91   111  1    -17   146   141  2    -1   139   148  1
  -4   136   155  1    -16    93    96  2     1    83    97  1
  -3   108   115  1    -15    90   100  2     3   107   120  1
  -2    86   100  1    -14    93    91  2     4   147   139  1
   3   132   143  1    -13   119   122  2     5    94   114  1
   4   101   123  1    -12    89   101  2   * H=    9   K= 11
 * H=    8   K= 12     -11   178   182  2   -14   129   109  2
  -8    72    57  2    -10   184   169  2   -13    66    67  2
  -4   175   196  1     -9   355   324  2   -12   109    96  2
 * H=    9   K=  1      -8   170   174  1   -10    54    49  2
 -20    56    49  2     -7   331   334  1    -9    60    62  2
 -19    73    66  2     -6   196   206  1    -8   180   166  2
 -17    62    62  2     -5   228   240  1    -6   173   174  1
 -16   158   170  2     -4    70    62  1   * H=    9   K= 13
 -15    74    56  2     -3   109   112  1    -9    73    63  2
 -14   217   228  2     -1   288   300  1    -6    94    82  2
 -13   115   118  2      0   251   245  1    -4    99   102  1
 -12   107   105  2      1   224   233  1    -3   105   141  1
 -11   182   177  2      2   177   170  1   * H=   10   K=  0
  -9   232   211  2      3   142   145  1   -20    91    80  2
  -8    87    93  1      4   175   166  1   -18   126   129  2
  -6   132   133  1      7   126   123  1   -16   223   226  2
  -5   289   277  1      9    93    97  2   -14    95   109  2
  -4   105   127  1     10    60    48  2   -12   183   190  2
  -3    84    80  1   * H=    9   K=  7     -10   129   127  2
  -1    58    61  1    -18    58    45  2    -6   229   231  1
   0   336   321  1    -17    56    53  2    -4   339   346  1
   1   140   127  1    -16    64    54  2    -2   105   114  1
   2   251   250  1    -15    47    42  2     0   429   432  1
   4   176   179  1    -14    96   106  2     2   200   210  1
   5   145   146  1    -13    70    66  2     4   317   319  1
   6   114   114  1    -12   130   127  2   * H=   10   K=  2
  11   106    88  2    -10   293   293  2   -17   101   107  2
 * H=    9   K=  3      -9   203   190  2   -15    47    63  2
 -20    64    60  2     -8   170   176  1   -13   233   244  2
 -19    57    52  2     -7   225   233  1   -11    72    75  2
 -18    92   101  2     -6   163   171  1   -10   332   304  2
 -17    98    96  2     -5    94    87  1    -9   443   379  2
 -16    81    89  2     -4   194   211  1    -8   205   214  1
 -15    44    47  2     -3   109   102  1    -7   259   267  1
```

TABLE B.15 (continued)

-6	255	250	1
-5	506	505	1
-4	133	128	1
-3	73	39	1
-2	111	93	1
-1	170	130	1
0	60	67	1
1	60	68	1
2	73	88	1
3	100	103	1
6	87	90	1
7	173	133	1
* H=	10	K= 4	
-20	158	143	2
-19	54	51	2
-18	124	131	2
-17	72	93	2
-16	169	170	2
-14	81	89	2
-12	175	186	2
-10	191	194	2
-9	69	66	2
-8	77	87	1
-5	84	91	1
-4	184	185	1
-2	170	181	1
-1	140	132	1
0	163	170	1
4	151	167	1
5	95	85	1
6	87	86	1
8	122	113	1
10	70	61	1
* H=	10	K= 6	
-16	60	66	2
-15	86	94	2
-13	155	159	2
-12	63	60	2
-11	193	196	2
-10	53	71	2
-9	293	258	2
-7	246	243	1
-6	178	180	1
-5	159	143	1
-4	98	83	1
-3	174	164	1
-1	186	192	1
1	258	270	1
3	152	171	1
5	143	142	1
7	118	107	1
9	124	127	2
* H=	10	K= 8	
-16	89	88	2
-15	118	121	2
-14	75	74	2
-12	86	83	2
-10	49	27	2
-9	58	69	2
-6	174	195	1

-4	154	159	1
-2	195	202	1
-1	86	58	1
0	169	170	1
1	98	94	1
* H=	10	K= 10	
-15	67	64	2
-13	63	74	2
-11	175	170	2
-10	87	79	2
-9	160	154	2
-8	40	89	2
-7	163	173	1
-6	126	127	1
-4	141	160	1
-3	179	150	1
1	98	69	1
* H=	10	K= 12	
-12	70	51	2
-11	101	96	2
-10	80	64	2
-8	66	64	2
-6	103	132	1
* H=	11	K= 1	
-21	60	62	2
-19	82	75	2
-18	56	68	2
-17	102	106	2
-16	230	245	2
-15	138	143	2
-14	110	101	2
-12	108	100	2
-11	222	216	2
-10	241	218	2
-9	224	209	2
-8	227	238	1
-6	234	236	1
-5	182	190	1
-3	75	65	1
-1	76	52	1
0	169	173	1
1	56	31	1
2	74	79	1
9	47	56	2
* H=	11	K= 3	
-20	90	80	2
-19	52	54	2
-16	95	101	2
-14	97	106	2
-13	134	141	2
-12	155	157	2
-11	50	38	2
-9	73	63	2
-8	130	140	1
-6	75	79	1
-5	264	207	1
-4	232	225	1
-3	238	233	1
-2	138	151	1
-1	135	145	1

0	146	160	1
1	162	172	1
2	147	169	1
3	197	203	1
5	122	135	1
* H=	11	K= 5	
-19	118	115	2
-17	85	93	2
-15	52	56	2
-14	81	85	2
-13	77	83	2
-12	180	187	2
-11	153	158	2
-10	82	77	2
-9	117	111	2
-8	107	115	1
-7	77	67	1
-6	264	257	1
-5	88	79	1
-4	124	112	1
-3	277	236	1
-2	128	124	1
-1	192	204	1
1	253	230	1
2	91	86	1
3	132	126	1
4	149	149	1
5	110	122	1
* H=	11	K= 7	
-17	74	83	2
-16	95	86	2
-15	75	82	2
-14	69	73	2
-13	41	27	2
-12	141	138	2
-10	242	256	2
-9	100	93	2
-8	234	221	1
-6	223	209	1
-4	154	156	1
-2	113	111	1
-1	155	155	1
0	147	152	1
1	75	76	1
4	97	92	1
5	86	8	1
6	113	113	1
* H=	11	K= 9	
-17	90	72	2
-15	94	92	2
-13	130	129	2
-12	115	112	2
-11	101	98	2
-10	125	122	2
-9	43	44	2
-5	170	186	1
-3	177	140	1
1	100	105	1
3	114	122	1
* H=	11	K= 11	

TABLE B.15 (continued)

```
-14   126   106  2    * H= 12   K=  6          -4   122   130  1
-13    68    61  2    -19    67    58  2       -2   125   125  1
-10    83    73  2    -18    47    37  2       -1    83   113  1
 -8   139   125  2    -15    67    71  2        0    77    69  1
  2   115   116  1    -14    71    62  2        1    75    88  1
* H= 12   K=  0       -13   115   114  2        3   160   159  1
-20   118   121  2    -12   115   115  2        5    83    77  1
-16   186   196  2    -11   264   268  2     * H= 13   K=  3
-14    91   104  2    -10    66    77  2      -20   143   105  2
-12   177   177  2     -9   294   275  2      -18    62    65  2
-10    68    79  2     -7   173   171  1      -17    55    56  2
 -8   332   366  1     -5   126   115  1      -16    60    87  2
 -4   190   197  1     -4   113   128  1      -15   161   163  2
  0   122   126  1     -1   112   129  1      -14   243   263  2
  2   206   212  1      0    74    62  1      -12 [illegible] 109  2
  4   175   177  1      7   112   126  1      -10   215   219  2
  6   101   105  1    * H= 12   K=  8         -9    47    40  2
* H= 12   K=  2       -19   109    93  2       -8   224   230  1
-19   113   113  2    -16    62    60  2       -6   174   173  1
-18    76    82  2    -14   123   121  2       -5    99   102  1
-17    86    92  2    -13    46    45  2       -4   192   206  1
-15   269   283  2    -12   110   112  2       -2   151   148  1
-14    79    79  2     -6   106    94  1       -1   133   133  1
-13   120   122  2     -4   180   192  1        1   279   282  1
-11   173   173  2     -2   211   219  1        2   104   111  1
-10   101    97  2      0   104   103  1        3   146   163  1
 -9   214   205  2      2   172   160  1        5   130   125  1
 -8    80    63  1      4   103   118  1     * H= 13   K=  5
 -7   275   266  1    * H= 12   K= 10        -20    60    50  2
 -6    93    61  1    -15   112    97  2      -19    84    87  2
 -5   221   218  1    -14    82    72  2      -16    43    42  2
 -3   262   266  1    -13   127   117  2      -13    65    62  2
 -2    98    99  1    -11    75    63  2      -12   189   196  2
  0   126   119  1    -10    87    74  2      -11   193   206  2
  1   223   233  1     -9   224   215  2      -10    86    82  2
  4    91   109  1     -7   132   136  1       -9   130   135  2
  5   134   143  1     -6    86    52  1       -8   140   143  1
  9   107    95  2     -5   109   121  1       -5   105   120  1
* H= 12   K=  4       * H= 12   K= 12          -4   180   186  1
-20    85    85  2    -10    79    74  2       -3   248   262  1
-18    84   100  2     -9    72    65  2       -1   115   116  1
-17    75    77  2     -8   123   116  2     * H= 13   K=  7
-16   126   128  2     -6   100   144  1      -19    67    57  2
-15    87    91  2    * H= 13   K=  1        -18    57    47  2
-12   208   203  2    -21    79    74  2      -17    53    57  2
-11    71    59  2    -19   113   127  2      -16   117   116  2
-10   110   119  2    -18    70    87  2      -15    72    74  2
 -9   117   116  2    -17    72    77  2      -14    70    72  2
 -8   154   161  1    -16    63    78  2      -13    65    71  2
 -6   137   153  1    -15   247   253  2      -11   135   137  2
 -5    92    71  1    -14    63    58  2      -10    74    71  2
 -4   280   291  1    -13   231   234  2       -8   113   112  1
 -3    67    76  1    -12    56    55  2       -6   114   109  1
 -2   257   262  1    -11   200   189  2       -2   144   144  1
 -1    69    60  1    -10    62    67  2       -1   127   132  1
  0   210   219  1     -9   102   106  2        0   111   125  1
  2   141   144  1     -8   337   339  1        2   108   117  1
  3   114   115  1     -7   186   197  1        6    96    96  1
  4    88   106  1     -6   169   169  1     * H= 13   K=  9
  6   110 [illegible] 1  -5   120   137  1      -17    77    77  2
```

TABLE B.15 (continued)

```
-15     97     90   2    -14    237    249   2    -11    266    262   2
-14     64     66   2    -12    150    159   2    -10    137    128   2
-13    172    115   2    -11     50     36   2     -9    171    164   2
-12     99    102   2    -10    165    155   2     -8     73     83   1
-11     93     85   2     -9     63     51   2     -7    240    250   1
 -9    173     98   2     -8    219    219   1     -5    132    115   1
 -8    172    143   1     -6    164    162   1     -4    170    172   1
 -7    117    136   1     -4    183    183   1     -3     93    112   1
 -6    113    138   1     -2    131    136   1     -2    132    134   1
 -5    175    184   1     -1     96    106   1     -1     99     99   1
 -4     85     94   1      0     91     60   1      1    149    139   1
 -3    178    123   1      2    130    139   1      3    123    139   1
 -1     81     65   1      4     86     76   1    * H= 15    K=  3
  0     85     61   1    * H= 14    K=  6          -19     49     42   2
  1    115    101   1    -20     61     55   2    -18     87     85   2
  3    112    104   1    -15     55     61   2    -16    119    131   2
* H= 13    K= 11         -14     54     45   2    -15    235    250   2
-14     95     75   2    -11     76     71   2    -14     93     92   2
-12     83     82   2    -10    121    118   2    -11     73     57   2
-11     70     58   2     -9    117    112   2    -10    145    150   2
-10    175    165   2     -7    131    123   1     -8    234    244   1
 -8    159    142   2     -3    144    140   1     -7    243    244   1
 -4     95     96   1     -1    144    159   1     -6    227    238   1
* H= 14    K=  0         * H= 14    K=  8          -4    211    228   1
-22     85     66   2    -18     91     85   2     -2    191    199   1
-20     64     65   2    -16    110    111   2      0    205    209   1
-18    193    196   2    -14    121    128   2      1    137    133   1
-16     55     42   2    -12    220    228   2    * H= 15    K=  5
-14     92    102   2    -10    152    151   2    -19     96     90   2
-12    107    112   2     -9    221    222   2    -16     45     41   2
-10    285    283   2     -8    106     97   1    -13    202    202   2
 -8    340    342   1     -7    178    195   1    -12     66     72   2
 -6    403    424   1     -4    181    209   1    -11    137    142   2
 -4    169    186   1     -2     87     89   1    -10     61     66   2
 -2    209    204   1      0    106    113   1     -9     55     56   2
  2    133    148   1      4    110     89   1     -5    121    116   1
* H= 14    K=  2         * H= 14    K= 10          -4     76     64   1
-21     67     65   2    -15     96     83   2     -3    119    121   1
-20     60     46   2    -14     70     54   2     -2    105     92   1
-19    164    164   2    -13     93     65   2      3     97    102   1
-17    136    155   2    -11    125    114   2      5     94    105   1
-16     50     46   2    -10     72     78   2    * H= 15    K=  7
-15    241    259   2     -9    106    112   2    -19     65     59   2
-13    116    122   2     -7    118    132   1    -17     64     67   2
-12    203    191   2     -5    120    143   1    -16     79     73   2
-11    178    189   2      1     91     90   1    -15    115    127   2
 -9     79     88   2    * H= 14    K= 12         -14    145    150   2
 -7    114    116   1    -10     68     52   2    -13     75     85   2
 -6    174    170   1     -9    119    103   2    -11    203    218   2
 -5     70     99   1     -8    148    133   2     -8    142    147   1
 -3    123    137   1    * H= 15    K=  1          -3    146    146   1
 -1    193    208   1    -21     68     70   2      2     82     81   1
  0     96     84   1    -20     69     68   2    * H= 15    K=  9
  1    127    155   1    -19     81     86   2    -17    113    103   2
  3    142    167   1    -18    156    155   2    -15    106    106   2
  5    101    100   1    -17    130    136   2    -14     93     91   2
* H= 14    K=  4         -15    123    123   2    -13     94     94   2
-18     89     93   2    -14     51     60   2    -11     85     82   2
-16     68     70   2    -13    237    240   2    -10     94     92   2
-15     63     7    2    -12     73     71   2     -9    113    115   2
```

TABLE B.15 (continued)

```
  -8   103   107  1    -11    82    83  2    -19    90    86  2
  -7   119   130  1    -10    57    53  2    -18    91    99  2
  -6   173   180  1     -9    57    58  2    -17    45    42  2
  -5   101   117  1     -7   221   231  1    -15    64    59  2
  -4   141   153  1     -6    94    77  1    -14    99    98  2
 * H= 15   K= 11        -5   148   154  1    -13   131   139  2
 -12   124   109  2     -3   186   196  1    -11   169   177  2
 -11   116   107  2   * H= 16   K=  8        -10    71    77  2
 -10   215   206  2    -18   103    95  2     -7   104   112  1
  -8   111   107  2    -16   121   127  2     -5   163   170  1
  -2   106   104  1    -14   142   141  2     -3   101   107  1
 * H= 16   K=  0       -12    88    96  2   * H= 17   K=  7
 -22    99    91  2    -10   153   158  2    -18    70    72  2
 -20    74    77  2     -9    82    76  2    -13   105   116  2
 -18   137   146  2     -2   100    78  1    -12    84    86  2
 -16   106   117  2   * H= 16   K= 10        -10    94    93  2
 -14   153   159  2    -15   105    91  2     -9    44    49  2
 -12   189   200  2    -12   105   109  2     -5    90   108  1
 -10   247   242  2    -11    98    68  2     -4   120   130  1
  -8   352   372  1     -9    57    61  2     -3   125   135  1
  -6   236   240  1     -3   110   127  1      0   100    57  1
  -4   142   159  1   * H= 17   K=  1       * H= 17   K=  9
   0   125   138  1    -21    91    89  2    -17   110    91  2
   4    88    73  1    -20    78    78  2    -16    75    51  2
 * H= 16   K=  2       -19    45    47  2    -15   112   112  2
 -21    54    61  2    -18   108   110  2    -14   140   136  2
 -19    96    98  2    -16    44    54  2    -13   120   118  2
 -18    56    61  2    -15    43    25  2    -11    76    84  2
 -17   209   223  2    -14    91    93  2    -10   124   122  2
 -15    71    81  2    -13    77    67  2     -9    96    98  2
 -14    51    61  2    -12   124   124  2   * H= 17   K= 11
 -13    74    81  2    -11    78    93  2    -12   107    89  2
 -12    67    74  2    -10   267   267  2    -11    52    26  2
 -11   132   140  2     -9   185   195  2    -10   121   102  2
 -10    71    73  2     -7   252   270  1     -9   110    86  2
  -9   138   144  2     -6   119   119  1     -8   170   144  2
  -7   115   134  1     -5    83   107  1     -6   106   132  1
  -5    87    98  1     -4   170   162  1   * H= 18   K=  0
  -4   109   129  1     -3   128   139  1    -22   118   117  2
  -3   194   199  1     -2   185   161  1    -20   142   143  2
  -1   236   250  1      0   104   111  1    -18   121   137  2
   0    98   100  1      1   120   125  1    -16   155   162  2
   1   131   136  1   * H= 17   K=  3        -14   300   308  2
   3   110   125  1    -21    73    63  2    -12   209   218  2
 * H= 16   K=  4       -18   100   116  2    -10   127   132  2
 -20    96   102  2    -17   107   127  2     -8   136   167  1
 -18    66    68  2    -16   231   249  2     -6   226   236  1
 -15    64    60  2    -14   144   152  2      0    90   116  1
 -14   217   235  2    -13    92   104  2      2   109   128  1
 -13   121   125  2    -12   101   108  2   * H= 18   K=  2
 -12   189   199  2    -11    66    64  2    -21    50    39  2
 -10   121   122  2    -10    58    59  2    -19    78    93  2
  -6   108   132  1     -9    76    74  2    -17   147   156  2
  -4   114   112  1     -8    86   106  1    -15    62    75  2
  -1    97    88  1     -7    84    78  1    -13    70    87  2
   4    94   102  1     -6    89   103  1    -11   106   201  2
 * H= 16   K=  6        -2   135   139  1     -9   183   189  2
 -15    73    71  2      0   120   130  1     -7   162   194  1
 -14    62    68  2   * H= 17   K=  5         -4    99    97  1
 -13   174   136  2    -21    88    80  2     -3   184   189  1
```

TABLE B.15 (continued)

```
 -1    93   121  1    -17    54    58  2    -3    94    69  1
  2    86    43  1    -16   103   106  2    -1    93    97  1
* H= 18   K=   4      -14   149   157  2   * H= 20   K=   4
-20    55    62  2    -12   123   130  2   -21    61    62  2
-16    56    56  2    -11    51    58  2   -20    61    60  2
-15    99    94  2    -10   126   124  2   -18    79    90  2
-13    66    66  2     -9   127   130  2   -16   149   157  2
-12    59    68  2     -3   106   116  1   -15    44    35  2
-10   148   150  2     -2    93   102  1   -14    95   103  2
 -7    89    70  1   * H= 19   K=   5     -12    97   103  2
 -6   113   132  1    -20    89    94  2   -11    74    66  2
 -2   116   104  1    -18    57    46  2   -10    48    70  2
  2    88    95  1    -17   107   105  2    -8   127   139  1
* H= 18   K=   6      -16   120   124  2    -6   128   138  1
-19   111   102  2    -15   186   182  2    -2   106   105  1
-17   145   144  2    -14    82    86  2   * H= 20   K=   6
-15   127   131  2    -13   142   149  2   -20    59    36  2
-13   159   163  2    -12    87    90  2   -19    99    98  2
-12    60    58  2    -11    73    75  2   -17   123   124  2
-11    63    74  2    -10    53    61  2   -15   137   138  2
-10    45    33  2     -9   109   118  2   -14    64    53  2
 -9   109   108  2     -7   168   174  1   -13    92   104  2
 -8   101    84  1     -5   128   153  1   -12    58    60  2
 -5   146   160  1   * H= 19   K=   7      -9   127   122  2
 -3   102   125  1    -18   131   114  2    -6    91    43  1
* H= 18   K=   8      -16    89    91  2   * H= 20   K=   8
-18    66    52  2    -13   117   116  2   -16    99    99  2
-17    64    51  2    -10   148   149  2   -14    75    82  2
-16    92    83  2     -9    77    66  2   -12   105   103  2
-14   136   141  2     -7   106   115  1   -11    84    78  2
-13    49    50  2     -5   105   128  1   -10    61    72  2
-12    96    98  2     -4    97    98  1    -4    97   110  1
-11    98    99  2     -2    91    66  1   * H= 20   K=  10
-10   108   115  2   * H= 19   K=   9     -11   145   120  2
 -5    96   131  1    -16    99    60  2   -10    83    74  2
* H= 18   K=  10      -15    81    83  2    -9    99    76  2
-13   158   146  2    -13    73    67  2    -8    67    56  2
-12    77    79  2    -12    80    79  2   * H= 21   K=   1
-11    70    76  2     -9    60    72  2   -21    90    91  2
 -9   100    94  2   * H= 20   K=   0     -19    81    67  2
 -8    71    66  2    -22   105    67  2   -17    74    75  2
* H= 19   K=   1      -20   107   116  2   -16    93    87  2
-21    88    87  2    -16    52    54  2   -15    64    70  2
-20    60    62  2    -14   100   107  2   -14    81    87  2
-19    60    58  2    -12   125   129  2   -12    65    77  2
-18   110   114  2    -10   204   209  2   -11    53    57  2
-16   204   210  2     -8    96    93  1    -9   123   125  2
-15    73    69  2     -6   193   200  1    -6    97    95  1
-14   138   139  2     -4   184   192  1    -5   141   140  1
-12   177   185  2     -2   127   136  1   * H= 21   K=   3
-10   159   154  2   * H= 20   K=   2     -21    45    50  2
 -9   123   123  2    -21    85    76  2   -20    75    66  2
 -7   158   157  1    -19    79    76  2   -19   109   105  2
 -5   244   250  1    -17   117   122  2   -17    58    57  2
 -3   119   119  1    -16    64    53  2   -16    61    58  2
 -2    80    54  1    -15    70    82  2   -15    65    72  2
  0    83    85  1    -13   137   152  2   -13   148   155  2
  1    97    86  1    -11   119   125  2   -12   123   125  2
* H= 19   K=   3       -9   194   198  2   -11   147   171  2
[illegible]            -8   113   129  1   [illegible]
```

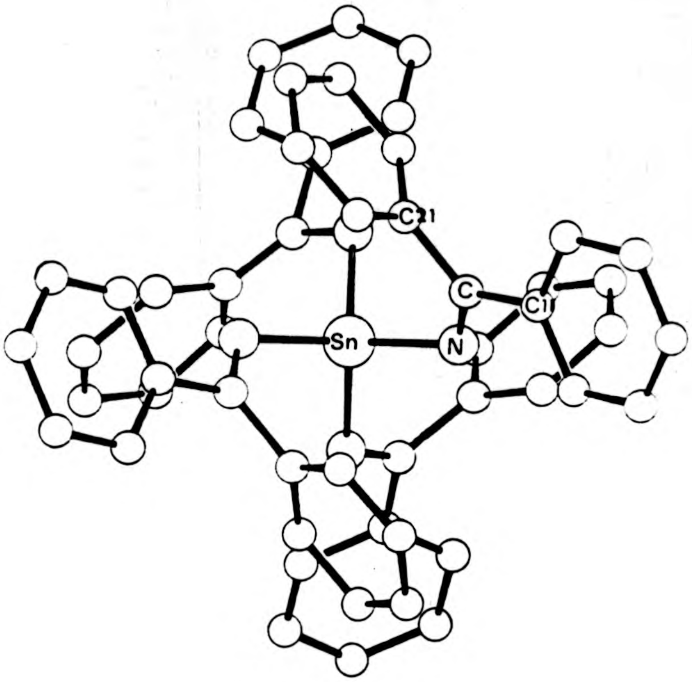
TABLE B.15 (continued)

```
  -9    94   108  2      * H= 22   K=  8        -16   120   115  2
  -4   112   124  1     -16   130   114  2      -15    60    58  2
* H= 21   K=  5         -14   119   103  2      -14   171   158  2
 -20    79    82  2     -13    80    65  2      -12    55    51  2
 -18    52    59  2     -12    77    69  2      -10    97    94  2
 -17    82    85  2     -10    70    74  2      * H= 24   K=  6
 -16    62    53  2      -9    50     9  2      -17   115   102  2
 -15   149   145  2      * H= 23   K=  1        -16    95    84  2
 -13    72    76  2     -19    91    93  2      -14    72    70  2
 -11    60    54  2     -18    66    56  2      -11   111   110  2
  -9    86    88  2     -17   101    96  2       -9   112   103  2
  -7   117   161  1     -16    56    47  2      * H= 25   K=  1
* H= 21   K=  7         -15   148   154  2      -20   120   109  2
 -18   111    97  2     -13    88    80  2      -18    73    66  2
 -16   115   115  2     -11    65    59  2      -17    95    95  2
 -15    86    92  2      -8   132   136  1      -16    51    46  2
 -14    86    88  2      -4    99   101  1      -15    75    78  2
 -12   154   154  2      * H= 23   K=  3        -14    80    85  2
 -10   115   122  2     -21   101    81  2      -13    82    76  2
  -9    59    60  2     -20    95    76  2      -12    70    76  2
* H= 21   K=  9         -19    88    77  2      -11    49    42  2
 -13    92    80  2     -18    91    89  2      -10    84    85  2
 -12    87    63  2     -17    91    93  2      * H= 25   K=  3
 -11   140   128  2     -15    92    85  2      -18    53    56  2
  -9   123   106  2     -13   118   116  2      -15    93    78  2
* H= 22   K=  0         -12   101   102  2      -14    48    47  2
 -20   165   159  2     -11   106   126  2      -13    55    45  2
 -18    84    88  2     -10   104   111  2      -12    59    55  2
 -16   103   103  2      * H= 23   K=  5        -10    74    81  2
 -14    51    52  2     -19    72    71  2      * H= 25   K=  5
  -8   127   109  1     -18    80    74  2      -17   126   104  2
  -4    92   114  1     -17    74    62  2      -16    62    61  2
  -2    85    97  1     -16    79    60  2      -15    53    60  2
* H= 22   K=  2         -15   135   127  2      -14    66    52  2
 -21    52    44  2     -12    79    83  2      -13    69    63  2
 -18    74    66  2     -10    69    75  2      -11    56    59  2
 -15   127   130  2      -9    94    90  2       -9   125   111  2
 -13   152   159  2      -7   121   108  1      * H= 26   K=  0
 -12    51    62  2      * H= 23   K=  7        -18    72    69  2
 -11   145   148  2     -17    97    90  2      -16    92    92  2
  -9   123   121  2     -16    62    61  2      -14   122   114  2
  -6    90    74  1     -15    89    74  2      -12    78    76  2
* H= 22   K=  4         -14   119   112  2      -10    82    70  2
 -21    86    68  2     -12   131   125  2      * H= 26   K=  2
 -20   121   105  2     -10   113   102  2      -19    93    80  2
 -18   109   109  2      * H= 24   K=  0        -17    69    67  2
 -16   135   145  2     -20    57    42  2      -14    53    39  2
 -14   145   147  2     -18   111   102  2      -12    74    58  2
 -12   138   145  2      * H= 24   K=  2        * H= 26   K=  4
  -9    84    75  2     -21    60    46  2      -18    79    70  2
  -6   155   196  1     -19    50    64  2      -16   128   114  2
  -4   143   139  1     -15   140   142  2      -14    99    98  2
* H= 22   K=  6         -13   160   167  2      -13    63    39  2
 -19   100    90  2     -12    47    51  2      -12   109   100  2
 -17   114   110  2     -11   173   174  2      -11    99    79  2
 -16    51    47  2     -10    90    95  2      -10   177   142  2
 -15    77    80  2      -9    47    56  2       -9    61    35  2
 -14    67    58  2      * H= 24   K=  4        * H= 27   K=  1
 -11   137   141  2     -20   133   116  2      -19    55    47  2
  -9    95    95  2     -18   117   114  2      -16    55    55  2
```

TABLE B.15 (continued)

-17	90	72	2	-9	74	59	2	-16	197	174	2
-16	70	62	2	* H=	27	K=	3	-14	209	191	2
-15	57	49	2	-17	54	41	2	-12	149	132	2
-14	57	56	2	-15	90	65	2	* H=	28	K=	2
-12	99	100	2	-12	80	71	2	-15	56	34	2
-10	102	89	2	* H=	28	K=	0				

Figure B.6



$Sn(NC(C_6H_5)_2)_4$

TABLE B.16

Final Atomic Positions For $Sn(NC(C_6H_5)_2)_4$

ATOM	X	Y	Z
Sn	.00000	.25000	.12500
N	.07123	.30830	.20934
C	.04698	.34533	.28218
C11	.09947	.37589	.34995
C12	.01828	.43468	.40533
C13	.13414	.46163	.46749
C14	.20135	.42791	.47395
C15	.21898	.36969	.41732
C16	.16936	.34241	.35709
C21	.03250	.14022	.30221
C22	.06510	.16401	.37318
C23	.13743	.15534	.39565
C24	.17925	.11658	.33123
C25	.14932	.09051	.25378
C26	.07590	.10134	.23651
H12	.02695	.44725	.39057
H13	.11540	.50035	.49875
H14	.21892	.43876	.49745
H15	.26668	.33839	.42020
H16	.16954	.29606	.33418
H22	.03108	.20917	.39196
H23	.15654	.17624	.44942
H24	.20391	.12105	.32874
H25	.16934	.07347	.21930
H26	.04828	.09511	.19729

TABLE B.17

Anisotropic Temprature Factors For $Sn(NC(C_6H_5)_2)_4$

ATOM	U11	U22	U33	U12	U13	U23
Sn	3.40252	3.40252	3.44502	0.00000	0.00000	0.00000
N	2.87359	3.50661	5.44439	-1.25409	-1.46679	-1.27916
C	3.14964	1.79888	7.25620	-1.05325	0.00336	0.62085
C11	3.70112	4.27902	3.80840	-2.04128	-0.64251	0.17469
C12	5.98239	5.79374	5.83330	-2.33526	-0.39156	-0.69074
C13	10.48335	6.57758	7.04460	-2.82176	0.40948	-1.92075
C14	9.95752	12.06681	8.29332	-6.71429	-4.01342	-2.77689
C15	7.82405	6.48150	8.90454	-1.56779	-2.21738	0.93666
C16	4.00346	7.33963	4.81011	-2.37996	-1.95708	0.95772
C21	4.28442	2.28945	5.47432	0.49608	0.60363	0.39675
C22	5.59931	4.95218	3.55161	1.67868	-1.17357	-0.37720
C23	8.11331	5.82561	4.28263	0.37023	-1.81894	-0.83769
C24	7.71922	7.13812	10.20634	1.41019	-3.20627	-0.15445
C25	6.98057	11.20963	7.64334	3.13572	0.19503	-2.39826
C26	3.89519	6.21112	7.56993	-0.24110	-1.20843	-0.22878

Isotropic Temprature Factors For $Sn(NC(C_6H_5)_2)_4$

ATOM	U
H12	7.32688
H13	5.26998
H14	4.17112
H15	11.72865
H16	13.60354
H22	2.53287
H23	5.79136
H24	8.88146
H25	6.76051
H26	7.57717

TABLE B.18

Internuclear Distances In $Sn(NC(C_6H_5)_2)_4$

	Distance (Å)(σ)		Distance (Å) (σ)
Sn-N	2.069 (37)	C15-C16	1.347 (49)
N-C	1.330 (36)	C16-C11	1.410 (38)
C-C11	1.470 (36)	C21-C22	1.332 (36)
C-C21	1.492 (30)	C22-C23	1.343 (37)
C11-C12	1.37 4 (40)	C23-C24	1.392 (51)
C12-C13	1.402 (49)	C24-C25	1.332 (56)
C13-C14	1.376 (63)	C25-C26	1.369 (43)
C14-C15	1.374 (62)	C26-C21	1.421 (41)

TABLE B.19

Bond Angles In $Sn(NC(C_6H_5)_2)_4$

	Angle° (σ)		Angle° (σ)
N-Sn-N'	107.7 1 (67)	C13-C14-C15	120.7 (38)
N-Sn-N''	110.36 (64)	C14-C15-C16	120.8 (34)
Sn-N-C	121.5 (13)	C15-C16-C11	119.4 (28)
N-C-C11	120.2 (19)	C-C21-C22	122.4 (20)
N-C-C21	124.0 (18)	C-C21-C26	119.3 (20)
C11-C-C21	115.7 (18)	C22-C21-C26	118.3 (20)
C-C11-C12	121.3 (20)	C21-C22-C23	123.0 (22)
C-C11-C16	118.2 (20)	C22-C23-C24	118.2 (26)
C12-C11-C16	120.5 (22)	C23-C24-C25	121.3 (33)
C11-C12-C13	118.7 (26)	C24-C25-C26	119.9 (33)
C12-C13-C14	119.8 (32)	C25-C26-C21	119.2 (26)

TABLE B.20

Comparison of observed and calculated Fs for $Sn(NC(C_6H_5)_2)_4$

0,0,L

4	2067	-1839
8	1931	1743
12	1169	-936
16	337	243

0,1,L

1	2085	-2826
3	320	-611
5	173	709
7	412	819
9	402	-670
11	574	-815
13	380	472
15	275	318

0,2,L

0	3432	-2290
2	517	-435
4	3074	1970
6	314	-245
8	1414	-1067
12	1223	1090
16	527	-462

0,3,L

1	471	730
3	716	924
5	1356	-1565
7	1149	-1192
9	254	381
11	591	662
13	516	-531

0,4,L

0	2276	-2202
2	1360	1064
4	1148	-823
8	636	633
12	777	-786

0,5,L

1	558	515
3	1035	-939
5	1209	990
7	1031	949
9	825	-845
11	593	-507
15	292	276

0,6,L

0	646	-653
4	741	660
6	509	502
8	974	-1074
12	263	315

0,7,L

1	1356	1304
3	457	452
5	1618	-1299
7	874	-695
9	525	561
13	214	-316
15	358	-302

0,8,L

0	302	433
2	1038	-898
4	1552	-1557
6	250	221
8	699	733
12	355	-402

0,9,L

1	969	-1051
3	1456	-1553
5	1161	1158
7	596	692
9	519	-582
11	467	-480
13	406	460

0,10,L

0	1159	-1257
4	1462	1605
6	209	270
8	618	-715
10	205	-306
12	411	476

0,11,L

1	827	972
3	742	927
5	500	-597
7	351	-448
9	570	669
11	494	542
13	312	-403

0,12,L

0	942	1090
2	196	161
4	693	-1117
8	859	1057
12	394	-472

0,13,L

1	473	-606
3	476	-625
7	280	415
9	499	-595
11	299	-331

0,14,L

0	721	-918
4	422	548
6	334	-407
8	580	-747

0,15,L

1	366	450
3	665	880
5	233	-332
7	230	-228
9	266	328
11	323	314

0,16,L

0	495	584
4	481	-651
8	314	370

0,17,L

1	333	-446
3	275	-371
5	297	326

0,18,L

0	407	-520
4	369	443

0,19,L

1	376	414

0,20,L

0	370	452

1,0,L

1	1781	2826
3	327	-611
5	154	-709
7	367	819
9	352	670
11	532	-815
13	371	-422

1,1,L

2	624	839
4	1197	-1159
6	1374	846
8	305	-372
10	993	-910
14	768	533
16	274	-128

1,2,L

1	2289	-2936
3	211	660
5	469	872
7	355	-561
9	427	-580
11	823	945
13	439	460

TABLE 3.20 (continued)

	1,3,L	
4	479	-421
6	2085	-1652
10	915	613
14	582	-497
	1,4,L	
1	870	975
3	2412	-2118
5	1086	-1017
7	972	888
11	556	-568
13	351	-338
15	384	401
	1,5,L	
2	1788	-1780
4	1168	1041
6	1901	1886
8	337	285
10	875	-964
14	744	723
	1,6,L	
1	1428	-1245
3	1447	1286
5	594	645
7	1028	-1042
9	662	-855
11	486	429
13	466	452
15	308	-236
	1,7,L	
2	1943	1961
4	545	339
6	1383	-1447
10	714	857
14	467	-466
	1,8,L	
1	313	-252
3	392	-417
5	1372	-1405
7	639	721
9	738	846
11	240	-281
13	297	-430
	1,9,L	
2	1032	-1070
4	517	-613
6	1435	1693
10	505	-651
14	399	433
	1,10,L	
1	239	-195
3	504	508
5	843	1034
7	496	-568
9	316	-434
11	207	208
	1,11,L	
2	752	908
4	176	168
6	568	-740
8	633	735
10	414	496
	1,12,L	
1	[illegible]	987
3	590	-664
5	517	-611
7	653	807
9	450	573
	1,13,L	
2	[illegible]	-1015
10	672	-478
	1,14,L	
1	460	-626
3	617	1037
7	308	-440
9	329	-382
11	359	412
	1,15,L	
2	606	794
6	219	-204
10	577	594
	1,16,L	
1	268	321
3	400	-581
5	265	-235
9	344	359
	1,17,L	
2	572	-729
6	387	495
	1,18,L	
1	320	-412
3	352	367
5	380	514
7	343	-361
	1,19,L	
2	455	520
	1,20,L	
1	285	299
3	262	-250
	2,0,L	
0	3105	2290
2	475	-435
4	3270	-1970
6	300	-245
8	1288	1067
12	1128	-1090
16	597	462
	2,1,L	
1	1081	-1807
3	935	286
5	274	674
7	964	1166
9	392	-597
11	411	-547
13	615	680
15	534	488
	2,2,L	
0	3414	-2894
2	1387	1347
4	1332	990
6	1005	843
8	1394	-1117
12	1025	923
14	423	408
16	523	-433
	2,3,L	
1	1021	1149
3	2390	2250
5	1145	-1163
7	625	-715
9	889	908
11	551	614
13	428	-361
15	491	-571
	2,4,L	
0	2121	2069
2	2298	2520
4	2173	-2001
8	1030	951
12	450	-465
	2,5,L	
1	251	216
3	2804	-2470
5	1411	1270
7	1422	1425
9	480	-529
11	352	-420
13	402	458
15	450	406

TABLE B.20 (continued)

	2,6,L	
4	1945	2162
6	564	-496
8	1042	-1155
10	305	344
12	300	325
	2,7,L	
1	908	821
3	667	753
5	891	-919
7	735	-829
9	726	793
13	403	-497
15	243	-204
	2,8,L	
0	381	524
2	423	-485
4	326	-428
8	965	1140
10	205	-240
12	462	-517
	2,9,L	
1	1452	-1532
3	414	-424
5	587	721
7	485	484
9	568	-691
11	424	-482
13	230	286
	2,10,L	
0	875	-1008
2	247	290
4	699	796
8	560	-624
10	406	-432
12	378	444
	2,11,L	
1	453	623
3	679	855
5	618	-752
7	346	-337
9	231	238
11	335	389
13	351	-329
	2,12,L	
0	923	1030
4	899	-1056
8	700	840
12	459	-554
	2,13,L	
1	528	-604
3	538	-663
7	221	253
9	316	-432
11	267	-340
	2,14,L	
0	897	-1053
4	916	1185
8	603	-768
	2,15,L	
1	509	623
3	518	668
5	205	-234
7	364	-542
9	406	449
	2,16,L	
0	462	560
4	527	-689
8	358	395
	2,17,L	
1	364	-464
3	387	-496
5	283	391
	2,18,L	
0	357	-444
4	273	309
	2,19,L	
1	326	373
5	252	-252
	2,20,L	
0	521	551
	3,0,L	
1	345	230
3	635	-924
5	1305	-1565
7	1240	1192
11	532	-662
13	511	-531
15	375	295
	3,1,L	
2	3905	-3730
4	170	-76
6	1492	1316
8	426	-352
10	930	-997
12	407	440
14	484	368
	3,2,L	
1	470	-673
3	1179	1334
5	1193	1281
7	569	-621
9	560	-644
11	384	481
13	365	347
	3,3,L	
2	663	696
4	752	-581
6	1391	-1407
8	656	589
10	842	805
12	378	-392
14	748	-695
	3,4,L	
1	697	686
3	639	563
7	705	719
9	799	701
11	521	-537
13	407	-388
15	280	271
	3,5,L	
2	546	-809
4	1020	-991
6	466	527
10	790	-956
14	641	688
	3,6,L	
1	1362	-1296
3	879	836
5	718	579
7	826	-854
9	607	-561
11	287	299
13	392	493
	3,7,L	
2	1473	1515
4	443	478
6	1283	-1446
8	329	-352
10	415	528
14	436	-521
	3,8,L	
1	1013	992
3	1102	-1211
5	1303	-1331
7	809	900
9	566	675
11	222	-306
13	231	-333

TABLE B.20 (continued)

3,9,L

4	220	241
6	1186	1428
8	207	-177
10	488	-691
14	291	360

3,10,L

1	908	-998
3	545	617
5	551	622
7	1092	-1351
9	412	-510
11	365	449
13	236	304

3,11,L

2	869	1052
6	904	-1077
10	452	622

3,12,L

1	369	449
3	845	-1031
5	585	-701
7	304	364
9	526	636
11	528	-420

3,13,L

2	484	-604
4	269	300
6	333	377
10	289	-372

3,14,L

1	372	-514
3	542	790
5	356	408
9	335	-407
11	325	357

3,15,L

2	515	678
4	203	-264
10	533	529

3,16,L

1	360	457
3	290	-436

3,17,L

2	667	-795
6	679	535

3,18,L

1	350	-380
3	259	226
5	364	455
7	367	-370

3,19,L

2	366	360

3,20,L

1	341	279

4,0,L

0	2157	-2202
2	1159	-1064
4	975	-823
8	708	633
12	768	-786

4,1,L

1	1853	-1982
3	1601	-1828
5	300	511
7	400	509
9	935	-951
11	580	-644
13	560	614
15	427	376

4,2,L

0	1963	-1882
2	1494	-1507
4	933	1016
8	1032	-1144
12	614	606

4,3,L

1	1776	1721
3	1944	1952
5	972	-1006
7	687	-772
9	1293	1348
11	405	406
13	441	-524
15	565	-446

4,4,L

0	1439	1768
2	285	377
4	1967	-2149
8	1431	1583
12	395	-497

4,5,L

1	1357	-1222
3	2254	-2184
5	1682	1589
7	631	669
9	847	-953
11	261	-308
13	274	385
15	418	398

4,6,L

0	1200	-1274
2	845	-695
4	1415	1542
6	703	-733
8	823	-1053
12	512	640

4,7,L

1	356	285
3	982	957
5	589	-613
7	451	-444
9	645	770
11	486	531
13	326	-356

4,8,L

0	1823	1807
4	523	-617
6	416	-415
8	772	858
10	233	382
12	430	-562

4,9,L

1	823	-883
5	363	406
7	906	994
11	253	-352
13	281	292

4,10,L

0	836	-979
2	427	550
4	582	723
8	628	-697
12	456	518

4,11,L

1	684	790
3	224	272
5	319	-427
7	618	-686
11	377	461
13	313	-277

4,12,L

0	785	943
2	233	-234
4	839	-1029
6	318	456
8	325	454
12	519	-573

TABLE B.20 (continued)

4,13,L

3	376	-469
5	894	1065
7	318	332
9	392	-465

4,14,L

0	778	-968
4	835	1085
6	254	242
8	509	-616

4,15,L

1	495	553
3	449	520
5	471	-524
7	422	-504
9	374	445

4,16,L

0	583	737
4	305	-408
8	457	515

4,17,L

1	386	-495
3	358	-476
7	393	347

4,18,L

0	545	-542
4	342	329

4,19,L

3	304	327

4,20,L

0	599	519

5,0,L

1	520	-515
3	971	-939
5	1181	-990
7	1177	949
9	993	845
11	538	-507
13	308	-255
15	379	276

5,1,L

2	2511	-2559
4	888	-824
6	1904	1901
10	1174	-970
14	524	470

5,2,L

1	1719	-1440
3	342	395
5	1122	963
7	835	-816
9	714	-686

5,3,L

2	1312	1463
4	1033	950
6	254	-314
8	308	238
10	1174	1055
14	300	-403

5,4,L

1	1331	1185
3	344	-277
5	713	-603
7	757	656
9	707	530
11	530	-492
13	533	-499

5,5,L

2	1855	-1921
4	299	-260
6	723	820
10	599	-546
14	528	488

5,6,L

1	971	-765
3	800	778
5	1201	1118
7	659	-645
9	539	-474
11	446	387
13	441	467
15	437	-348

5,7,L

2	921	962
4	618	-574
6	1224	-1276
8	365	377
10	623	741
14	581	-512

5,8,L

1	1731	1602
3	780	-806
5	573	-501
7	940	946
9	513	620
11	578	-578
13	476	-440

5,9,L

2	813	-870
4	313	394
6	1059	1046
10	451	-535
14	431	378

5,10,L

1	727	-683
3	1158	1186
5	854	784
7	652	-685
9	538	-506
11	587	633
13	324	336

5,11,L

2	887	889
6	1033	-1090
8	893	-945
10	377	396

5,12,L

1	631	662
3	753	-782
5	609	-663
9	285	304
11	340	-310

5,13,L

2	645	-665
6	644	624
10	613	-627

5,14,L

1	696	-745
3	282	270
7	266	-183
9	508	-508
11	366	323

5,15,L

2	654	651
4	280	-287
6	502	-506
10	549	466

5,16,L

1	412	511
3	458	-433
5	301	-292
7	387	332
9	305	243

5,17,L

2	633	-614
6	574	537

TABLE B.20 (continued)

	5,18,L	
3	276	135
5	438	411
	5,19,L	
2	395	341
4	325	193
	6,0,L	
0	563	653
4	711	-660
6	554	502
8	1155	1074
12	355	-315
	6,1,L	
1	1067	-878
3	1757	-1707
5	1567	1566
9	1009	-1008
11	904	-645
13	346	311
15	483	444
	6,2,L	
0	1497	-1361
4	1799	1830
6	660	-570
8	850	-958
12	572	516
	6,3,L	
1	738	639
3	1701	1571
5	420	-481
7	756	-798
9	647	710
11	617	604
15	398	-370
	6,4,L	
0	1518	1440
2	216	101
4	1545	-1560
8	982	1054
10	317	-268
12	705	-743
	6,5,L	
1	881	-885
3	1459	-1311
5	308	328
7	533	470
9	831	-825
11	514	-528
15	350	330
	6,6,L	
0	1239	-1271
2	967	-807
4	694	740
6	601	509
8	879	-847
12	619	708
	6,7,L	
1	1003	928
3	424	428
5	953	-843
7	881	-752
9	394	355
11	414	451
13	421	-409
	6,8,L	
0	1759	1689
4	1465	-1431
6	352	-379
8	674	639
12	630	-625
	6,9,L	
1	940	-1003
3	279	-251
5	769	796
7	591	538
9	293	-238
11	292	-326
13	423	300
	6,10,L	
0	1743	-1778
2	491	465
4	725	758
8	669	-742
12	782	737
	6,11,L	
1	818	766
3	240	189
5	843	-854
7	533	-557
11	413	414
	6,12,L	
0	851	875
4	722	-702
8	440	479
12	376	-341
	6,13,L	
1	401	-460
3	509	-535
5	792	815
7	821	921
11	380	-303
	6,14,L	
0	516	-595
2	391	-464
4	456	505
8	408	-457
	6,15,L	
3	542	557
5	342	-350
7	408	-369
9	400	353
	6,16,L	
0	620	624
4	400	-354
8	575	469
	6,17,L	
1	337	-327
5	299	280
7	446	362
	6,18,L	
0	639	-538
4	542	499
	6,19,L	
1	503	431
3	451	390
	7,0,L	
1	1335	1304
3	446	-452
5	1441	-1299
7	937	995
9	633	591
13	563	-716
15	427	302
	7,1,L	
2	1324	-1272
6	1476	1443
10	1021	-741
14	53[illegible]	[illegible]
	7,2,L	
1	306	-356
3	813	729
5	862	892
7	856	-849
9	562	-544
11	955	917
15	531	-313
	7,3,L	
2	616	711

TABLE B.20 (continued)

	7,3,L	
4	563	537
6	903	-855
10	926	937
14	441	-436
	7,4,L	
1	954	964
3	1711	-1725
5	849	-847
7	802	803
9	445	402
11	772	-689
13	428	-349
	7,5,L	
2	1490	-1508
6	1047	1097
10	703	-609
14	356	332
	7,6,L	
1	1631	-1611
3	828	857
5	703	708
7	492	-531
9	441	-369
11	463	436
13	475	379
	7,7,L	
2	1484	1437
6	578	-612
10	505	577
14	430	-418
	7,8,L	
1	863	824
3	803	-824
5	731	-727
7	434	438
11	435	-435
13	514	-475
	7,9,L	
2	564	-559
6	572	620
10	532	-536
	7,10,L	
1	692	-656
3	626	646
5	754	774
7	304	-146
9	657	-734
11	363	416
13	398	341
	7,11,L	
2	706	676
6	782	-776
10	550	656
	7,12,L	
1	756	805
7	515	518
9	423	493
11	406	-400
	7,13,L	
2	850	-930
6	856	908
10	570	-617
	7,14,L	
1	380	-373
3	614	555
5	302	281
7	526	-528
	7,15,L	
2	796	836
6	742	-783
	7,16,L	
1	591	586
3	446	-374
5	613	-526
7	322	300
	7,17,L	
2	347	-368
6	423	404
	7,18,L	
1	325	-255
5	347	356
	8,0,L	
0	347	433
2	902	898
4	1557	-1557
8	905	733
12	545	-402
	8,1,L	
1	734	-741
3	936	-987
5	1089	1027
7	882	926
9	367	-457
11	402	-376
	8,2,L	
0	1322	-1298
4	1605	1697
6	346	299
8	715	-813
12	606	475
	8,3,L	
1	1225	1211
3	904	932
5	775	-790
7	539	-635
9	394	239
11	481	501
	8,4,L	
0	1981	1988
4	1169	-1280
8	607	664
12	778	-704
	8,5,L	
1	737	-668
3	293	-281
5	600	637
7	560	519
9	695	-600
11	546	-605
13	473	410
	8,6,L	
0	1233	-1254
2	369	371
4	918	937
8	809	-770
12	795	843
	8,7,L	
1	1026	971
3	955	889
5	491	-487
7	648	-649
9	553	510
11	510	606
13	320	-301
	8,8,L	
0	1645	1565
4	974	-1009
8	698	817
12	592	-616
	8,9,L	
1	1004	-936
3	625	-580
5	353	328
7	401	368
9	582	-614
11	535	-482
13	463	375

TABLE B.20 (continued)

	8,10,L	
0	1548	-1403
4	823	941
8	498	-575
12	374	358
	8,11,L	
1	756	682
3	440	375
5	623	-745
7	356	-380
9	379	357
11	316	215
	8,12,L	
0	578	673
4	482	-484
8	513	535
	8,13,L	
1	473	-415
3	778	-777
5	343	414
7	491	494
9	314	-255
	8,14,L	
4	553	375
8	463	-448
	8,15,L	
3	392	341
5	445	-483
7	483	-449
	8,16,L	
0	373	296
4	777	-654
	8,17,L	
1	383	-391
3	329	-312
5	385	375
	8,18,L	
0	866	-754
4	556	478
	9,0,L	
1	1047	1051
3	1571	-1553
5	1113	-1158
7	694	692
9	605	582
11	681	-489
13	689	-460
	9,1,L	
2	656	-689
4	515	549
6	1293	1328
10	662	-643
14	740	487
	9,2,L	
1	567	-476
3	872	890
5	849	863
7	722	-740
9	513	-520
11	640	634
13	622	491
	9,3,L	
2	1089	1079
4	398	-397
6	1061	-1053
10	526	595
	9,4,L	
1	1167	1237
3	585	-625
5	1006	-992
7	403	368
9	578	644
	9,5,L	
2	1042	-1043
6	557	586
10	677	-706
	9,6,L	
1	681	-714
3	770	775
5	350	444
7	410	-398
9	348	-342
11	561	495
13	432	372
	9,7,L	
2	1054	1119
6	471	-487
10	534	510
	9,8,L	
1	595	506
3	865	-862
7	531	504
9	331	331
11	433	-410
13	350	-283
	9,9,L	
2	1068	-906
6	410	485
10	733	-768
	9,10,L	
1	1112	-1071
3	512	527
5	484	475
7	501	-462
9	521	-554
	9,11,L	
2	953	1003
6	551	-548
10	728	734
	9,12,L	
1	366	241
3	550	-579
5	567	-589
7	512	471
9	511	503
	9,13,L	
2	754	-777
6	727	850
10	412	-367
	9,14,L	
3	502	474
5	568	568
7	364	-429
	9,15,L	
2	489	503
6	559	-585
	9,16,L	
7	434	341
	10,0,L	
0	1263	1257
4	1569	-1605
8	710	715
12	758	-476
	10,1,L	
3	520	-577
5	935	1056
7	732	775
	10,2,L	
0	1051	-1066
4	1175	1214
8	756	-755
12	771	587

TABLE B.20 (continued)

10,3,L

1	1050	1002
5	952	-978
7	543	-529
9	407	452
13	465	-337

10,4,L

0	1747	1655
4	566	-619
6	357	-356
8	795	815
12	751	-648

10,5,L

1	1441	-1394
3	493	-418
5	421	442
7	436	484
9	433	-465
11	576	-554
13	422	350

10,6,L

0	1611	-1565
4	1054	1051
8	745	-754
12	563	570

10,7,L

1	1120	1154
3	1250	1244
7	521	-485
9	468	436
11	495	484

10,8,L

0	952	872
4	677	-691
8	637	652
12	390	-461

10,9,L

1	422	-373
3	836	-794
5	469	405
9	621	-662
11	547	-418

10,10,L

0	336	-330
4	526	571
8	612	-601

10,11,L

1	462	420
3	617	600
7	342	-287
9	527	537

10,12,L

4	694	-727
8	376	507

10,13,L

1	471	-420
3	517	-532
5	352	368
9	450	-250

10,14,L

0	443	-366
4	884	842
8	506	-423

10,15,L

1	362	340
5	525	-494
7	371	-336

10,16,L

0	629	577
4	574	-554

10,17,L

1	449	-403
3	500	-399

11,0,L

1	911	972
3	850	-927
5	552	-597
7	435	448
9	767	689
11	773	-547

11,1,L

2	634	-661
6	721	727
8	475	518
10	567	-546

11,2,L

1	1242	-1202
3	849	865
5	602	638
7	602	-730
9	718	-637

11,3,L

2	1129	1098
4	297	-342
6	1189	-1211
10	524	533

11,4,L

1	768	736
3	802	-825
5	649	-668
7	562	588
9	590	599

11,5,L

2	993	-946
6	647	630
10	643	-625

11,6,L

1	475	-466
3	641	607
5	428	271
7	614	-667
9	459	-470
11	495	435

11,7,L

2	920	908
6	392	-399
10	686	640

11,8,L

1	592	577
3	410	-313
5	387	-390
9	441	425

11,9,L

2	1296	-1250
6	597	604
10	398	-507

11,10,L

1	406	-318
3	606	613
5	442	461

11,11,L

2	794	874
6	595	-587
10	479	454

11,12,L

3	710	-595
5	650	-590
7	524	443
9	427	326

11,13,L

2	407	-415
6	484	486

TABLE B.20 (continued)

11,14,L		
1	460	-372
3	406	308
5	674	593
7	541	-457
11,15,L		
2	411	273
6	506	-477
12,0,L		
0	1076	1090
4	1028	-1117
6	341	201
8	1094	1057
12	732	-472
12,1,L		
1	508	-590
3	552	-554
5	590	647
7	480	486
13	556	353
12,2,L		
0	1064	-1133
4	697	731
6	345	-333
8	486	-495
12	598	463
12,3,L		
1	609	603
3	350	330
5	409	-410
11	551	506
12,4,L		
0	845	867
2	379	-382
4	369	-393
8	518	533
12,5,L		
1	845	-885
7	755	635
12,6,L		
0	1286	-1317
4	715	710
8	764	-787
12,7,L		
1	667	610
3	593	557
5	561	-498
7	562	-468
9	581	581
12,8,L		
0	468	419
4	868	-855
8	672	664
12,9,L		
1	576	-488
3	1059	-979
5	791	694
7	395	390
9	560	-561
11	393	-236
12,10,L		
4	763	761
8	477	-484
12,11,L		
1	501	455
3	868	863
5	391	-328
7	430	-403
12,12,L		
0	691	596
4	728	-640
8	474	416
12,14,L		
0	759	-632
4	420	487
12,16,L		
0	402	445
13,0,L		
1	581	606
3	579	-625
9	587	595
13,1,L		
2	1081	-1120
6	517	600
10	512	-516
13,2,L		
1	547	-568
3	865	914
5	622	657
7	590	-583
9	566	-537
13,3,L		
2	1142	1209
6	983	-1085
10	631	605
13,4,L		
1	545	543
3	557	-508
5	649	-649
7	724	777
9	475	453
13,5,L		
2	803	-770
6	933	908
10	558	-509
13,6,L		
1	675	-601
3	614	581
5	504	518
7	440	-408
13,7,L		
2	520	453
6	616	-623
10	478	415
13,8,L		
1	518	444
3	390	-470
5	448	-428
13,9,L		
2	798	-752
6	418	462
13,10,L		
7	476	-409
13,11,L		
2	578	513
6	553	-539
13,12,L		
1	645	564
5	464	-456
7	490	367
13,13,L		
2	525	-462
4	426	-201
6	502	477
13,14,L		
1	529	-477

TABLE B.20 (continued)

13,14,L		
5	603	503
13,15,L		
2	676	442
14,0,L		
0	766	918
4	514	-548
8	734	747
14,1,L		
1	736	-625
3	451	-498
9	571	-542
14,2,L		
0	407	-398
4	430	383
8	577	-546
14,3,L		
1	710	655
3	386	386
5	637	-624
7	472	-445
14,4,L		
0	469	412
2	432	-359
4	657	-697
8	440	394
14,5,L		
1	864	-756
3	479	-397
5	774	687
7	476	463
14,6,L		
0	979	-987
4	653	628
8	610	-529
14,7,L		
5	564	-525
7	553	-544
9	503	474
14,8,L		
0	600	496
4	806	-716
8	686	571
14,9,L		
3	627	-684
7	563	525
14,10,L		
0	652	-506
2	545	-518
4	660	663
8	567	-444
14,11,L		
3	571	463
5	596	-407
14,12,L		
0	1076	883
4	502	-394
14,13,L		
1	652	-461
14,14,L		
0	626	-666
15,0,L		
1	432	450
3	786	-880
5	427	-332
9	523	328
15,1,L		
2	1036	-1108
6	446	483
15,2,L		
1	381	-465
3	426	482
15,3,L		
2	642	680
6	678	-714
15,4,L		
5	502	-525
15,5,L		
2	590	-391
6	1014	941
15,6,L		
5	695	626
15,7,L		
2	768	686
6	831	-724
15,8,L		
1	919	761
3	556	-484
7	553	396
15,9,L		
2	587	-546
6	617	536
15,10,L		
1	817	-684
7	459	-382
15,11,L		
6	463	-399
15,12,L		
1	630	541
15,13,L		
2	539	-293
16,0,L		
0	529	554
4	608	-651
16,1,L		
1	666	-652
5	443	368
16,2,L		
0	851	-737
4	700	683
8	725	-578
16,3,L		
1	731	662
3	573	505
5	550	-436
7	501	-481
9	525	325
16,4,L		
0	1079	981
4	694	-711
8	618	662
16,5,L		
3	576	-531
5	724	621

TABLE B.20 (continued)

16,7,L		
5	546	-497
16,8,L		
0	477	305
16,10,L		
0	1025	-831
4	607	476
16,12,L		
0	644	717
17,0,L		
1	542	446
3	434	-371
17,1,L		
2	550	-508
17,2,L		
5	458	414
17,3,L		
6	534	-462
17,4,L		
3	434	-372
5	563	-523
17,5,L		
2	619	-525
6	721	660
17,6,L		
1	513	-492
7	625	-429
17,7,L		
2	898	795
6	803	-611
17,8,L		
3	490	-414
5	547	-322
17,10,L		
1	526	-404
18,0,L		
0	509	520
4	530	-443
18,1,L		
3	690	-488
7	565	341
18,2,L		
0	966	-869
4	529	543
18,3,L		
1	467	392
18,4,L		
0	676	548
4	697	-576
18,6,L		
4	502	437
18,7,L		
3	692	455
18,8,L		
0	666	439
4	819	-505
19,1,L		
2	569	-436
19,2,L		
1	720	-437
19,3,L		
2	658	419
19,5,L		
2	609	-477
19,6,L		
3	655	456
20,0,L		
0	673	452
20,2,L		
0	579	-452

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