SOME STUDIES on CRYSTAL and MOLECULAR STRUCTURE.

A thesis submitted for the degree of

Doctor of Philosophy

at the University of Glasgow

by

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Summary.

The work which is described in this thesis is principally concerned with X-ray crystallography. Some other work, which involved molecular orbital calculations, was also carried out and is described in Appendix I.

Three compounds in all were studied by X-ray diffraction techniques, and the results of these investigations are summarised below.

(1) Dimethylcorticrocin: This compound, which has the formula $CH_3O.CO.(CH = CH)_6.COOCH_3$, and which is the dimethyl ester of an acid isolated from a fungus, crystallises as yellow needles from chloroform. The crystals are triclinic, space goup $C_1^1 - P\,1$ or $C_i^1 - P\,\bar{1}$,* and the unit cell dimensions are a = 9.06, b = 7.52, c = 6.07 Å; α = 104.8°, β = 104.0°, γ = 103.7°. Unfortunately due to all the crystals which could be obtained being twinned, only the projection on (001) was studied. However this has been sufficient to show that the compound adopts the trans configuration throughout the molecule.

(2) n - Dodecylammonium Chloride: The samples of this compound were prepared, and all the photographs taken, in Sweden. Preliminary work was carried out on it in this department by C.J. McCron. The crystals are monoclinic, space group $C_2^2 - P2_1$, and the unit cell dimensions are a = 5.68, b = 7.16, c = 17.86 Å; β = 92°16. The projections on (010) and (100) have been studied and sub-cell theory has been applied to the calculation of the structure factors. The figures of merit are 15.8% and 21.2% respectively, the higher value being due to difficulties which were encountered in that projection.

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ADD

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The bond lengths etc. have been calculated and no abnormalities discovered. The standard deviations of these bond lengths are also given.

(3) L - Serine Phosphoric acid: This compound is an important amino acid which possesses an especially interesting feature in the phosphate group. The crystals are orthorhombic, space group $D_2^4 - P2_12_12_1$, and the unit cell dimensions are a = 7.79, b = 10.24, c = 9.09 Å. The projections on (010) and (100) have been studied and a variety of methods was employed in an attempt to affect an analysis of the structure. Unfortunately none of these was successful. Consequently complete three-dimensional data have been collected and a three-dimensional Patterson synthesis has been computed on X-RAC. It is hoped that this will lead to a complete analysis of the structure being possible.

In Appendix I is an account of some molecular orbital calculations which were performed on dimethylcorticrocin. These show that the molecule has a large amount of resonance energy and that this leads to the formal double bonds being considerable longer, and the formal single ones being considerably shorter, than "pure" double or single bonds respectively. The bond orders are compared with those in the corresponding conjugated hydrocarbon and a discussion of probably reactivity is also given.

Appendix II contains a short note on the re-determination of the film absorbtion factor for Ilford Industrial G film with Cu K_α radiation.

Acknowledgements.

I should like to thank my two supervisors, Professor J.M. Robertson and Dr. V. Vand,[*] for their generous help and cooperation during the progress of this research, and to thank Dr. T.H. Goodwin, who gave me a great deal of useful advice on how to write up the molecular orbital calculations.

My gratitude is due also to Professor Ray Pepinsky and his staff at the Pennsylvania State University who evaluated the sections of a three-dimensional Patterson synthesis on X-RAC, and to the Department of Scientific and Industrial Research for their maintenance grant, during the tenure of which this work was carried out.

[*] Now at the Pennsylvania State University, State College, Pa., U.S.A.

Introduction.

1. General:

It is less than fifty years since X-rays were first employed to study matter in the solid state, and during this period our knowledge of the intimate structure of solids has increased enormously. Before the advent of X-ray crystal analysis and other allied techniques it was not possible to make any direct study of the details of molecular structure as it exists in the solid state. Chemical studies could, in general, only be made if the solids were first vapourised, melted, or dissolved in a suitable solvent, and there could be no guarantee that this had not brought about some fundamental change. This position has now been completely changed due to these newer methods and, in certain instances, our ideas concerning the solid state revolutionised. Also certain theories, such as that of hydrogen bonding, have been confirmed in a way which would not have been possible by any other known method.

The study of organic crystals by these methods has enabled us to confirm very nearly all the structural deductions of the organic chemist and to differentiate between structures of equal chemical plausibility.[1, 2.] Further than this, accurate measurements have been made of a whole range of organic molecules,[3, 4.] and attempts are now being made to elucidate the structures of molecules so complex that they have not yet yielded to the ordinary methods of chemistry.[1, 5, 6, 7.]

It is also a consequence of these studies that nowadays a great deal of attention is being paid to the more theoretical aspects of chemistry, since the theoreticians have now got a sound basis on which to work.[8]

2. Methods of Structure Solution:

When we record the diffraction pattern of a crystal the knowledge of the relative phases of the reflections is lost. Consequently the process of structure solution cannot in general be direct. Various methods[3,9,10] have been devised to assist in overcoming this difficulty, but none of these is infallible. An account of some which found application in the present work is given below.

2 (a). Trial and Error:

This is the simplest and oldest method. It consists of postulating a set of atomic positions which conform with space group requirements and which are chemically plausible. A general survey of the intensities is usually of great assistance in this.[11] The structure factors which are calculated on the basis of these positions (F_c) are then compared with the observed ones (F_o), which are obtained from the measured intensities. The overall agreement is tested by means of the discrepancy or figure of merit (R) which is given by,

$$R = \frac{\Sigma\,|F_o - F_c|}{\Sigma\,|F_c|} \times 100\%$$

It is not possible to lay down cast-iron rules about the maximum acceptable value of R. The only reliable guide is individual experience.

We can only use this method when dealing with fairly simple or regular structures. If it were applied as outlined above to complex ones it would involve a vast amount of computational work. The method has, however, been used with great success in many instances.[3, 9.]

2 (b) Utilisation of the Patterson Synthesis:

In this treatment we use only the observed data in order to evaluate a function P (UVW) which gives information about interatomic vectors. It is normally called the Patterson[12] synthesis and can be represented by the Fourier series,[13]

$$P(UVW) = \frac{1}{V_c} \sum_{-\infty}^{\infty} h \sum_{-\infty}^{\infty} k \sum_{-\infty}^{\infty} \ell \left| F(hk\ell) \right|^2 \cos 2\pi (hU + kV + \ell W)$$

Evaluation of this function for a unit cell of N atoms leads to N^2 peaks, which represent weighted interatomic vectors and of which N are at the origin, so that there will normally be a great deal of overlapping due to the limited resolving power of the wavelengths employed. Consequently various modifying functions [9] have been proposed in attempts to improve the resolution, which will obviously be much poorer if the function is evaluated in only one or two dimensions instead of three.

It is possible in the course of structure analysis to employ the vector map which this method gives, because, as Wrinch first showed, we can always recover the fundemental set of points from its vector set. [9] In theory, therefore, it should always be possible to interpret a Patterson synthesis. Unfortunately, however, due to the complication of non-resolution of peaks, which has already been discussed, a Patterson synthesis does not yield a set of points, and a further difficulty arises from the fact that two or more fundemental sets of points, which Patterson has called homometric, can have the same weighted vector set. This means that we cannot always obtain the vector set of points from the map and, when we can, we cannot distinguish between homometric pairs from the map alone.

When this method is employed in practice our task is somewhat simplified because we can always make use of additional pieces of information, such as bond lengths and known configurations. Nevertheless even with this help success cannot be guaranteed, although it seems probable that trial and error methods based on inspection of the Patterson synthesis are the most powerful available at present. The usual application of the method are: [9]

(1) to locate a heavy atom, whence the analysis may proceed by Fourier methods if we use the phase constants calculated for this atom as a first approximation. [14, 15] (see Section 3 (a))

(2) to determine the fundemental set of points from superposition methods. [16, 17.] This process may be assisted by the presence of a heavy atom. [5]

(3) to determine interatomic vectors from known interatomic distances. [18.]

2 (c) Relationships Between Structure Factors.

In a crystal the electron density can never be negative and this alone is sufficient to impose limitations on the magnitudes and phases of the structure factors. [9, 19, 20.] Hence it is possible to derive relationships between structure factors which are known as Harker-Kasper inequalities. When only a centre of symmetry is present the most powerful of these is, [23]

$$\left|U_H \pm U_K\right| \leqslant \left(1 \pm U_{H+K}\right)\left(1 \pm U_{H-K}\right)$$

Here H and K refer to Miller indices and the U's to the sharpened structure factors on a unitary scale (i.e. F(000) = 1). When further elements of symmetry are present more inequalities can be deduced.[9, 13.]

Statistical relationships between the signs (S) of the structure factors in centrosymmetrical crystals have also been discussed.[21, 22, 23.] If the unitary structure factors involved are about 1,5 times the root mean square value then the relationship,

$$S_H = \overline{S(S_{K_i} \cdot S_{H+K_i})}$$

is probably, but not necessarily, true.

Unfortunately the practical utility of these relations is limited because of their insistance on strong unitary structure factors. In complicated structures, where the method would be of greatest use, the average value of the structure factors is small and there are few much greater than average. Nevertheless successful use has been made of the method.[23, 24.]

3. Methods of Refining Atomic Parameters:

In this section we shall assume that approximate atomic coordinates have been arrived at by some means or another and we shall consider how these can be improved.

3. (a) The F_o Synthesis:[9]

The electron density (ρ) in a crystal is periodic and can be represented by the Fourier series,

$$\rho(xyz) = \frac{1}{V_c} \sum_{-\infty}^{\infty} h \sum_{-\infty}^{\infty} k \sum_{-\infty}^{\infty} l \left| F_o(hkl) \right| \cos 2\pi \left\{ \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} - \alpha(hkl) \right\}$$

which can be evaluated in one, two, or three dimensions.

In practice one evaluates the series using observed coefficients (F_o (hkl)), and phase angles (α(hkl)) calculated for the postulated structure. If this has not been too wide of the mark a density distribution will be obtained which should enable us to choose improved coordinates. The process is now one of successive approximation to the true structure.

If there is a centre of symmetry present the complexity of the problem is greatly reduced since, if the centre of symmetry is chosen as origin, the phase angles can only have the values 0 or π. In these cases the principal thing is the determination of the correct signs and the refinement can proceed much more rapidly.

Even if all the phase angles included in the synthesis are correct, the coordinates normally obtained from an F_o synthesis are not the true ones. This is because the F_o values are subject to random errors of measurement as well as to certain systematic ones, and because the series may not contain all terms of appreciable magnitude due to the limitations of the wavelengths employed. It is possible to correct for errors caused by series termination and absorption, but not for extinction and random errors, although their effects may be minimised.

3. (b) The (F_o - F_c) Synthesis: [9,25,26]

We compute this synthesis from a Fourier series similar to that given in section 3. (a), but with (F_o - F_c) replacing F_o as its coefficients and normally only in two dimensions. It has properties which make it particularly useful in the final stages of crystal structure analysis as a complete picture of the causes of discrepancies between F_o and F_c is obtained.

From the resulting difference map we are able to decide on the magnitude and direction of the required atomic shifts, which are in the direction of the steepest ascents and which eliminate errors due to termination of series. Errors due to wrongly assumed atomic scattering factors and anisotropic thermal motion are also detectable as well as peaks due to hydrogen atoms. In the recent very accurate study of salicylic acid[27] the effects of bonding were even allowed for.

It should be emphasised that several $(F_o - F_c)$ syntheses are normally required before all these corrections can be properly allowed for, and that fine details will only show up if the initial intensities have been measured with sufficient accuracy. In the most accurate two dimensional work Geiger-counters are used for this purpose.[26, 27, 28.]

4. Sub-Cell Theory:[29, 30.]

Regions of structural periodicity are often to be found within a molecule, e. g. hydrocarbon chains and proteins. Thus, in the unit cell (axes a_k) of their crystals, there may be one or more regions where the electron density is periodic and can be described by a sub-cell (axes A_j). The suffixes mean that the symbols refer to all three axes, k being used for the main-cell and j for the sub-cell.

The equivalent positions in a sub-cell region are given by,

$$x_k = u_k + t_j A_j + X_j$$

where x and X refer to main and sub-cell parameters respectively,

t_j enumerates the required sub-cell, and u_k gives the coordinates of the nearest corner of the block-shaped sub-cell region referred to the main-cell origin. The centre of gravity (x_m) referred to the main cell origin is given by the similar expression,

$$x_m = u_k + \tfrac{1}{2} \sum (N_j - 1)\, A_j,$$

where $N_j\, A_j$ gives the edges of the sub-cell region.

The sub-cell region has finite volume and therefore each of its reciprocal lattice points will be surrounded by an interference function,

$$I = \prod_j \frac{\sin \pi N_j H_j}{\sin \pi H_j} ,$$

where H_j refers to the sub-cell Miller indices. To refer the sub-cell diffraction amplitude to the origin of the main-cell, I must be multiplied by a modulating factor exp. $(2\pi i\, x_m\, h_k)$, where h_k refers to the main-cell Miller indices. Then, since the contribution of the different parts of the main-cell to the structure factors are additive, we can write for F_h, the main cell structure factor, that $F_h = F_h^\circ + \prod_j \frac{\sin \pi N_j H_j}{\sin \pi H_j} F_H \cdot \exp\left(2\pi i\, x_m\, h_k\right)$, where F_h^o is the contribution of atoms not included in the sub-cell region and F_H is the structure factor of the sub-cell.

The main and sub-cell translations, diffraction orders, etc. can be interrelated by the same transformation matrix,[13] e.g.

$$(H_j) = (s_j^k)(h_k),$$

where s_j^k are the transformation coefficients.

When the number of non-sublattice atoms is small it is sometimes possible to use this theory in structure solution,[30, 31] and a suggestion has been made that it might be possible to apply it to some very large molecules.[3] In our case, however, it was employed only to simplify the structure factor calculations.

5. Accuracy of Crystal Structure Determination:[4]

In order to discuss quantitatively the results of our investigations we must have some means of assessing the experimental errors, and proper significance tests to apply before drawing conclusions from comparisons. These errors result chiefly from errors in the F_o values and imperfections in the model used to calculate the F_c's. Errors in cell dimensions and approximation errors in computation are normally of much less consequence.

Cruickshank[32] has studied these errors and has arrived at the following formulae for the standard deviation of electron density $\sigma(\rho_o)$ and of the x-coordinate of the n-atom $\sigma(x_n)$,

$$\sigma(\rho_o) = \frac{1}{V_c}\left\{\sum_3 (F_o - F_c)^2\right\}^{\frac{1}{2}}, \text{ and } \sigma(x_n) = \frac{2\pi\left\{\sum_3 h^2 (F_o - F_c)^2\right\}^{\frac{1}{2}}}{a V_c C_n}.$$

Here C_n represents the central curvature, $\frac{\partial^2 \rho}{\partial x^2}$, at the centre of the n-th atom, $\sum_3$ means summation over all the F_o's including $F(hkl)$ and $F(\overline{hkl})$, and the other symbols a, V_c, and h, have their usual significance. With regard to reflections which are accidentally absent, Cruickshank[32] suggests leaving them out if series termination has been corrected for by an F_c $\{$or the equivalent $(F_o - F_c)\}$ synthesis.

These standard deviations are liable to be an under-estimate if many of the phases are badly wrong. They also require modification in the following circumstances:

(1) The structure is non-centrosymmetrical. Each must then be

multiplied by two if the structure does not have a centrosymmetrical projection[33] on a plane or line and by a value between one and two if it does.[18]

(2) The number of unknown parameters is not much less than the number of independant F_o values.[34]

The standard deviation of a bond $\sigma(d_{12})$, provided that

$$\sigma(x_n) \approx \sigma(y_n) \approx \sigma(z_n),$$

is given by

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

since errors at right angles to the bond do not affect its length. The value of $\sigma(d_{12})$ will be greater, however, should the atoms concerned be related by symmetry.

It is often desirable to be able to compare bond lengths, either experimental with theoretical ones or two sets of experimentally derived ones. In the latter case let the determinations be l_1 and l_2 with estimated standard deviations $\sigma(l_1)$ and $\sigma(l_2)$ respectively. Then, following the treatment of Cruickshank and Robertson,[8] we can write that,

$$t_0 = \frac{(l_1 - l_2)}{\{\sigma^2(l_1) + \sigma^2(l_2)\}^{\frac{1}{2}}}$$

The following arbitrary conventions can now be applied to decide on the significance of any difference,

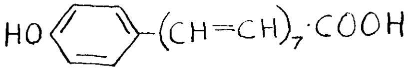
$t_o \leqslant 1{,}960$	not significant,
$1.960 < t_o \leqslant 2.576$	possibly significant,
$2{,}576 < t_o \leqslant 3{,}291$	significant,
$3.291 < t_o$	highly significant.

When a theoretical bond length is used for comparison the expression is modified by considering that it has zero standard deviation.

The Crystal and Molecular Structure of Dimethylcorticrocin.

Introduction.

Corticrocin, a new pigment, was first isolated by Erdtman[35] from the mycelium of a mycorrhiza fungus. He reported it to be a polyene dicarboxylic acid, of formula $HO.CO.(CH = CH)_6.COOH$, whose role in fungal metabolism is not yet known. Since then, cortisalin, another compound which possesses a polyene chain without isoprenoid methyl substitution, has been isolated from a fungus by Grippenberg.[36] It has the formula:



and it therefore seems possible that such compounds are of general importance among the fungi.

The acids of general structure $HO.CO.(CH = CH)_n.COOH$, where n = 3, 4, 5, and 7, were prepared by Kuhn and his collaborators.[37] Corticrocin itself, which is the missing link in this series, has also been synthesised recently.[38] None of these workers, however, were able to establish the geometrical configuration of the compounds, although it appears very likely from the study of its ultra-violet absorbtion spectra that dimethylcorticrocin is <u>trans</u> throughout.[35] The present work shows that this is indeed the case.

The bond lengths etc. in corticrocin are also of great interest because of the conjugated chain. Unfortunately, due to the adverse crystal habit, it was only possible to obtain one two dimensional projection of the structure so that no measurements of the molecule could be made. Theoretical bond lengths have however been calculated, and are to be found in the appendix.

Experimental.

A supply of corticrocin and of its dimethyl ester was obtained from Erdtman.[35] It was decided to work on the dimethyl ester rather than the free acid since the latter was either insoluble or only sparingly soluble in most solvents.[35] The ester was recrystallised from chloroform in the form of yellow needles by very slow evaporation. When examined under the polarising microscope these showed two extinction positions, with the exception of one part which remained dark all the time.* DELETE ~~also marked dichroism.~~ DELETE ~~This proved to be due to twinning.~~

A previous investigator (Dr. G. Todd) obtained c-axis rotation and oscillation photographs, as well as the corresponding zero-layer moving film, without interference from the twin. Unfortunately this has not been possible with the other axes. Accordingly attempts were made to cut the crystals but the fragments o obtained still showed evidence of twinning. Different solvents and other corticrocin derivatives were also investigated but the crystals obtained still* DELETE ~~showed pronounced dichroism.~~ This meant that only the projection of the structure on (001) could be examined because of the interference of the twin with the photographs about the other axes, and with the first-layer Weissenberg photographs about the c-axis.

Unit cell dimensions were determined purely from photographs about the c-axis which was itself measured from a rotation photograph. The remaining unit cell parameters were determined from the superposition of a first-layer precession photograph[39] on a zero-layer one. The precession photographs were taken using M_o K_α radiation $(\lambda = 0{\cdot}711$ Å$)$

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Twinning was later found to be the cause of this difference.
AND IN LINE 17 BY,
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and the remainder with Cu K_α ($\lambda = 1{\cdot}542$ Å)

Crystal Data.

Dimethylcorticrocin, $CH_3O.CO.(CH = CH).COOCH_3$, molecular weight 274,2, melting point 225° C, density calculated 1,225 $g.cm^{-3}$., found 1.237 $g.cm.^{-3}$
Triclinic, elongated in the direction of the c-axis.

$a = 9.06,\ b = 7.52,\ c = 6.07$ Å;

$\alpha = 104{,}8^\circ,\ \beta = 104{,}0^\circ,\ \gamma = 103{,}7^\circ$

No absent spectra, space group $C_1^1 - P\,1$ or $C_i^1 - P\,\bar{1}$.* One molecule per unit cell.

Intensity data for the (h k 0) reflections were recorded on a moving film photograph using the Robertson multiple film technique.[40] Measurement was by eye estimation and Lorentz and polarisation corrections were applied. This gave a set of structure factors on a relative scale. The film used was Ilford Industrial G which has an absorbtion factor of 3.22 (see Appendix II)

Analysis of the c-axis Projection.

The true unit cell has a projection on (001) which is not particularly convenient so that one was chosen which has the dimensions,

$$a' = 16.76,\ b' = 7.28\ \text{Å},\ \beta' = 95.7^\circ$$

The advantage of this choice is that the molecule now lies along the centre of the projection unit, and that the asymmetric unit is one quarter of the projected area which is face-centred.

An approximate structure was obtained by trial and error. This was refined using first F_o, and then $(F_o - F_c)$ syntheses.

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Hydrogen atoms, which were placed using a model combined with inspection of a difference map, were included in the later stages of the work.

The chief difficulty associated with this projection was due to the lack of resolution of individual atoms. This necessitated the use of $(F_o - F_c)$ syntheses from an early stage and probably added to the amount of work necessary for refinement. The discrepancy R stands at 21.1% when all the observed reflections are taken into account and an F_o synthesis using signs calculated for the final atomic coordinates is given in Figure I. The positions of the carbon and oxygen atoms are indicated on this, while the positions chosen for hydrogen atoms are shown by small crosses. The atomic coordinates are given in Table I.

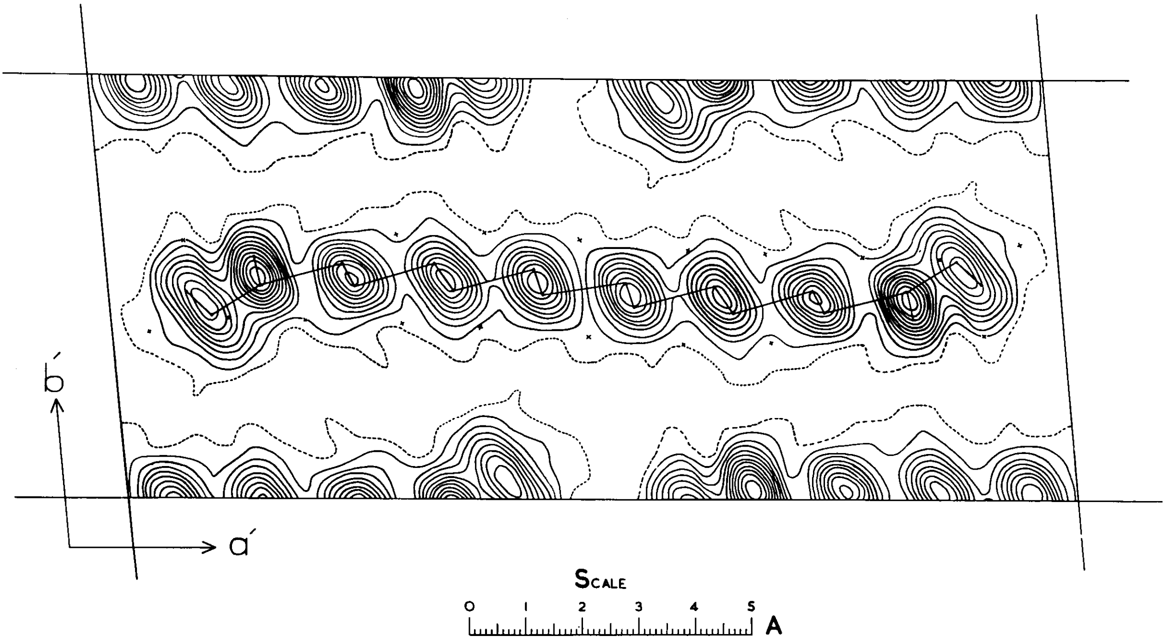

Figure I.

Electron density projected on (001). The contour line interval is one electron Å^{-2}, the one electron line being broken.

Table I. Atomic Coordinates.

These are referred to the projection unit origin at centre of symmetry. Equivalent positions:

(x, y); $(\bar{x}, \bar{y})$; $(\frac{1}{2} + x, \frac{1}{2} + y)$; $(\frac{1}{2} - x, \frac{1}{2} - y)$

Atom	$\frac{x}{a}$	$\frac{y}{b}$
C_1	0.045	0.016
C_2	0.051	0.955
C_3	0.138	0.008
C_4	0.155	0.942

Atom	$\frac{x}{a}$	$\frac{y}{b}$
C_5	0.241	0.998
C_6	0.252	0.943
C_7	0.340	0.995
C_8	0.419	0.012
O_1	0.395	0.067
O_2	0.344	0.927
H_1	0.113	0.093
H_2	0.000	0.885
H_3	0.195	0.085
H_4	0.099	0.868
H_5	0.296	0.077
H_6	0.192	0.874
H_7	0.377	0.070
H_8	0.462	0.107
H_9	0.416	0.890

The atomic scattering curve used for both carbon and oxygen atom was a McWeeney[41] curve for an isotropic carbon atom with a temperature factor of exp. $\left[-2.5\left(\frac{\sin\theta}{\lambda}\right)^2\right]$. No allowances were made for the different scattering powers of oxygen and carbon etc. The curve for hydrogen was also an approximation, being a carbon curve similar to the above with a factor of exp. $\left[-4\left(\frac{\sin\theta}{\lambda}\right)^2\right]$ and weighted for hydrogen. All these approximations probably contributed to raise the discrepancy, but would be unlikely to change any signs or affect the atomic positions by more than a very small amount. Since no bond lengths or angles have been measured this will not affect our conclusions.

Discussion.

The electron density map obtained, and the reasonable agreement between observed and calculated structure factors, show that Erdtman's structural deductions[35] were correct and that the dimethyl ester does indeed have the trans configuration. It is disappointing, however, that no measurements of the molecule could be made due to all the crystals which could be obtained being twinned.

The atomic positions and the electron density map seem to indicate that there is a lack of regularity along the chain. No definite pronouncements on this are possible though, unless single crystals of this, or a related compound, can be prepared. An accurate study of the molecular configuration would then be possible.

Table II.

Observed and calculated structure Factors; values of F(h k 0).
Indexing for projection unit, F(h k 0) absent when h + k ≠ 2 n.

h k	sinθ	F_o	F_c
00	0	-	292.0
20	0.092	24.0	-18.3
40	0.185	47.0	-33.8
60	0.277	10.5	-10.5
80	0.370	10.9	9.9
10,0	0.462	40.5	-41.4
12,0	0.554	14.7	14.5
14,0	0.647	3.1	5.3
16,0	0.739	6.7	-6.0
$\overline{15}$,1	0.689	5.9	4.8
$\overline{13}$,1	0.599	6.3	-11.7
$\overline{11}$,1	0.509	13.8	-18.3
$\overline{9}$,1	0.419	6.9	-13.7
$\overline{7}$ 1	0.330	14.9	-4.9
$\overline{5}$ 1	0.243	27.4	26.6
$\overline{3}$ 1	0.166	46.5	36.5
$\overline{1}$ 1	0.112	6.5	-4.7
1 1	0.120	10.6	26. 3
3 1	0.184	22.5	19.7
5.1	0.266	23.8	20.9
7 1	0.351	5.9	6.0
9 1*	0.440	3.9	-0.5
11,1	0.531	41.0	-38.7
13,1	0.621	7.1	-8.9
15,1	0.712	8.9	6.5
17,1	0.802	< 2.8	3.0
19,1	0.895	4.0	-3.4

h k	sinθ	F_o	F_c
$\overline{12}$,2	0.574	6.1	6.7
$\overline{10}$,2	0.489	42.3	-38.0
$\overline{8}$ 2	0.408	13.5	12.4
$\overline{6}$ 2	0.332	7.3	-11.0
$\overline{4}$ 2	0.268	33.6	-31.5
$\overline{2}$ 2	0.223	31.9	-28.3
0 2	0.213	152.1	159.9
2 2	0.240	4.5	4.0
4 2	0.296	9.4	-5.5
6 2	0.367	10.7	-8.8
8 2*	0.447	6.9	1.2
10,2	0.528	25.8	-31.6
12,2	0.614	15.5	15.4
14,2	0.701	5.2	-4.8
16,2	0.789	8.1	-6.5
18,2	0.878	< 2.5	-3.0
20,2	0.967	7.4	9.5
$\overline{13}$,3	0.690	6.6	-7.2
$\overline{11}$,3	0.574	< 2.8	-1.5
$\overline{9}$ 3	0.489	< 2.5	19.2
$\overline{7}$ 3	0.431	13.1	-9.0
$\overline{5}$ 3	0.373	3.5	10.8
$\overline{3}$ 3	0.334	23.7	25.6
$\overline{1}$ 3	0.317	8.1	-11.1
13	0.327	20.2	28.3
3 3	0.360	< 2.0	-3.4
5 3	0.413	< 2.2	3.7
7 3	0.477	9.3	12.7

h k	sinθ	F_o	F_c
9 3	0.550	4.6	10.8
11,3	0.628	38.7	-39.3
13,3	0.708	9.0	- 6.3
15,3	0.790	7.0	3.6
17,3	0.875	< 2.5	2.7
19,3	0.963	2.9	-3.1
$\overline{10}$,4	0.595	13.2	-20.3
$\bar{8}$ 4	0.535	3.7	6.1
$\bar{6}$ 4	0.483	7.3	-7.7
$\bar{4}$ 4	0.447	7.9	-12.4
$\bar{2}$ 4	0.426	9.8	-12.0
0 4	0.425	39.8	38.0
2 4	0.444	< 2.3	7.4
4 4	0.481	6.4	9.0
6 4	0.531	< 2.6	-3.3
8 4	0.591	8.8	-3.3
10,4	0.659	6.6	-16.7
12,4	0.732	8.4	5.9
14,4	0.809	2.7	-1.2
16,4	0.888	2.6	-2.8
$\bar{9}$ 5	0.640	5.1	-7.8
$\underline{7}$ 5	0.594	< 2.8	-3.6
$\underline{5}$ 5	0.558	< 2.7	-0.4
$\underline{3}$ 5	0.536	< 2.6	11.0
1 5	0.528	6.3	-6.0
1 5	0.538	15.5	15.3
3 5	0.564	< 2.7	-9.7
5 5*	0.601	5.1	0
7 5	0.650	< 2.9	0
9 5	0.708	13.3	12.9
11,5	0.772	22.6	-24.0

h k	sinθ	F_o	F_c
13,5	0.841	2.6	-4.4
0 6	0.638	10.1	8.4
2 6	0.653	< 2.9	-7.6
4 6	0.681	< 3.0	7.1
8 6	0.721	< 3.0	-2.9
10,6	0.769	2.9	-3.7
$\bar{9}$ 7	0.813	6.2	3.4
$\bar{7}$ 7	0.782	< 2.9	-2.8
$\bar{5}$ 7	0.756	< 2.9	3.5
$\bar{3}$ 7	0.743	< 3.0	4.6
$\bar{1}$ 7	0.739	4.7	-0.7
1 7	0.748	5.1	4.9
3 7	0.770	< 2.9	1.6
5 7	0.801	< 2.8	0
7 7	0.841	< 2.6	2.9
9 7	0.887	7.6	8.8
080*	0.850	2.3	0

* These planes were left out of the Fourier shown in Figure I on account of uncertain sign. All non--observed planes were also left out.

The Crystal and Molecular Structure of n-Dodecylammonium Chloride.

Introduction.

Some preliminary details of this work have already been published by Gordon, Stenhagen, and Vand,[42] who detail the transitions undergone by the chloride on heating it to 75°C. They also give unit cell data and the results of a preliminary study of the projection on (010).

The N-mono-n-alkyl substituted ammonium halides are of interest because they exhibit surface activity and polymorphism, the latter property suggesting that the hydrocarbon chains can pack in different ways. It is also thought that the lower members exhibit some form of chain rotation since their crystals are tetragonal[43,44] at normal temperatures. Other points of interest concern the dimensions of the hydrocarbon chain and the packing of the chloride ions with the terminal groups, ionic ammonium and non-ionic methyl.

Crystal Data.

The samples were prepared and all photographs taken in Sweden using CuK_α radiation $(\lambda = 1{\cdot}542\text{Å})$. The unit cell dimensions were obtained from rotation, oscillation, and Weissenberg photographs.

n-Dodecylammonium chloride, molecular formula $C_{12}H_{25}NH_3Cl$ molecular weight 221,5, crystallises as thin yellowish needles which decompose at about 100°C.[45] The crystals are monoclinic with,

$$a = 5.68,\ b = 7.16,\ c = 17.86\text{Å},\ \beta = 92^\circ 16'$$

Two molecules per unit cell. Calculated density 1,015 $gm.cm.^{-3}$

Absent reflections; (0k0) when k is odd. Space group $C_2^2 - P2_1$. The space group $C_{2h}^2 - P2_{1/m}$ is also possible, but requires the atoms to lie in special positions, and was for this reason rejected. The above data are in good agreement with those of Clark and Hudgens.[46]

The intensities of the (h0ℓ) and (0kℓ) reflections were estimated using the Robertson multiple film technique.[40] The absorbtion factor of the Gevaert film used is 1.93.[47] Lorentz and polarisation factors were applied to the observed intensities giving a set of observed structure factors which were later scaled by comparison with the calculated values.

Analysis of the Structure.

(h0ℓ) zone. Approximate z-coordinates were obtained by McCron[48] who used one-dimensional Fourier syntheses on the (00ℓ) planes. He also obtained an indication of the x-coordinates. This structure was modified in the light of the bromide structure,[42] and on re-estimating intensities (McCron had used a wrong film factor), a discrepancy of 32% was obtained. An F_o synthesis of the electron density projected on (010) was then carried out from which it was seen that the hydrocarbon chain was arranged in a regular fashion. Consequently it was decided to use sub-cell theory in the calculation of the structure factors for these atoms. The sub-cell dimensions, projected on (010), were directly determined from this electron density map, and the sub-cell was chosen so that it contained two CH_2 groups related by a centre of symmetry. There were two such regions, one associated with each chain in the unit cell, and with their centroids related by normal space group symmetry. Further details of the sub-cell are given in another section.

An (F_o-F_c) synthesis was then carried out, over the whole projections, using sub-cell theory to calculate only the carbon atom contributions to the structure factors. The best positions of the sub-cell atoms, including hydrogen, were then found using trial and error systematically, The best position of the $C\ell^-$ ion was found directly from the difference map. Uncertainty exists, however, about the exact position of the nitrogen atom due to the x- and z- coordinates of it and the $C\ell^-$ ion being almost the same. The nitrogen coordinates were chosen therefore from consideration of the F_o synthesis and the hydrocarbon chain. The hydrogen atoms of the NH_3 group were positioned from a model and the final figure of merit over the observed reflections was 15.8%. The final x- and z-coordinates are given in Table III and the projection of the structure on (010) is shown in Figures II and III. The calculated and observed structure factors are in Table IV.

The atomic scattering curves employed were:

(a) carbon and nitrogen (as N^+). A McWeeney[41] curve for an isotropic carbon atom with a temperature factor of exp. $\left[-3{\cdot}9\left(\frac{\sin\theta}{\lambda}\right)^2\right]$

(b) chlorine (as $C\ell^-$). A James and Brindley curve[49] with a factor of exp. $\left[-3{\cdot}9\left(\frac{\sin\theta}{\lambda}\right)^2\right]$

(c) hydrogen. A McWeeney[41] hydrogen curve with a factor of exp. $\left[-4{\cdot}2\left(\frac{\sin\theta}{\lambda}\right)^2\right]$

(0 k 1) zone. It was found that all the even and odd C - C bonds as projected on (010) were approximately equal. Since the chain can be assumed regular and planar, and the plane of the chain is inclined to the (010) plane, it follows that the long axis of the chain must lie approximately parallel to (010). The angle between (010) and the plane containing the chain may then be calculated from the expected and the projected bond lengths. This method is very similar to that employed in finding the orientation of many polynuclear hydrocarbons using data derived from a single projection.[50]

The projection on (100) has no centre of symmetry and the origin can lie anywhere on the b-axis,[13] which means that the y-co-ordinate of any one atom can be arbitrarily chosen, and that the positions of the others are fixed relative to it. As the exact y-separation of the even and odd carbon atoms was not known, even though the chain had been assumed planar, it was decided to fix the chloride ion at y=o. The problex is now reduced to one of finding the best y-co-ordinates for the other atoms.

The dimensions of the sub-cell for this projection were found from the dimensions projected on (010) and space group considerations. There are again two related sub-cell regons, and each sub-cell has a centre of symmetry. The use of this theory meant that it was much easier to compute structure factors for trial structures involving systematic movement of the whole chain. The z-coordinates used were the same as those determined from the projection on (010) and the best y-coordinates which could be found by making use of the above facts gave an agreement of 21.9% between observed and calculated structure factors.

An $(F_o - F_c)$ synthesis then showed that all the even numbered carbon atoms required to be slightly moved in the same direction, This was done by trial and error and was found to have very little effect on the agreement between the calculated and observed structure factors. It was found that shifting all these even numbered atoms by 0.06Å gave the best agreement, reducing the figure of merit from 21.9% to 21.2%, but that a further shift of 0.02Å only increased it to 21.8%. Since this work indicated that the agreement between the calculated and observed values for the structure factors was not particularly sensitive to changes in atomic coordinates, it was decided not to proceed any further with the refinement.

The reasons for the above facts are uncertain, especially as the $(F_c - F_o)$ synthesis did not yield any large peaks or troughs, however they may have their origin in:

(a) the number of reflections available not being so great as in the other zone.

(b) the fact that the projection does not possess a centre of symmetry.

(c) a possible unfavourable crystal form.

The scattering curves used were the same as in the other zone.

The projected structure is shown schematically in Figure IV and the y-coordinates are in Table III. The calculated and observed structure factors are given in Table IV.

$(F_o - F_c)$ Synthesis on the Projection on (100)[25]

The normal Fourier coefficients used in our computations are:

$$\left.\begin{array}{l} \text{A terms} - F_o \cos\alpha \\ \text{B terms} - F_o \sin\alpha \end{array}\right\} - \text{where } \alpha \text{ is a calculated value for the phase constant.}$$

In the computation of the difference map, F_o was replaced by $(F_o - F_c)$ with appropriate sign, after which normal procedures were used. The value of α was left unchanged.

Cochrane[25] gives a formula for the shift required by any atom which lies on a slope in the $(F_o - F_c)$ synthesis. In the projection on (100) the magnitude of the required shift was found, by trial and error, to be 1.5 times greater than the shift which would have been required had the origin been at a centre of symmetry. This is due to phase-angle lag and the value of 1.5 was taken to be the constant required in the expression for standard deviation of coordinates in the $(0k\ell)$ zone.[13]

Application of Sub-Cell Theory.

There are two hydrocarbon chains in each unit cell, and the sub-cell was chosen so that it included only one of these chains, which means that there are two sub-cell regions related by the normal space-group symmetry for $C_2^2 - P2_1$. The only symmetry element present in the sub-cell is a centre of symmetry so that the sub-cell space group is $C_i^1 - P\bar{1}$, although it contains two right angles. The sub-cell dimensions, which were found as previously discussed, are:

$$A = 5.68, \quad B = 7.16, \quad C = 2.526 Å, \quad \beta_s = 114^\circ\ 9.$$

(capitals have been used to differentiate these translations from the main cell ones, similarly β has a subscript s). Two CH_2 groups per sub-cell. Each sub-cell region contains six sub-cells, the centroid of one region being at,

$$\frac{x}{a} = 0.296, \quad \frac{y}{b} = 0.452, \quad \frac{z}{c} = 0.463,$$

while the centroid of the other region is at the equivalent position for $C_2^2 - P2_1$.

The transformation matrix,[13] where a_j^k are the transformation coefficients, was determined by measuring the sub-cell edges, in fractional coordinates, as vectors relative to the edges of the main cell. This employs the following relationship

where x_k are the main-cell vectors and X_j are the sub-cell ones.

where x_k are the main-cell vectors and X_j are the sub-cell ones,

$$(x_k) = (a_j^k)\,(X_j)$$

The numerical values of the transformation matrix are,

$$\begin{vmatrix} a_1^1 & a_2^1 & a_3^1 \\ a_1^2 & a_2^2 & a_3^2 \\ a_1^3 & a_2^3 & a_3^3 \end{vmatrix} = \begin{vmatrix} 1 & 0 & -0.167 \\ 0 & 1 & 0 \\ 0 & 0 & 0.129 \end{vmatrix}$$

The main-cell structure factors were calculated, as set out in the introduction , from the relationship,

$$F_h = F_h^\circ + \prod_j \frac{\sin.\pi N_j H_j}{\sin \pi H_j} F_H \cdot \exp\left(2\pi i x_m h_k\right)$$

This was used in the two projections as follows:

(1) $(h0\ell)$ zone. The plane group involved is p 2. F_h^o was calculated normally. F_H values were calculated normally also after the sub-cell indices had been transformed into equivalent main-cell ones by making use of the relationship,

$$(H_j) = (s_j^k)\,(h_k),$$

which is discussed in the introduction. The term exp $(2\pi i x_m h_k)$ was simplified to $2\cos 2\pi x_m h_k$ since the centroid at x_m is related by a centre of symmetry to one at $\bar{x}_m$. The value of the interference function was found graphically by plotting it against H_3 values (which corresponds to the normal Miller index ℓ) since this is the only index which varies. The H_3 value for each plane may be easily found.

(2) $(0k\ell)$ zone. The plane group here is pg which has no centre of symmetry. F_H can be found as before, however, since the sub-cell has a centre of symmetry. F_h^o and exp $(2\pi i x_m h_k)$ must be evaluated using the structure factor equations for pg,[13] while the evaluation of the interference function is entirely analasous with the method used in the $(h0\ell)$ zone.

The use of this method substantially shortens the structure factor calculations as compared with the orthodox methods, the only disadvantage being that the chain must be assumed strictly periodic.

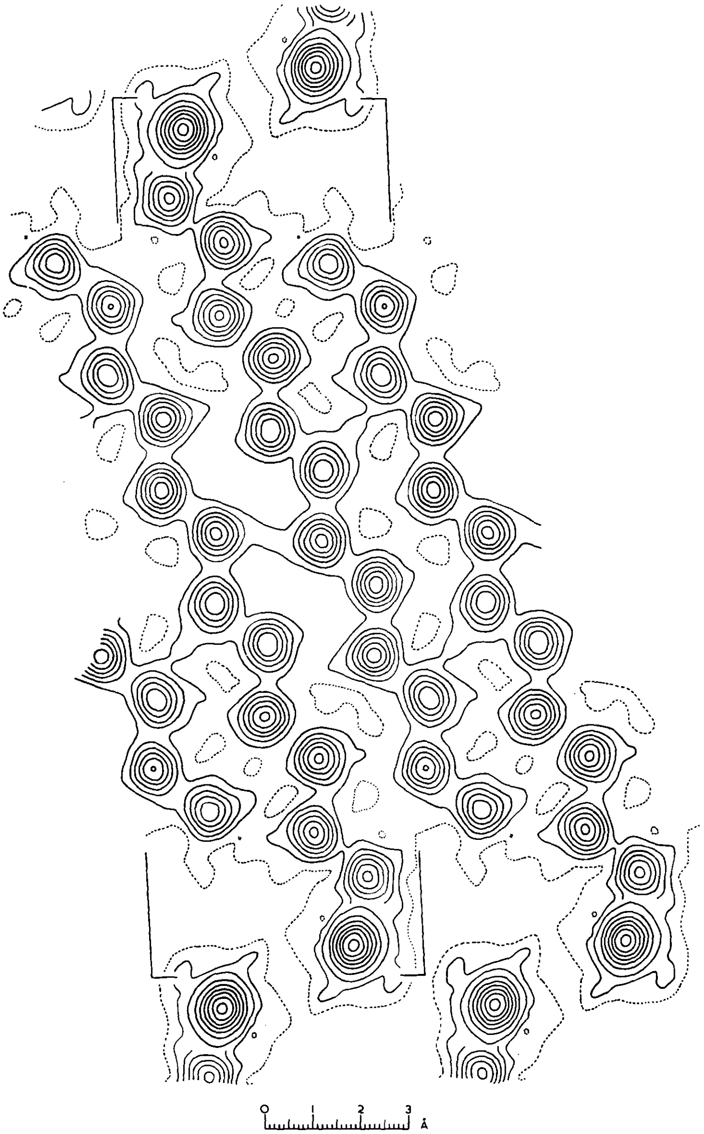

Figure II.

Electron density projected on (010). Interval of contours, one electron per Å^2, except round the chloride ions where only every fourth is plotted. The one electron line is dotted.

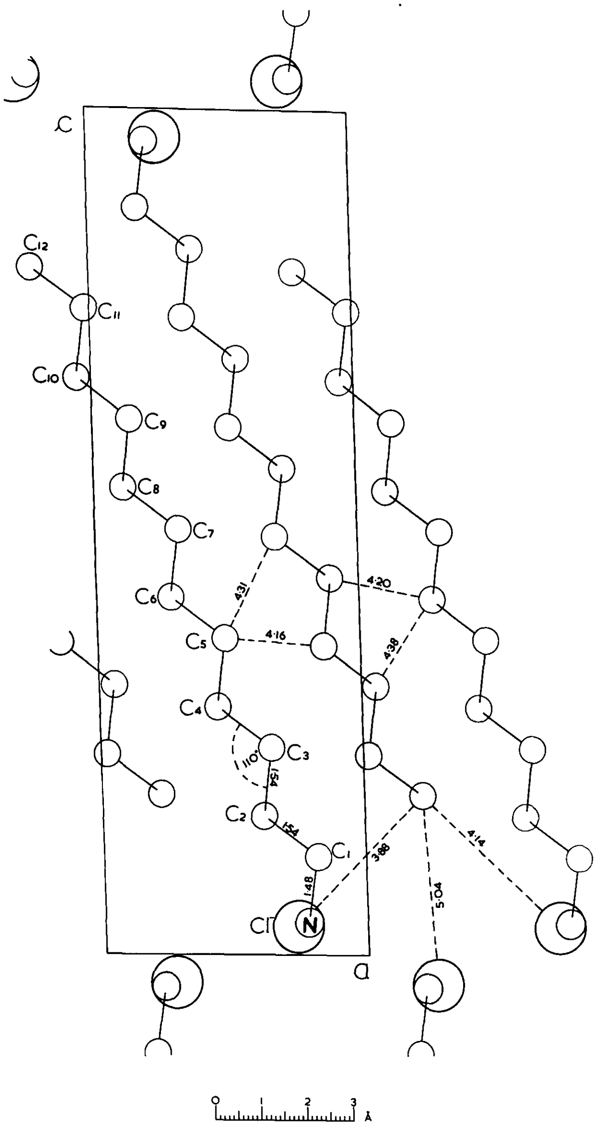

Figure III.

Diagram of structure projected on (010) showing certain interatomic distances. The spatial arrangement is indicated.

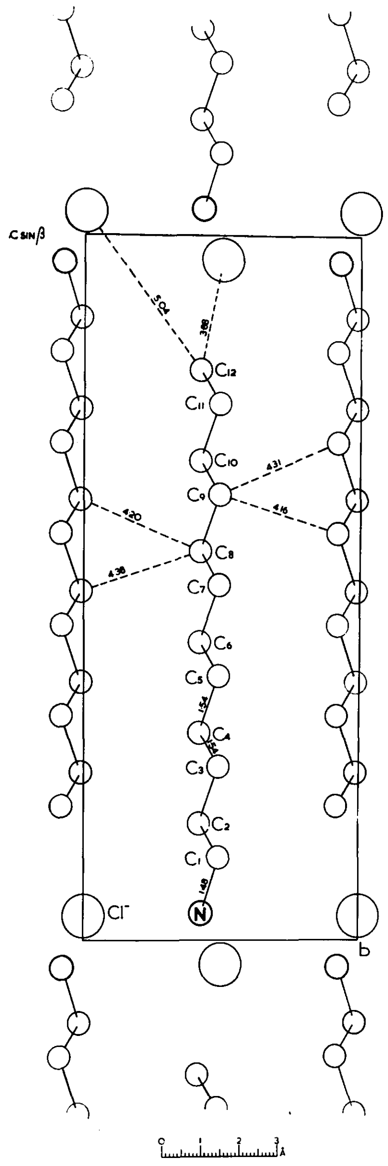

Figure IV.

Diagram of projection of structure projected on (100) showing certain interatomic distances. The spatial arrangement is indicated.

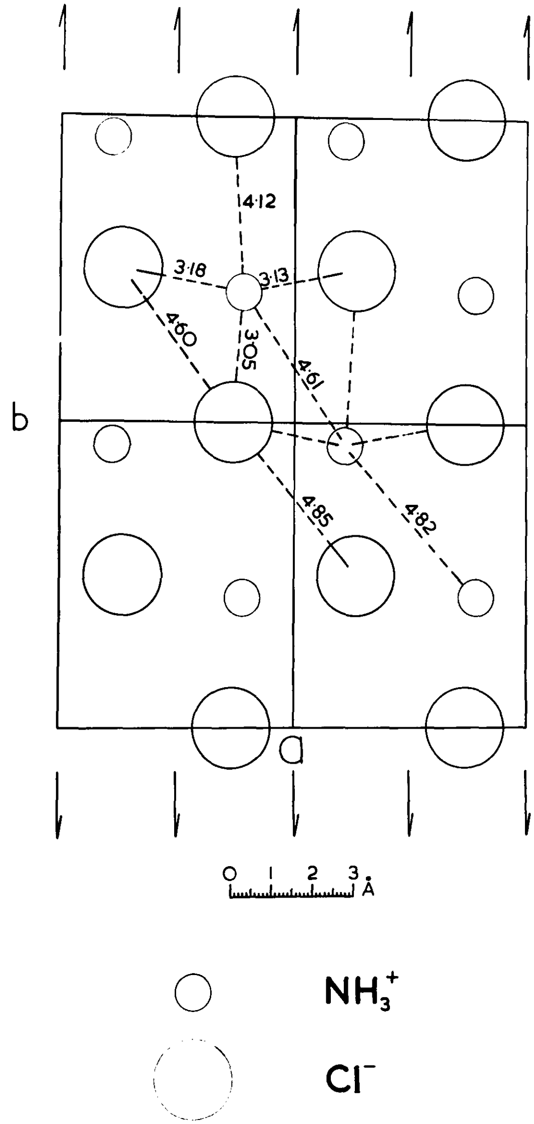

Figure V.

Diagram showing the arrangement of the ionic groups, viewed perpindicular to the a b crystal face.

Table III. Atomic Coordinates.

(1) Sub-Cell Coordinates:

	$\frac{X}{A}$	$\frac{Y}{B}$	$\frac{Z}{C}$
C	0.930	0.965	0.188
H_1	0.917	0.817	0.172
H_2	0.735	0.025	0.015

(2) Main-Cell Coordinates: The sub-cell coordinates were converted into main-cell ones, as set out in the introduction, using the relationship,

$$x_k = u_k + t_j A_j + X_j.$$

The coordinates of u_k are $\frac{x}{a} = 0.714$, $\frac{y}{b} = 0.452$, $\frac{z}{c} = 0.141$; and the sub-cell coordinates can be converted to equivalent main-cell ones by the use of the transformation matrix. The coordinates of all the atoms, excepting sub-cell hydrogen are then as follows:

	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$
C	0.736	0.000	0.034
N	0.778	0.425	0.038
C_1	0.815	0.487	0.117
C_2	0.613	0.417	0.165
C_3	0.648	0.487	0.246
C_4	0.446	0.417	0.294
C_5	0.481	0.487	0.375
C_6	0.279	0.417	0.423
C_7	0.314	0.487	0.504
C_8	0.112	0.417	0.552

	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$
C_9	0.147	0.487	0.633
C_{10}	-0.055	0.417	0.681
C_{11}	-0.020	0.487	0.762
C_{12}	-0.222	0.417	0.810
(H_1	0.761	0.273	0.036
N –(H_2	0.612	0.481	0.015
(H_3	0.112	0.520	0.007
N	0.193	0.515	0.130

(at end of chain)

These coordinates were referred to orthogonal coordinates (in Å) in order to calculate interatomic distances. These are referred to axes a, b, and c′ where DELETE ~~b′ is chosen normal to a in the a b plane and~~ c′ is mutually perpindicular to a and b. The relationships are,

$$x' = x + z\cos\beta$$

$$y' = y$$

$$z' = z\sin\beta$$

where x′, y′, and z′ are the orthogonal coordinates in Å and x, y, and z are the unit cell coordinates also in Å.

Errors in Coordinates.

The observed electron density (ρ_0) near the centre of an atom can be closely approximated to by the relation[9],

$$\rho_0 = Z\left(\frac{p}{\pi}\right)^{\frac{3}{2}} \exp.\left[pr^2\right]$$

where Z is the atomic number of the atom in question, r is the distance from its centre in Å, and p is a constant for that particular atom. We can thus calculate a value for p from measurement on an electron density map and the value so obtained for carbon from the (010) projection is 3.2

It is also possible to obtain a value for the curvature at the centre of the nth atom $\left\{\left(\frac{\partial^2\rho_0}{\partial x^2}\right)_n\right\}$ by the use of this relationship, i.e.

$$\left(\frac{\partial^2\rho_0}{\partial x^2}\right)_n = 2pZ\left(\frac{p}{\pi}\right)^{\frac{3}{2}}$$

We can now utilise the formula for standard deviation of a coordinate which is discussed in the introduction. This gives us for carbon,

$$\sigma(x_n) = \sigma(z_n) = \pm 0{\cdot}045\,\text{Å}$$

$$\sigma(y_n) = \pm 0{\cdot}049\,\text{Å}$$

all the carbon atoms having the same standard deviation. The position of the nitrogen atom is much less certain due to overlap, however it will not have a smaller standard deviation than the carbon values. For chlorine the values are much smaller,

$$\sigma(x_{Cl^-}) = \sigma(y_{Cl^-}) = \sigma(z_{Cl^-}) = \pm 0{\cdot}003\,\text{Å}$$

The standard deviations of bond lengths and angles can now be calculated.[4] We use the root mean square value for the standard deviation of carbon coordinates for this purpose,[51] since the value for the y coordinate differs from those for the x - and z - coordinates.

atoms.	standard deviation of bond. length.	angle.
C-C and C-N	±0·065 Å	± 4°
Cl^--C and N-Cl^-	±0·049 Å	± 1°
Cl^--Cl^-	±0·004 Å	—

This method of calculation neglects the fact that the carbon positions were obtained from a sub-cell, i.e. treated collectively, and it therefore refers to individual distances. The averaged distances, as such, are probably more accurate. Indeed it is possible that the standard deviation for the averaged bond length is less, by a factor of the square root of the number of bonds over which averaging has taken place, than the standard deviation of any one bond. This means that, if we average all six carbon-carbon bonds, the standard deviation of the average value is ± 0.027 Å, with ± 0.03Å being acceptable as a maximum value for the average standard deviation.

Interatomic Distances and Angles.

(1) Hydrocarbon chain. This must be very regular as shown by a low figure of merit being obtained upon application of sub-cell theory which gives only any variation in alternate bonds and all the angles equal, i.e. no fine details (if any) along the chain are shown up. The actual distances and angles are:

$C_1 - N$	1·48 ± 0·065 Å
$C_n - C_{n\pm1}$	1·54 ± 0·03 Å
all angles	110° ± 2·5°
$C_n - C_{n\pm2}$	2·526 ± 0·030 Å

These bond lengths and angles were obtained by the use of sub-cell theory and are averaged over the whole chain. They agree well with the normally accepted values.[31,57]

The interchain distances of closest approach have also been calculated and are shown in Figure III. The chains are about

4.2Å apart, which separation is in good agreement with the values found in n-hexatriacontane[31] and polythene.[52] The packing is in the manner most economical as regards space, the chains being interlocked, as can be seen upon inspection of Figures III and IV. This type of arrangement is typical of hydrocarbon chains in general and accounts for the fact that there is a certain constancy about their angles of tilt to (001). For our compound the tilt is 66° (deduced from the sub-cell angle β_s). This value is exactly the same as that for the hydrobromide,[42] though in the opposite direction, and is closely similar to the 62½° tilt in n-hexatriacontane.[31] Values about 70° have also been found for a series of silver salts of fatty acids,[58] although other angles of tilt are possible if the chains slip over one another so that different zig-zags are interlocked. Such angles have been measured.[57, 59, 60]

The distances between the terminal methyl groups of the hydrocarbon chain and the chloride ions are also shown in Figure III. The closest approach is 3.88± 0.05Å which is in good agreement with the 3.81Å, the sum of their van der Waals radii.[53]*

(2) Ionic groups. The Cl^- and NH_3^+ ions form a layer between the rows of hydrocarbon chains. The arrangement can best be seen viewed perpindicular to the ab crystal face as in Figure V. In each vertical row the Cl^- and NH_3^+ ions have approximately the same z-coordinates and the rows are related by screw axes, so that they are alternately above and below the ab face.

Each nitrogen atom is surrounded by three chloride ions at 3.05, 3.13, and 3.18Å (average 3.12Å) and by one at 4.12Å which

* see leaf opposite

4.2Å apart, which separation is in good agreement with the values found in n-hexatriacontane[31] and polythene.[52] The packing is in the manner most economical as regards space, the chains being interlocked, as can be seen upon inspection of Figures III and IV. This type of arrangement is typical of hydrocarbon chains in general and accounts for the fact that there is a certain constancy about their angles of tilt to (001). For our compound the tilt is 66° (deduced from the sub-cell angle β_s). This value is exactly the same as that for the hydrobromide,[42] though in the opposite direction, and is closely similar to the 62½° tilt in n-hexatriacontane.[31] Values about 70° have also been found for a series of silver salts of fatty acids,[58] although other angles of tilt are possible if the chains slip over one another so that different zig-zags are interlocked. Such angles have been measured.[57, 59, 60.]

LINE 18 AFTER
van der Waal radii.
ADD
(This term is used since the contact is between an ionic and a non-ionic grouping)

rminal methyl groups of the
are also shown in Figure
5Å which is in good
r van der Waals radii.[53]*
form a layer between the
he arrangement can best be seen viewed perpindicular to the ab crystal face as in Figure V. In each vertical row the Cl^- and NH_3^+ ions have approximately the same z-coordinates and the rows are related by screw axes, so that they are alternately above and below the ab face.

Each nitrogen atom is surrounded by three chloride ions at 3.05, 3.13, and 3.18Å (average 3.12Å) and by one at 4.12Å which

* see leaf opposite

is a highly significant difference (see introduction section 5). The fourth chloride ion can therefore exert only a very weak attraction on the substituted ammonium ion. However the distance of 3.05 Å is significantly shorter than 3.21 Å, the sum of the ionic ~~van der Waals~~ radii,[53] but the other two distances do not differ significantly. This seems to indicate that at least one hydrogen bond is formed between the ammonium group and the chloride ion. Binnie and Robertson found evidence of similar behaviour in hexamethylene diamine dihydrochloride[54] where the interionic distances are ~~of~~ 3.01, 3.07, 3.15, and 3.24Å.[55] * ~~correspond very well to those found in our compound.~~

Discussion.

The fact that we have been able to apply sub-cell theory shows that the hydrocarbon chains, although occupying general positions in the space group, are built up of a series of regular repetitions. This has been called hypersymmetry,[56] and it has been shown that where this is present the figure of merit for a trial structure is likely to be higher and probably will not drop quite so low on refinement. It is possible, therefore, that some of the present disagreement between calculated and observed structure factors is due to this.

The interatomic distances and angles have already been discussed. These are shown not to differ appreciably from the expected values. As regards the general packing of the molecules two arrangements appear possible, the one actually adopted and one with two chains between successive ionic layers, as for example

* see leaf opposite

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ammonium group

found evidence of

hydrochloride[54]

3.15, and 3.24 Å.[55] *

~~mpound.~~

LINE 10 AFTER
3·24 Å
ADD
It will be noticed that the three shorter of these distances correspond very well with the three short interionic contacts found in our compound.

The fact that we have been able to apply sub-cell theory shows that the hydrocarbon chains, although occupying general positions in the space group, are built up of a series of regular repetitions. This has been called hypersymmetry,[56] and it has been shown that where this is present the figure of merit for a trial structure is likely to be higher and probably will not drop quite so low on refinement. It is possible, therefore, that some of the present disagreement between calculated and observed structure factors is due to this.

The interatomic distances and angles have already been discussed. These are shown not to differ appreciably from the expected values. As regards the general packing of the molecules two arrangements appear possible, the one actually adopted and one with two chains between successive ionic layers, as for example

* see leaf opposite

in the fatty acids.[57, 59, 60.] The favoured arrangement, however, allows more room for the chloride ion and this is probably the reason for its adoption.

TABLE IV.

Observed and calculated Structure factors.

(1) Values of $F(h0\ell)$.

$h\ell$	$2\sin\theta$	F_o	F_c
00	0	-	248.0
01	0.086	*	2.8
02	0.172	11.8	11.0
03	0.258	19.3	18.2
04	0.344	22.0	22.0
05	0.430	19.7	20.0
06	0.516	13.4	12.6
07	0.602	2.7	1.8
08	0.688	2.7	6.7
09	0.774	9.6	-7.6
0,10	0.860	10.4	-11.2
0,11	0.946	11.1	-11.8
0,12	1.032	13.0	-11.7
0,13	1.118	10.2	-11.6
0,14	1.204	9.9	-12.6
0,15	1.290	18.6	-18.2
0,16	1.376	2.7	1.3
0,17	1.462	3.4	-4.9
0,18	1.548	3.6	-5.0
0,19	1.634	3.4	-3.6
1,$\overline{22}$	1.907	4.2	7.8
1,$\overline{21}$	1.823	<2.0	1.7
1,$\overline{20}$	1.738	<2.3	2.2
1,$\overline{19}$	1.653	3.0	3.1
1,$\overline{18}$	1.570	3.7	4.1
1,$\overline{17}$	1.486	5.7	5.3
1,$\overline{16}$	1.400	6.5	6.5

$h\ell$	$2\sin\theta$	F_o	F_c
1,$\overline{15}$	1.313	5.7	7.8
1,$\overline{14}$	1.230	4.5	-8.7
1,$\overline{13}$	1.146	3.4	-3.1
1,$\overline{12}$	1.061	7.0	-7.0
1,$\overline{11}$	0.980	3.2	-11.7
1,$\overline{10}$	0.898	13.3	-15.4
1 $\overline{9}$	0.817	16.3	-17.9
1 $\overline{8}$	0.738	18.4	-19.1
1 $\overline{7}$	0.658	19.3	-17.5
1 $\overline{6}$	0.580	26.8	-27.4
1 $\overline{5}$	0.507	29.8	-27.4
1 $\overline{4}$	0.437	31.5	-25.6
1 $\overline{3}$	0.373	29.5	-30.1
1 $\overline{2}$	0.321	27.1	-24.8
1 $\overline{1}$	0.284	13.3	-14.8
1 0	0.271	<1.1	1.3
1 1	0.288	13.5	15.5
1 2	0.326	28.2	27.2
1 3	0.379	37.9	31.6
1 4	0.443	30.7	29.0
1 5	0.513	24.9	22.7
1 6	0.588	15.3	17.8
1 7	0.667	10.9	10.5
1 8	0.743	8.4	9.1
19	0.828	59.9	59.2
1,10	0.908	3.6	4.8
1,11	0.990	5.5	6.9
1,12	1.073	5.6	6.0

* not observed due to the construction of the camera.

h ℓ	$2\sin\theta$	F_o	F_c
1,13	1.153	3.1	4.2
1,14	1.240	< 2.6	1.3
1,15	1.322	< 2.7	1.4
1,16	1.408	3.1	-2.0
1,17	1.491	4.6	-6.2
1,18	1.576	3.6	-3.7
1,19	1.661	3.0	-3.2
1,20	1.747	2.5	-2.9
2,$\overline{18}$	1.632	2.9	3.6
2,$\overline{17}$	1.552	3.9	5.1
2,$\overline{16}$	1.470	3.7	6.1
2,$\overline{15}$	1.390	4.6	5.9
2,$\overline{14}$	1.311	7.0	6.3
2,$\overline{13}$	1.233	32.1	34.5
2,$\overline{12}$ §	1.158	4.0	-0.3
2,$\overline{11}$	1.082	2.9	2.6
2,$\overline{10}$	1.009	6.1	4.9
2 $\overline{9}$	0.939	7.1	6.9
2 $\overline{8}$	0.870	6.7	8.2
2 $\overline{7}$	0.803	4.5	6.8
2 $\overline{6}$	0.774	< 1.8	3.5
2 $\overline{5}$	0.688	15.4	-15.5
2 $\overline{4}$	0.639	16.7	-14.6
2 $\overline{3}$	0.598	27.3	-20.3
2 $\overline{2}$	0.568	29.3	-24.8
2 $\overline{1}$	0.549	31.2	-27.6
2 0	0.542	33.4	-29.4
2 1	0.551	36.0	-34.0
2 2	0.572	51.3	-53.7
2 3	0.607	19.8	19.0
2 4	0.648	14.9	-11.7
2 5	0.698	15.0	-14.6

h ℓ	$2\sin\theta$	F_o	F_c
2 6	0.753	8.5	-11.9
2 7	0.818	2.7	- 6.5
2 8	0.883	< 2.0	- 0.2
2 9	0.953	3.7	4.4
2,10	1.024	3.1	1.6
2,11	1.099	12.3	15.5
2,12	1.173	11.5	11.9
2,13	1.249	8.6	9.6
2,14	1.331	6.2	7.4
2,15	1.408	4.7	6.0
2,16	1.488	3.6	5.2
2,17	1.568	3.8	4.5
2,18	1.648	3.0	5.6
3,$\overline{19}$	1.815	3.4	-3.6
3,$\overline{18}$	1.740	2.8	-3.6
3,$\overline{17}$	1.662	3.4	-3.7
3,$\overline{16}$	1.587	3.6	-3.6
3,$\overline{15}$	1.513	< 2.7	-2.8
3,$\overline{14}$	1.442	< 2.8	-1.0
3,$\overline{13}$	1.371	< 2.8	2.3
3,$\overline{12}$	1.303	12.3	11.9
3,$\overline{11}$	1.239	6.2	1.9
3,$\overline{10}$	1.174	11.6	8.1
3 $\overline{9}$	1.115	11.6	10.7
3 $\overline{8}$	1.059	11.6	11.6
3 $\overline{7}$	1.005	11.5	10.7
3 $\overline{6}$	0.958	13.0	9.5
3 $\overline{5}$	0.915	18.3	10.5
3 $\overline{4}$	0.879	54.1	51.5
3 $\overline{3}$	0.850	6.6	-2.3
3 $\overline{2}$	0.830	3.4	4.4
3 $\overline{1}$	0.818	3.4	2.5

h ℓ	$2\sin\theta$	F_o	F_o	h ℓ	$2\sin\theta$	F_o	F_o
3 0	0.813	<2.0	1.4	4 1	1.089	10.9	10.3
3 1	0.820	3.3	-1.9	4 2	1.100	8.3	8.6
3 2	0.833	8.5	-5.9	4 3	1.119	8.4	8.4
3 3	0.858	11.1	-9.5	4.4	1.143	8.2	7.0
3 4	0.890	12.5	-12.1	4 5	1.173	4.3	10.9
3 5	0.928	13.6	-12.2	4 6	1.209	3.6	3.4
3 6	0.970	11.7	- 9.9	4 7	1.250	< 2.6	2.5
3 7	1.020	10.3	-10.8	4 8	1.295	< 2.7	0.3
3 8	1.073	10.6	-10.6	4 9	1.340	3.0	-2.0
3 9	0.132	11.0	-11.8	4,10	1.397	4.0	-3.5
3,10	1.194	11.7	-14.2	4,11	1.451	4.6	-4.9
3,11	1.259	16.8	-21.4	4,12	1.512	5.0	-4.0
3,12	1.327	12.4	12.5	4,13	1.570	6.2	-8.4
				4,14	1.635	3.7	-3.4
4,$\overline{18}$	1.873	3.0	1.5				
4,$\overline{17}$	1.804	2.7	-2.8	5,$\overline{16}$	1.912	2.6	-4.8
4,$\overline{16}$	1.735	3.6	-4.1	5,$\overline{15}$	1.852	< 1.8	-0.3
4,$\overline{15}$	1.670	5.8	-5.1	5,$\overline{14}$	1.796	< 2.1	-0.1
4,$\overline{14}$	1.606	6.0	-5.7	5,$\overline{13}$	1.740	< 2.3	-0.3
4,$\overline{13}$	1.541	5.9	-6.3	5,$\overline{12}$	1.689	< 2.4	-1.2
4,$\overline{12}$	1.482	7.0	-7.4	5,$\overline{11}$	1.639	2.6	-2.5
4,$\overline{11}$	1.427	12.5	-12.4	5,$\overline{10}$	1.591	4.4	-3.9
4,$\overline{10}$	1.370	3.8	5.2	5 $\overline{9}$	1.548	6.3	-3.9
4 $\overline{9}$	1.320	6.6	-4.2	5 $\overline{8}$	1.509	7.6	-6.1
4 $\overline{8}$	1.272	6.3	-5.4	5 $\overline{7}$	1.472	7.1	-6.5
4 $\overline{7}$	1.230	3.0	-4.4	5 $\overline{6}$	1.441	7.8	-6.7
4 $\overline{6}$	1.191	<2.6	-1.0	5 $\overline{5}$	1.414	9.0	-6.6
4 $\overline{5}$	1.159	4.1	2.1	5 $\overline{4}$	1.392	9.5	-5.7
4 $\overline{4}$	1.130	6.4	7.2	5 $\overline{3}$	1.375	11.1	-9.3
4 $\overline{3}$	1.110	12.3	14.7	5 $\overline{2}$	1.361	12.6	-15.0
4 $\overline{2}$	1.095	11.8	8.1	5 $\overline{1}$	1.357	16.4	15.1
4 $\overline{1}$	1.085	13.0	11.3	5 0	1.355	3.8	- 1.9
4 0	1.084	11.8	11.8	5 1	1.360	< 2.8	- 2.7

h ℓ	$2\sin\theta$	F_o	F_c	h ℓ	$2\sin\theta$	F_o	F_c
5 2	1.369	<2.8	−1.2	6 $\bar{4}$	1.657	3.0	−0.8
5 3	1.382	3.4	1.3	6 $\bar{3}$	1.641	4.2	−1.5
5 4	1.402	4.6	3.9	6 $\bar{2}$	1.631	5.7	−4.0
5 5	1.430	4.7	5.6	6 $\bar{1}$	1.628	6.5	−4.8
5 6	1.458	6.4	6.2	6 0	1.626	5.1	−3.1
5 7	1.492	7.0	6.9	6 1	1.630	5.9	−5.1
5 8	1.530	6.1	6.1	6 2	1.639	3.1	−4.7
5 9	1.572	3.4	5.2	6 3	1.650	3.6	−4.6
5,10	1.618	3.1	4.4	6 4	1.669	3.5	−4.8
5,11	1.666	3.0	3.9	6 5	1.690	3.4	−5.4
5,12	1.719	2.3	3.2	6 6	1.712	3.4	−6.4
5,13	1.770	<2.2	2.2	6 7	1.742	3.2	−8.8
5,14	1.829	3.6	−3.1	6 8	1.778	6.1	6.4
5,15	1.886	2.4	3.6				
				7 $\bar{5}$	1.933	2.4	2.6
6,$\overline{12}$	1.910	2.6	3.2	7 $\bar{4}$	1.920	2.5	2.5
6,$\overline{11}$	1.866	2.2	3.3	7 $\bar{3}$	1.908	2.4	2.2
6,$\overline{10}$	1.825	2.3	3.2	7 $\bar{2}$	1.898	2.0	1.9
6 $\bar{9}$	1.789	2.2	3.4	7 $\bar{1}$	1.893	1.8	1.5
6 $\bar{8}$	1.753	2.3	5.7	7 0	1.897	<1.6	0.9
6 $\bar{7}$	1.722	2.3	1.3	7 1	1.899	3.2	−2.8
6 $\bar{6}$	1.697	<2.4	0	7 2	1.904	2.7	2.5
6 $\bar{5}$	1.674	<2.5	−0.9				

§ **This plane was left out of the final F_o synthesis on account of uncertain sign.**

(2) Values of F (0kℓ).

k ℓ	$2\sin\theta$	A'	B'	$\lvert F_c \rvert$	$\lvert F_o \rvert$
1 1	0.233	−4.5	−6.8	5.5	8.2
1 2	0.280	−7.2	−8.8	6.3	11.4
1 3	0.338	−7.8	−3.8	5.1	8.7
1 4	0.409	−5.8	7.1	9.0	9.2

k ℓ	$2\sin\theta$	A′	B′	$\lvert F_o \rvert$	$\lvert F_c \rvert$
1 5	0.483	-2.4	20.8	16.0	20.9
1 6	0.561	1.3	32.8	24.3	32.8
1 7	0.642	6.6	47.8	41.8	48.2
1 8	0.727	-6.5	-27.0	20.6	27.8
1 9	0.808	-1.8	11.7	11.5	11.8
1,10	0.891	-1.0	11.2	9.8	11.2
2 0	0.430	111.7	-62.1	108.1	127.7
2 1	0.440	8.2	8.7	10.9	11.9
2 2	0.467	9.9	5.7	13.8	11.4
2 3	0.503	13.1	1.3	16.4	13.1
2 4	0.552	14.8	-2.1	17.2	14.9
2 5	0.611	13.9	-3.3	13.4	14.3
2 6	0.676	9.9	-2.2	12.2	10.9
2 7	0.743	2.1	1.5	18.1	2.6
2 8	0.817	8.9	-5.3	22.2	10.3
2 9	0.889	-4.6	2.3	< 9.3	5.1
2,10	0.969	-8.6	3.2	10.5	9.4
2,11	1.042	-10.3	6.1	12.3	12.0
2,12	1.121	-10.2	5.5	12.9	11.6
2,13	1.204	- 9.3	1.8	< 11.6	9.5
2,14	1.284	- 7.0	1.7	< 11.9	7.2
2,15	1.368	-10.5	2.7	16.0	10.8
3 1	0.656	- 4.8	0.3	< 7.6	4.8
3 2	0.672	- 8.3	1.6	< 7.8	8.5
3 3	0.700	- 8.8	4.9	< 7.9	10.1
3 4	0.734	- 5.7	10.4	10.8	11.8
3 5	0.780	- 1.2	15.7	13.4	15.7
3 6	0.830	4.7	20.9	16.1	21.4
3 7	0.880	14.3	27.2	23.5	30.7

k ℓ	$2\sin\theta$	A'	B'	$\lvert F_o \rvert$	$\lvert F_c \rvert$
4 0	0.860	26.9	-29.9	44.5	40.1
4 1	0.868	8.9	7.4	< 9.0	11.6
4 2	0.880	9.7	4.7	< 9.2	10.8
4.3	0.900	8.8	2.1	< 9.4	9.0
4 4	0.929	7.9	-0.6	< 9.6	7.9
4 5	0.965	6.4	-2.0	< 9.8	6.7
4 6	1.008	4.8	-1.5	< 10.3	5.0
4 7	1.054	1.4	1.2	11.2	1.8
4 8	1.106	5.4	-6.0	17.2	8.1
5 1	1.080	-1.9	3.6	< 10.8	4.1
5 2	1.090	-3.4	4.5	< 9.6	5.6
5 3	1.107	-3.9	7.7	< 10.9	8.6
5 4	1.130	-2.7	8.8	< 11.1	9.2
5 5	1.160	0.1	9.4	< 11.2	9.4
5 6	1.193	4.2	10.6	12.1	11.4
5 7	1.233	11.6	10.7	12.4	15.8

Studies on the Crystal and Molecular Structure of L-Serine Phosphoric Acid.

Introduction.

Of recent years a great deal of work has been carried out on the structural analysis of the individual amino acids which go to make up the polypeptide chains of the proteins. The information thus gained has enabled model structures of the proteins themselves to be proposed.[61] However there still remains much work to be done in order to determine fully the nature of all the individual amino acids which are associated with the polypeptide chains. L-Serine phosphoric acid, which occurs naturally in silk fibroin, vitellin (from egg-yolk), and casein, is an important compound to study by X-ray diffraction methods not only for this reason, but also because it contains an orthophosphate group directly attached to an organic residue. So far no X-ray work on this type of linkage has been reported.

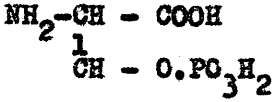
Part I. Two-Dimensional Work.

Experimental.

Crystals of the compound were obtained from Ågren, de Verdier, and Glomset,[62] and take the form of flattened needles showing extinctions under the polarising microscope in directions parallel to, and perpindicular to, the needle axis. The crystal data were obtained from rotation, oscillation, and Weissenberg photographs taken about all three axes using Cu K_α radiation ($\lambda = 1{\cdot}542$ Å)

Crystal Data.

L-serine phosphoric acid, $C_3H_7O_6NP$, structural formula,



$$\begin{array}{l}NH_2\text{-}CH - COOH\\ \qquad\;\; 1\\ \qquad\;\; CH - O.PO_3H_2\end{array}$$

Observed density 1.707 $g.cm^{-3}$, calculated 1.712 $g.cm^{-3}$, m. pt. 167° C (with decomposition). The crystals are orthorhombic with

$a = 7.79 \pm 0.01$, $b = 10.24 \pm 0.04$, $c = 9.09 \pm 0.02$ Å

Absent spectra, (h00) when h is odd, (0k0) when k is odd, (00ℓ) when ℓ is odd. Space group $D_2^4 - P\,2_12_12_1$. Four molecules per unit cell.

Intensity data for the (hk0), $(h0\ell)$, and $(ok\ell)$ reflections were recorded using the Robertson multiple film technique[40], and were estimated by eye. The normal Lorentz and polarisation factors were applied and structure factors on a relative scale obtained. The film used was Ilford Industrial G which has an obsorbtion factor of 3.22 (see Appendix II).

Attempts at Structure Determination.

The projection on (010). A sharpened Patterson synthesis with the origin removed[12] was carried out and the highest peaks assumed to correspond to phosphorus-phosphorus vectors. After the position of the phosphorus had been determined in this way the origin was shifted from the one given in International Tables,[13] which is not at a centre of symmetry, to one at ¼ of the way along one axis which is at a centre of symmetry in projection. This is because although the three screw axes are not concurrent, in the three main projections any two will appear concurrent.

An F_o synthesis was then carried out using only planes where the phosphorus contribution was more than one quarter of the possible value. It proved to be impossible to fit a model onto the peaks which appeared, although the phosphorus atom was clearly defined, and another F_o synthesis, which used signs derived from the peaks which appeared, gave an electron density map worse than the first one.

A new line of attack using Harker-Kasper inequalities and statistical relationships between signs was then tried. The phosphorus position was assumed to be correct and signs were allotted to the four planes to which it made the greatest contribution. Nineteen further signs of strong reflections were then determined and all twenty-three were used in another F_o synthesis.

Positions for all the atoms were then chosen in regions which appeared positive in both sets of electron density maps, although only the phosphorus atom was positively identified. Structure factors calculated from these gave a discrepancy of 43% and another F_o synthesis using the new signs gave well defined peaks except in one instance. The map is shown in Figure VI. Unfortunately it was again impossible to fit a model onto the peaks, even the position of the oxygen atoms in the PO_4 group being uncertain. The coordinates of the peaks which were obtained are given in Table V.

At this point it was decided to investigate the a-axis projection in order to see if the two could be correlated.

<u>The projection on (100).</u> Here again the origin was shifted in order that it might be at a centre of symmetry.

The first method of analysis tried involved the use of inequality and statistical relationships as before, two of the (00ℓ) planes being sufficiently strong to be included with known sign (allowing for the change in origin). Only the signs of reflections with $(k+\ell)$ even could be determined in this way, although the odd ones could be interrelated. An F_o synthesis was then carried out using only reflections with $(k+\ell)$ even and thus introducing false symmetry. A large peak appeared for phosphorus at $y = \frac{1}{2}$, and an attempt was made, using the map, to determine some of the signs of the odd planes with the aid of structure factor graphs. Another F_o synthesis was then done which gave reasonably resolved peaks.

A model was then used in an attempt to interrelate the two projections. Only one plausible structure could be found by this method and $(0k\ell)$ structure factors calculated for it bore no resemblance to the F_o values so that this line of attack was abandoned.

A sharpened Patterson synthesis with the origin removed[12] was then computed and interpreted by superposition methods.[9] This gave seven atoms only, one of which appeared to be phosphorus, and an F_o synthesis using 40 out of 119 possible terms was then carried out. This gave a large peak, at the position chosen for the phosphorus atom surrounded by four smaller ones which were taken to be the oxygens of the PO_4 group.

Using signs determined by these five atoms another F_o synthesis gave peaks onto which it proved possible to fit a molecular model. On calculating structure factors a discrepancy of 40% was obtained but it did not prove possible to improve the agreement using either F_o synthesis or trial and error methods.

The best Fourier synthesis obtained is shown in Figure VII and the last set of atomic coordinates obtained are in table V.

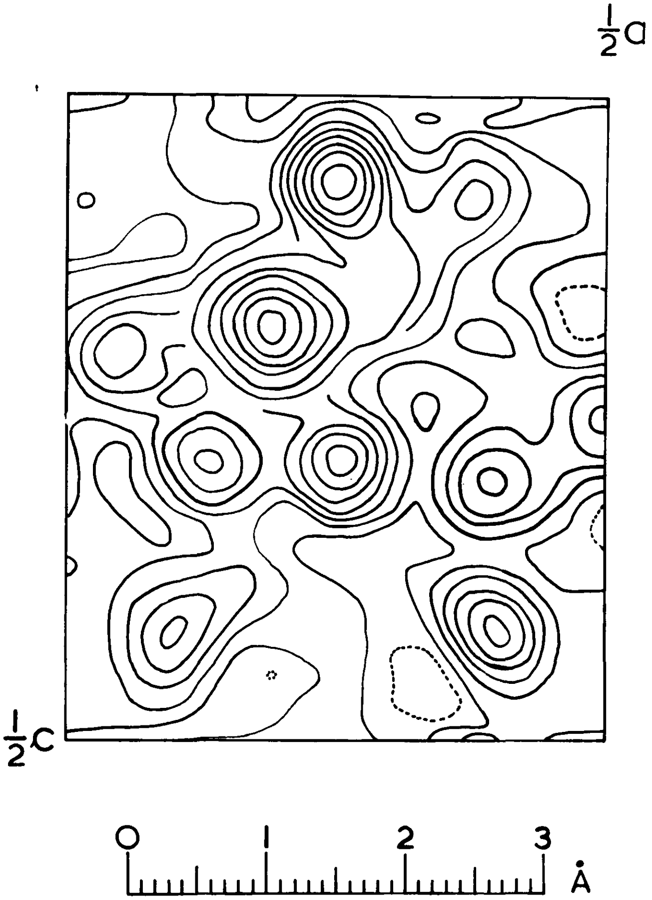


Figure VI.

Fourier map projected on (010). Contour scale arbitrary, the lowest line being dotted. In the region of the phosphorus peak only every second contour is plotted.

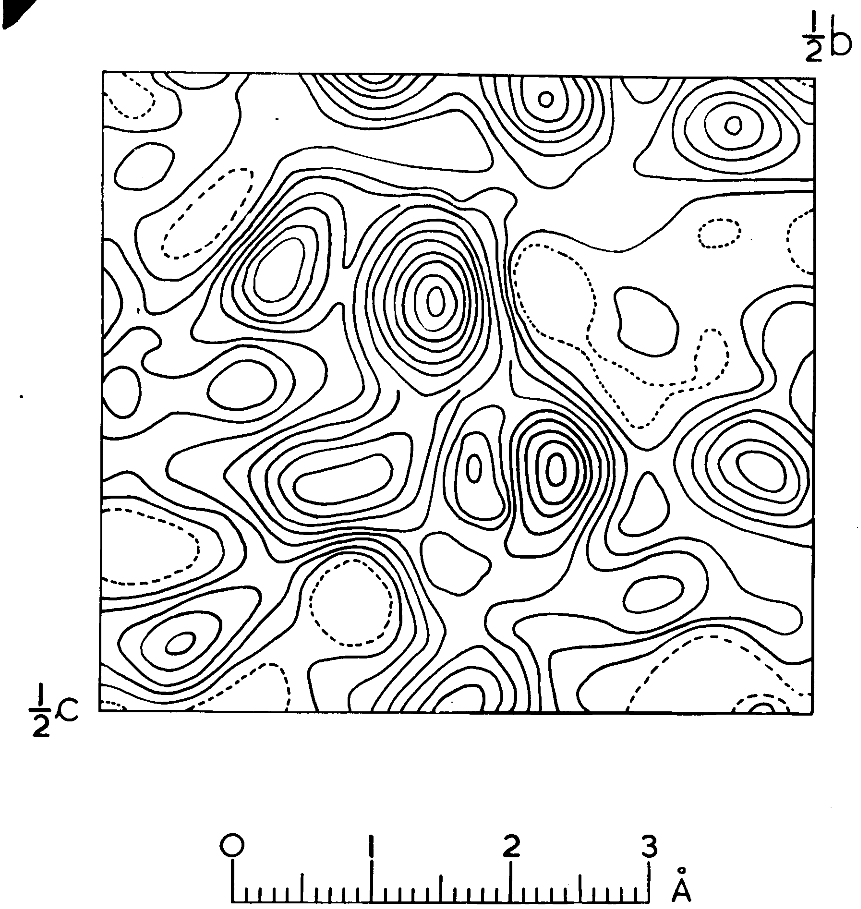


Figure VII.

Fourier map on (100). Arbitrary contour scale, lowest line dotted, and with only every second line plotted in neighbourhood of the phosphorus peak.

TABLE V.

Atomic Coordinates. Since the structure could not be refined these will, at best, be very approximate if not completely wrong. The origin is that given in International Tables.[13]

(1) Projection on (010).

Peak	$\frac{x}{a}$	$\frac{z}{c}$
P	0.191	0.179
1	0.105	-0.202
2	0.245	-0.217
3	0.370	-0.215
4	0.102	-0.086
5	0.403	-0.083
6	0.250	0.066
7	0.378	0.079
8	0.049	0.199
9	0.388	0.188

(2) Projection on (100). The atoms are in postulated positions which correspond to peaks on the Fourier map.

	Atom	$\frac{y}{b}$	$\frac{z}{c}$
PO$_4$ group	P	0.233	0.178
	O_1	0.191	0.312
	O_2	0.123	0.155
	O_3	-0.189	0.483
	O_4	-0.181	0.191
	O_5	-0.035	0.191
	O_6	0.191	0.387
	C_1	0.150	0.326
	C_2	0.057	0.447
	C_3	-0.112	0.094
	N	-0.057	0.463

Part II. Three-Dimensional Work.

Introduction.

The results which are given in Part I led us to the belief that it would be exceedingly difficult and laborious to solve the structure of serine phosphoric acid by two-dimensional methods. Consequently it was decided to collect three-dimensional data with a view to getting a three-dimensional Patterson synthesis done, as it appeared to be the most promising method of approach.[17,18]

Experimental.

The unit cell data etc. is given in Part I. Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs taken with unfiltered CuK_α radiation about each of the three principal axes for all equi-inclination angles less than 30°. Only three reflections, the (676), (686) and (677), all of which are very high order, were outwith the range of this method. Altogether nineteen different photographs were taken and the intensities were estimated by eye using the multiple film technique,[40] after which Tunell,[63] Lorentz, and polarisation factors were applied in the usual manner. The structure factors derived from the different photographs were all put on the same scale by utilising the fact that separate photographs of layers of the reciprocal lattice at right angles to one another have certain spots in common which enables an average scaling factor for each photograph to be found. The scaling was made approximately absolute by reference to a set of $F(h0\ell)$ values calculated during the two dimensional work and where more than one observed value was available an average was taken after the scaling had been completed.

The film used was Ilford Industrial G which has an absorbtion factor of 3.22 (see Appendix II) when the X-ray beam is normal to the film.* DELETE ~~However for angles of incidence other than 90° this factor G is increased.~~[64] ~~If G_o is the factor for 90° incidence and G' that for incidence at an angle ω then,~~

$$\log G' = \sec\omega \log G_o .$$

It can also be shown that in equi-inclination work $\omega = \mu$ where μ is the equi-inclination angle.

The sizes of the crystals used in this work were:

(1) for photographs taken about the a-axis

(0.24 x 0.27) x 0.55 m.m.

(2) about the b-axis

(0.38 x 0.43) x 1.24 m.m.

(3) about the c-axis

(0.64 x 0.58) x 0.30 m.m.

In each case the axis of rotation was the one not included in the brackets.

The values of F (hk$l$) which were obtained are given in Table VI.

The Three-Dimensional Patterson Synthesis.

It was intended that this should be computed on X-RAC, consequently a scheme had to be worked out for presenting the data in a suitable form. This was done as follows:

* see opposite leaf

the scaling had been completed.

The film used was Ilford Industrial G which has an

(see Appendix II) when the X-ray beam is

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However when the X-ray beam is not normal to the film this factor G is increased.[64] If G_0 is the factor when the beam is normal to the film and G' that when the angle between the normal and the beam is ω then,

~~e other than~~ ~~ster for 90°~~ ~~ency~~

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(0.64 x 0.58) x 0.30 m.m.

In each case the axis of rotation was the one not included in the brackets.

The values of F $(hk\ell)$ which were obtained are given in Table VI.

The Three-Dimensional Patterson Synthesis.

It was intended that this should be computed on X-RAC, consequently a scheme had to be worked out for presenting the data in a suitable form. This was done as follows:

* see opposite leaf

X-RAC computes two-dimensional functions directly from the series[10]

$$\sum_{1}^{20}{}_{H_1}\sum_{-20}^{20}{}_{H_2} A_{H_1H_2}\cos 2\pi(H_1x_1+H_2x_2)+\sum_{1}^{20}{}_{H_1}\sum_{-20}^{20}{}_{H_2} B_{H_1H_2}\sin 2\pi(H_1x_1+H_2x_2)$$

Three-dimensional functions are computed from the same series in the form of sections at discrete levels of the third coordinate so that the three-dimensional Patterson function must be put in this form.

The Patterson function for orthorhombic crystals is,[13]

$$P(UVW)=\frac{8}{V_c}\sum_{0}^{\infty}h\sum_{0}^{\infty}k\sum_{0}^{\infty}\ell\,|F(hk\ell)|^2\cos 2\pi hU\cos 2\pi kV\cos 2\pi \ell W$$

$$=2\sum_{0}^{\infty}h\sum_{0}^{\infty}\ell\left\{\frac{4}{V_c}\sum_{0}^{\infty}k\,|F(hk\ell)|^2\cos 2\pi kV\right\}\cos 2\pi hU\cos 2\pi \ell W$$

The part within the curly brackets may be written as $C_{hy\ell}$ in shorthand and can be evaluated by summing one-dimensional Fourier series at sufficiently small intervals of y. In the present instance intervals of $\frac{y}{60}$ were used and $C_{hy\ell}$ was summed from $\frac{0}{60}y$ to $\frac{30}{60}y$. The three dimensional function can now be evaluated in the form of sections at intervals of $\frac{y}{60}$ since the Patterson function can be written as,

$$P(UVW)=\sum_{0}^{\infty}h\sum_{0}^{\infty}\ell\,C_{hy\ell}\cos 2\pi(hU+\ell W)+\sum_{0}^{\infty}h\sum_{0}^{\infty}\ell\,C_{hy\ell}\cos 2\pi(\bar{h}U+\ell W)$$

which is a form suitable for X-RAC (since the crystal is orthorhombic $C_{hy\ell}=C_{\bar{h}y\ell}$ and only one eighth of the total cell volume need be covered by the summation).

In the actual Patterson synthesis the coefficients employed were the $F(hk\ell)^2$ values without modification since it was felt that the presence of the phosphorus atom would lead to undesirable diffraction effects were any of the usual sharpening functions employed.[9] The origin was not removed since this is unnecessary in three-dimensional work[9] and the terms were all multiplied by a factor of $\frac{14}{V_c}$, where V_c is the volume of the unit cell in $Å^{-3}$, so that the terms for summation by X-RAC would not exceed 100[10].

Interpretation of the Patterson Synthesis.[9]

The equivalent positions in the space group $D_2^4 - P2_12_12_1$ are (x, y, z), $(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$, $(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z})$, $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$. There are only three essentially distinct vectors between these positions and they give rise to peaks in the Patterson synthesis at $(\frac{1}{2} + 2x, 2y, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2} + 2y, 2z)$, and $(2x, \frac{1}{2}, \frac{1}{2} + 2z)$, all of which are in the Harker sections. The phosphorus-phosphorus vectors ought to stand out clearly against the vectors between the lighter atoms, consequently an investigation of the Harker sections was made. When the largest peaks were chosen in these sections the following coordinates were obtained for the phosphorus atom;

$$\frac{x}{a} = 0.185, \frac{y}{b} = 0.025, \frac{z}{c} = -0.172.$$

These coordinates differ somewhat from the ones previously given and are likely to be nearer the truth.

At the moment these atomic coordinates for the phosphorus atom are being employed in an attempt to solve the structure by the method of Beevers and Robertson.[65] This method depends on the presence of a heavy atom and they employed it successfully in the case of strychnine hydrobromide.

As an approximation the Patterson synthesis, when a heavy atom (W) is present, may be considered as consisting solely of vectors of the W - W and W - V type, where V_1, V_2, ---V_n are lighter atoms. For any one atom V_r in $P2_12_12_1$ there occur four W - V_r peaks whose coordinates may be readily calculated from the equivalent positions, the first of them being $(x_w - x_r, y_w - y_r, z_w - z_r)$. The position of W (in this case phosphorus) has been found, hence V_r can be located directly from the Patterson synthesis peaks by four transcriptions of the synthesis, with its origin transferred to the four equivalent positions of the heavy atom. This will give rise to 16n possible atomic positions, of which 12n will be randomly spaced, and the remaining 4 n will show fourfold coincidences on n points in space. (Here n is the number of light atoms). These fourfold coincidences should allow the positions of the lighter atoms to be recognised. This method is very similar to that employed in the structural analysis of DL-serine.[17]

In Figure VIII the X-RAC photograph showing the section at $y = \frac{1}{2}$ for the Patterson synthesis is given. The large peak, which was taken to represent a phosphorus-phosphorus vector, can be clearly seen.

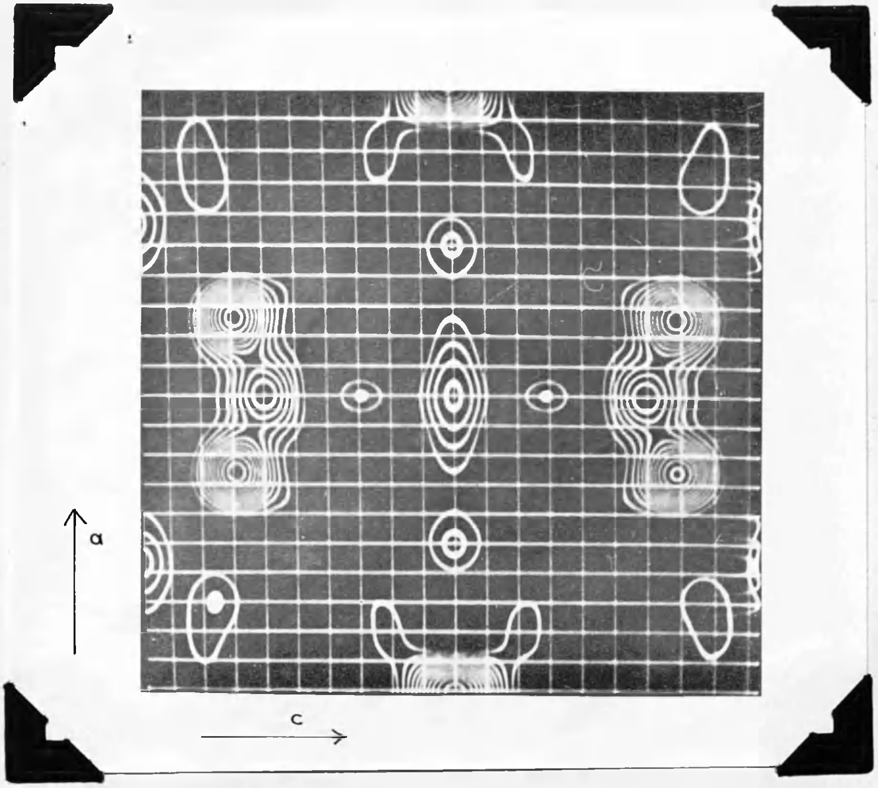

Figure VIII.

Section of the three-dimensional Patterson synthesis at $y = \frac{1}{2}$. Whole cell shown. The contours are at arbitrary intervals and go from 0 - 10. The mesh is at intervals of $\frac{1}{20}$ of the unit cell edge.

Table VI.

Observed structure factors, values of $F(hk\ell)$

$hk\ell$	$2\sin\theta$	$\lvert F_o \rvert$
200	0.398	63.3
400	0.796	15.9
600	1.194	20.0
800	1.592	10.8
002	0.340	67.0
004	0.680	6.8
006	1.020	38.8
008	1.360	29.8
0,0,10	1.700	9.5
020	0.301	59.4
040	0.601	34.4
060	0.902	11.1
080	1.202	5.6
0,10,0	1.503	9.3
0,12,0	1.804	5.9
011	0.228	14.5
021	0.346	31.1
031	0.482	1.4
041	0.625	20.8
051	0.771	13.0
061	0.918	2.1
071	1.066	6.7
081	1.214	20.8
091	1.364	13.4
0,10,1	1.513	16.7
0,11,1	1.662	4.9
0,12,1	1.812	16.4
0,13,1	1.961	4.2
012	0.373	15.6
022	0.455	24.6
032	0.565	17.9
042	0.691	9.6
052	0.826	23.4
062	0.964	4.3
072	1.105	5.6
082	1.249	7.5
092	1.395	8.6
0,10,2	1.541	1.9
0,11,2	1.687	< 1.7
0,12,2	1.836	4.0
013	0.532	25.5
023	0.592	14.6
033	0.680	30.7
043	0.789	11.3
053	0.909	26.2
063	1.036	4.0
073	1.169	39.9
083	1.305	6.6
093	1.446	22.7
0,10,3	1.587	6.0
0,11,3	1.730	2.6
0,12,3	1.874	3.7
014	0.696	29.1
024	0.744	4.7
034	0.815	5.1
044	0.907	14.1
054	1.014	10.1
064	1.129	5.0
074	1.252	16.3
084	1.380	16.4
094	1.514	3.2
0,10,4	1.649	2.7
0,11,4	1.787	2.6
0,12,4	1.927	4.4
015	0.864	6.8
025	0.902	25.1
035	0.962	6.3
045	1.041	17.4
055	1.135	17.9
065	1.239	5.2
075	1.352	24.1
085	1.462	9.5
095	1.598	5.3
0,10,5	1.726	11.2
016	1.031	18.8
026	1.064	28.4
036	1.115	< 2.6
046	1.184	5.2
056	1.267	< 1.5
066	1.361	1.4
076	1.470	< 3.0
086	1.586	< 2.8
096	1.702	< 2.6
0,10,6	1.824	< 2.1
0,11,6	1.856	3.1

017	1.200	9.1
027	1.227	12.3
037	1.272	9.6
047	1.333	<2.8
057	1.409	4.8
067	1.493	4.2
077	1.594	<2.7
087	1.702	8.4
097	1.810	2.8
0,10,7	1.926	14.1

018	1.369	13.8
028	1.393	18.6
038	1.433	10.2
048	1.487	3.6
058	1.554	3.5
068	1.632	2.0
078	1.724	<2.5
088	1.824	3.2
098	1.926	3.6

019	1.538	4.1
029	1.559	<2.2
039	1.595	<2.7
049	1.644	2.5
059	1.705	6.2
069	1.776	6.3
079	1.864	10.7
089	1.956	4.5

0,1,10	1.707	5.1
0,2,10	1.727	4.7
0,3,10	1.759	8.8
0,4,10	1.803	1.8
0,5,10	1.859	5.7
0,6,10	1.924	1.9

0,1,11	1.876	1.9
0,2,11	1.894	7.9
0,3,11	1.924	5.3
0,4,11	1.964	6.3

110	0.250	16.7
120	0.360	21.3
130	0.492	47.9
140	0.632	33.4
150	0.780	26.6
160	0.927	5.1
170	1.071	5.2
180	1.220	5.6
190	1.370	9.2
1,10,0	1.519	4.9
1,11,0	1.668	11.6
1,12,0	1.818	4.4

101	0.263	12.5
111	0.303	9.8
121	0.400	23.3
131	0.522	23.1
141	0.656	7 .6
151	0.797	7.3
161	0.939	4.5
171	1.085	12.3
181	1.231	4.4
191	1.381	27.1
1,10,1	1.528	3.1
1,11,1	1.677	12.6
1,12,1	1.826	6.3
0,13,1	1.973	4.7

102	0.394	45.1
112	0.422	6.8
122	0.491	27.3
132	0.598	13.3
142	0.718	36.1
152	0.849	19.0
162	0.984	14.3
172	1.123	12.6
182	1.266	18.1
192	1.411	5.9
1,10,2	1.556	5.0
1,11,2	1.702	4.2
1,12,2	1.849	11.3
1,13,2	1.995	6.3

103	0.548	8.3
113	0.568	15.7
123	0.625	38.9
133	0.709	21.1
143	0.813	37.9
153	0.931	18.4
163	1.055	12.9
173	1.186	5.7
183	1.322	10.7
193	1.462	1.4
1,10,3	1.602	11.7
1,11,3	1.744	<1.2
1,12,3	1.888	4.3

104	0.710	4.2
114	0.726	10.8
124	0.771	13.8
134	0.841	28.7
144	0.897	14.1
154	1.034	27.3
164	1.148	18.8

174	1.267	6.0
184	1.396	9.6
194	1.532	3.7
1,10,4	1.664	1.6
1,11,4	1.801	<1.4
1,12,4	1.941	5.8
105	0.873	6.8
115	0.886	13.7
125	0.924	23.5
135	0.982	16.5
145	1.059	16.8
155	1.152	7.7
165	1.255	4.6
175	1.366	16.1
185	1.486	2.9
195	1.612	11.0
1,10,5	1.740	8.6
1,11,5	1.872	4.0
106	1.040	5.0
116	1.051	21.7
126	1.083	13.5
136	1.133	12.6
146	1.201	16.4
156	1.284	12.9
166	1.377	4.8
176	1.484	11.0
186	1.599	2.1
196	1.714	2.6
1,10,6	1.835	3.9
1,11,6	1.867	8.6

107	1.208	8.2
117	1.217	2.5
127	1.245	10.2
137	1.289	2.9
147	1.349	6.2
157	1.423	8.1
167	1.507	2.7
177	1.607	11.8
187	1.714	3.6
197	1.821	8.0
1,10,7	1.936	2.8
108	1.375	19.2
118	1.383	9.2
128	1.408	11.3
138	1.447	9.0
148	1.501	9.0
158	1.567	5.8
168	1.644	3.8
178	1.735	5.4
188	1.835	3.5
109	1.542	3.4
119	1.550	3.1
129	1.571	13.5
139	1.607	7.3
149	1.655	3.3
159	1.716	6.7
169	1.786	<1.2
179	1.875	2.8
189	1.966	5.2

1,0,10	1.711	12.0
1,1,10	1.718	2.0
1,2,10	1.738	6.8
1,3,10	1.770	3.7
1,4,10	1.814	4.8
1,5,10	1.869	4.1
1,6,10	1.934	4.6
1,0,11	1.883	1.8
1,1,11	1.888	2.8
1,2,11	1.907	3.1
1,3,11	1.936	2.4
1,4,11	1.977	4.1
210	0.426	11.8
220	0.500	28.9
230	0.602	33.5
240	0.721	4.5
250	0.852	9.0
260	0.988	10.8
270	1.127	17.9
280	1.268	5.0
290	1.411	10.9
2,10,0	1.558	9.3
2,11,0	1.701	13.7
2,12,0	1.850	6.4
201	0.437	27.6
211	0.463	41.3
221	0.531	26.9
231	0.628	23.9
241	0.743	22.8

251	0.870	18.2
261	1.002	1.5
271	1.140	9.6
281	1.279	14.3
291	1.421	16.5
2,10,1	1.567	10.0
2,11,1	1.709	7.5
2,12,1	1.882	10.0

202	0.526	12.6
212	0.548	8 .9
222	0.607	9.2
232	0.693	10.6
242	0.799	13.9
252	0.918	18.8
262	1.044	17.5
272	1.177	17.3
282	1.313	11.7
292	1.451	9.2
2,10,2	1.594	9.1
2,11,2	1.734	8.5
2,12,2	1.881	8.0

203	0.649	17.0
213	0.666	24.6
223	0.716	8.0
233	0.790	16.2
243	0.884	11.2
253	0.993	7.9
263	1.111	11.9
273	1.237	20.6
283	1.366	7.9
293	1.466	21.1
2,10,3	1.669	10.5
2,11,3	1.775	5.2
2,12,3	1.919	2.5

204	0.790	12.1
214	0.804	8.0
224	0.846	9.7
234	0.909	13.8
244	0.992	12.8
254	1.091	23.4
264	1.199	20.3
274	1.316	28.8
284	1.438	21.0
294	1.566	6.9
2,10,4	1.700	10.0
2,11,4	1.831	4.3
2,12,4	1.971	4.6

205	0.940	20.0
215	0.952	1.4
225	0.987	14.9
235	1.043	14.4
245	1.116	10.1
255	1.204	13.1
265	1.303	6.1
275	1.411	16.8
285	1.526	7.4
295	1.647	6.8
2,10,5	1.774	5.6
2,11,5	1.901	4.1

206	1.098	14.2
216	1.109	11.7
226	1.139	14.3
236	1.187	4.5
246	1.252	12.2
256	1.331	14.3
266	1.420	5.6
276	1.523	14.3
286	1.635	7.3
296	1.748	5.5
2,10,6	1.867	2.2

207	1.257	<1 .7
217	1.266	20.4
227	1.293	11.1
237	1.335	17.8
247	1.393	4.2
257	1.465	7.4
267	1.547	3.6
277	1.643	3.0
287	1.748	7.1
297	1.853	3.8
2,10,7	1.967	7 .5

208	1.419	9.9
218	1.427	17.2
228	1.451	12.9
238	1.489	3.0
248	1.541	6.1
258	1.606	3.7
268	1.681	3.3
278	1.769	8.2
288	1.867	<1.2
298	1.967	5.5

209	1.582	6.4
219	1.589	5.6
229	1.611	10.7
239	1.645	1.6
249	1.692	6.6
259	1.752	1.5
269	1.821	1.5
279	1.906	5.9

2,0,10	1.748	2.0
2,1,10	1.755	4.2
2,2,10	1.772	2.4
2,3,10	1.805	4.6
2,4,10	1.851	5.9
2,5,10	1.914	5.2
2,6,10	1.967	4.7
2,0,11	1.913	4.3
2,1,11	1.919	2.4
2,2,11	1.937	8.0
2,3,11	1.966	3.3
310	0.618	24.2
320	0.670	32.1
330	0.750	3.0
340	0.850	10.6
350	0.961	2.6
360	1.084	18.5
370	1.211	5.7
380	1.345	12.3
390	1.481	7.2
3,10,0	1.620	17.1
3,11,0	1.760	< 1.5
3,12,0	1.904	9.9
301	0.625	23.7
311	0.643	18.4
321	0.694	20.4
331	0.771	24.6
341	0.867	30.6
351	0.978	20.3
361	1.096	12.7
371	1.223	6.4
381	1.356	8.7
391	1.491	16.7
3,10,1	1.629	2.6
3,11,1	1.768	8.6
3,12,1	1.912	5.5
302	0.690	25.5
312	0.706	26.2
322	0.753	8.0
332	0.824	6.9
342	0.915	20.9
352	1.021	15.5
362	1.135	16.7
372	1.258	5.4
382	1.387	13.0
392	1.519	6.9
3,10,2	1.655	12.4
3,11,2	1.792	10.2
3,12,2	1.934	4.1
303	0.789	16.5
313	0.804	12.1
323	0.845	6.5
333	0.909	31.5
343	0.974	5.9
353	1.085	22.5
363	1.198	7.5
373	1.314	14.6
383	1.438	7.9
393	1.566	8.5
3,10,3	1.698	2 .4
3,11,3	1.832	2.4
304	0.908	9.7
314	0.920	7.6
324	0.957	7.9
334	1.013	10.4
344	1.089	9.4
354	1.179	21.9
364	1.279	12.7
374	1.388	8.7
384	1.507	5.2
394	1.629	9.8
3,10,4	1.756	1.5
3,11,4	1.887	9.1
305	1.040	< 1.3
315	1.051	7.4
325	1.082	14.2
335	1.134	20.6
345	1.201	14.1
355	1.284	14.0
365	1.376	8.4
375	1.479	8.0
385	1.591	3.3
395	1.707	4.5
3,10,5	1.829	3.2
3,11,5	1.954	6.4
306	1.182	1.7
316	1.192	13.4
326	1.220	5.3
336	1.265	4.5
346	1.326	7.0
356	1.401	1.9
366	1.487	13.0
376	1.587	7.5
386	1.694	9.5

396	1.804	3.4
3,10,6	1.945	5.9
307	1.332	9.3
317	1.341	7.7
327	1.366	14.5
337	1.406	3.2
347	1.461	17.3
357	1.531	<1.5
367	1.608	8.5
377	1.702	8.1
387	1.804	<1.4
397	1.906	6.4
308	1.488	<1.8
318	1.496	8.5
328	1.518	3.2
338	1.555	<1.8
348	1.605	6.4
358	1.667	2.9
368	1.740	8.4
378	1.824	5.6
388	1.919	6.9
309	1.642	3.1
319	1.649	9.8
329	1.669	2.1
339	1.703	6.9
349	1.748	4.0
359	1.806	5.6
369	1.873	5.0
379	1.957	1.5
3,0,10	1.802	4.1
3,1,10	1.808	2.4
3,2,10	1.827	3.5
3,3,10	1.857	5.7
3,4,10	1.857	1.8
3,5,10	1.953	5.4
3,0,11	1.964	1.5
3,1,11	1.970	3.1
410	0.810	5.1
420	0.852	5.7
430	0.918	8.3
440	1.000	14.9
450	1.098	2.9
460	1.205	11.8
470	1.321	5.5
480	1.443	4.0
490	1.573	8.4
4,10,0	1.702	<2.3
4,11,0	1.840	14.5
401	0.819	7.6
411	0.833	39.6
421	0.873	14.1
431	0.935	27.5
441	1.016	19.2
451	1.117	8.9
461	1.218	5.7
471	1.332	4.5
481	1.453	10.6
491	1.582	3.0
4,10,1	1.711	3.9
4,11,1	1.848	<1.5
402	0.869	6.4
412	0.882	18.7
422	0.920	13.6
432	0.979	6.1
442	1.057	15.6
452	1.149	9.9
462	1.252	27.0
472	1.364	7.9
482	1.482	11.6
492	1.609	5.3
4,10,2	1.736	4.7
4,11,2	1.871	7.4
403	0.950	8.0
413	0.962	11.3
423	0.997	11.4
433	1.051	13.2
443	1.124	24.9
453	1.212	4.2
463	1.310	15.4
473	1.416	5.8
483	1.530	5.3
493	1.653	3.8
4,10,3	1.777	5.7
4,11,3	1.909	4.6
404	1.050	10.5
414	1.061	4.8
424	1.093	8.3
434	1.143	9.2
444	1.209	25.3
454	1.292	9.2
464	1.384	30.6
474	1.485	8.2

484	1.595	9.1
494	1.713	4.1
4,10,4	1.833	2.8
4,11,4	1.951	4.1
405	1.168	5.3
415	1.178	9.1
425	1.206	8.0
435	1.252	16.3
445	1.313	14.5
455	1.389	13.3
465	1.476	10.4
475	1.570	2.2
485	1.674	3.5
495	1.787	7.0
4,10,5	1.902	2.8
406	1.295	2.9
416	1.300	5.2
426	1.330	8.7
436	1.407	5.6
446	1.427	4.5
456	1.498	10.1
466	1.578	6.3
476	1.672	6.8
486	1.775	3.9
496	1.879	8.4
407	1.432	< 2.0
417	1.440	23.9
427	1.463	11.5
437	1.501	17.0

447	1.553	6.7
457	1.618	7.0
467	1.692	4.7
477	1.782	3.8
487	1.852	4.2
497	1.977	1.7
408	1.579	3.1
418	1.536	< 1.7
428	1.596	8.4
438	1.642	5.8
448	1.639	3.3
458	1.752	4.8
468	1.818	4.6
478	1.899	4.6
488	1.990	2.2
409	1.728	5.1
419	1.735	6.0
429	1.754	10.5
439	1.736	5.7
449	1.830	9.0
459	1.885	3.1
4,0,10	1.880	3.8
4,1,10	1.886	< 1.1
4,2,10	1.904	1.8
4,3,10	1.923	< 1.4
4,4,10	1.974	5.0
510	1.010	19.7
520	1.041	14.4

530	1.095	9.0
540	1.167	10.4
550	1.250	3.5
560	1.347	23.2
570	1.450	7.0
580	1.562	10.8
590	1.682	9.4
5,10,0	1.806	9.4
5,11,0	1.932	6.5
501	1.012	16.5
511	1.023	13.2
521	1.056	21.3
531	1.108	21.5
541	1.177	13.5
551	1.261	16.3
561	1.355	5.3
571	1.460	3.6
581	1.571	5.6
591	1.691	2.0
5,10,1	1.814	5.2
5,11,1	1.940	4.5
502	1.055	4.2
512	1.065	4.6
522	1.097	3.8
532	1.147	9.8
542	1.214	19.6
552	1.338	10.4
562	1.388	15.2
572	1.489	5.5
582	1.598	11.2

592	1.716	8.2
5,10,2	1.838	7.8
5,11,2	1.962	9.2
503	1.121	7.3
513	1.131	23.2
523	1.161	5.8
533	1.208	22.8
543	1.272	11.4
553	1.350	6.1
563	1.439	12.0
573	1.537	3.5
583	1.643	8.6
593	1.757	4.9
5,10,3	1.877	5.1
504	1.210	3.4
514	1.220	7.9
524	1.247	11.5
534	1.291	14.7
544	1.351	10.5
554	1.425	15.5
564	1.509	9.3
574	1.601	6.6
584	1.703	2.2
594	1.814	3.1
5,10,4	1.930	3.0
505	1.312	< 1.7
515	1.321	23.9
525	1.346	11.4
535	1.387	16.2
545	1.443	15.4

555	1.512	5.1
565	1.591	5.8
575	1.681	3.6
585	1.778	1.5
595	1.884	2.2
506	1.430	9.2
516	1.438	9.5
526	1.462	11.1
536	1.499	6.7
546	1.554	7.5
556	1.616	2.9
566	1.691	13.6
576	1.775	< 2.6
586	1.872	6.9
507	1.555	11.0
517	1.562	7.2
527	1.584	13.7
537	1.619	10.0
547	1.667	11.6
557	1.728	2.5
567	1.798	2.8
577	1.879	1.9
587	1.972	4.3
508	1.689	4.4
518	1.696	2.9
528	1.716	2.1
538	1.748	3.7
548	1.800	6.4
558	1.847	3.9
568	1.915	6.1

509	1.829	6.9
519	1.835	8.5
529	1.854	5.2
539	1.884	7.7
549	1.925	< 1.2
559	1.978	4.5
610	1.206	6.2
620	1.232	18.9
630	1.280	2.8
640	1.340	18.9
650	1.414	5.4
660	1.500	12.4
670	1.595	< 2.8
680	1.698	6.9
690	1.810	2.6
6,10,0	1.922	7.1
601	1.210	4.1
611	1.220	5.9
621	1.247	13.9
631	1.291	18.3
641	1.351	9.5
651	1.425	6.0
661	1.509	12.1
671	1.604	3.8
681	1.707	3.6
691	1.818	2.4
6,10,1	1.930	3.5
602	1.246	9.3
612	1.255	23.7
622	1.282	3.9

632	1.325	2.8
642	1.383	12.1
652	1.459	3.5
662	1.538	14.3
672	1.631	4.9
682	1.732	3.1
692	1.842	3.0
6,10,2	1.952	3.0
603	1.300	11.9
613	1.309	13.4
623	1.334	4.1
633	1.376	20.1
643	1.432	13.6
653	1.502	10.2
663	1.582	11.3
673	1.674	10.1
683	1.773	8.1
693	1.880	7.3
604	1.379	6.7
614	1.387	19.3
624	1.412	3.5
634	1.451	5.2
644	1.504	15.1
654	1.571	4.6
664	1.648	10.6
674	1.734	3.3
684	1.829	3.5
694	1.933	1.6
605	1.469	10.8
615	1.477	9.6

625	1.500	2.1
635	1.537	11.4
645	1.587	9.6
655	1.650	5.5
665	1.724	11.3
675	1.807	2.6
685	1.898	8.1
606	1.572	11.2
616	1.579	6.9
626	1.600	12.5
636	1.635	3.1
646	1.685	9.2
656	1.741	5.5
666	1.812	4.9
676	1.894	*
686	1.985	*
607	1.690	6.2
617	1.700	6.2
627	1.717	3.4
637	1.749	6.6
647	1.794	3.6
657	1.850	3.9
667	1.915	4.7
677	1.992	*
608	1.812	6.5
618	1.818	2.4
628	1.837	6.8
638	1.867	6.1
648	1.909	5.0

609	1.943	2.4
619	1.949	2.8
629	1.966	5.4
710	1.402	22.0
720	1.430	6.8
730	1.468	9.2
740	1.520	6.9
750	1.588	3.1
760	1.662	5.8
770	1.750	9.6
780	1.842	5.8
790	1.948	6.3
701	1.408	< 2.0
711	1.416	3.7
721	1.439	3.1
731	1.478	7.4
741	1.531	2.3
751	1.608	8.6
761	1.672	4.0
771	1.758	10.8
781	1.850	5.8
791	1.956	11.8
702	1.439	11.7
712	1.447	5.3
722	1.470	14.4
732	1.499	6.2
742	1.559	12.4
752	1.624	4.5
762	1.698	6.5
772	1.783	6.2
782	1.873	3.4
792	1.977	5.2

703	1.488	2.0
713	1.496	1.6
723	1.518	<1.4
733	1.555	6.7
743	1.605	1.8
753	1.667	6.1
763	1.740	8.4
773	1.823	2.6
783	1.911	13.6

704	1.555	14.3
714	1.562	7.0
724	1.584	14.5
734	1.619	3.4
744	1.667	8.6
754	1.728	1.5
764	1.798	6.0
774	1.877	4.4
784	1.963	3.6

705	1.637	<1.7
715	1.644	6.2
725	1.665	7.1
735	1.698	6.7
745	1.744	2.5
755	1.802	5.4
765	1.869	3.0
775	1.945	5.2

706	1.730	6.2
716	1.737	10.1
726	1.756	7.9
736	1.786	6.4
746	1.831	3.1
756	1.887	4.6
766	1.951	0.7

707	1.836	2.5
717	1.842	2.3
727	1.860	2.7
737	1.891	5.8
747	1.932	2.5

708	1.950	4.5
718	1.956	5.1

810	1.600	4.5
820	1.620	11.6
830	1.655	<2.6
840	1.702	10.2
850	1.761	<1.3
860	1.831	11.1
870	1.910	8.0

801	1.603	6.3
811	1.610	<1.6
821	1.631	6.0
831	1.665	4.6
841	1.712	2.5
851	1.771	7.4
861	1.839	<1.1
871	1.918	10.1

802	1.630	6.2
812	1.637	8.4
822	1.657	5.9
832	1.691	5.7
842	1.737	5.3
852	1.795	5.7
862	1.863	6.9
872	1.940	8.9

803	1.676	6.8
813	1.683	4.2
823	1.702	2.3
833	1.735	7.2
843	1.780	1.5
853	1.837	9.4
863	1.903	3.1
873	1.977	9.1

804	1.736	3.4
814	1.743	4.2
824	1.762	2.1
834	1.794	7.7
844	1.837	2.8
854	1.892	8.6
864	1.956	2.5

805	1.809	8.2
815	1.815	2.1
825	1.834	5.1
835	1.864	3.5
845	1.934	2.1
855	1.959	3.3

806	1.897	9.5
816	1.903	2.0
826	1.921	6.8
836	1.950	1.6

910	1.798	11.4
920	1.816	3.1
930	1.847	<2.0
940	1.889	3.8
950	1.943	2.9

901	1.800	5.1
911	1.806	6.4
921	1.825	7.4
931	1.855	8.1
941	1.898	3.0
951	1.951	6.4
902	1.827	14.7
912	1.833	5.8
922	1.852	6.7
932	1.882	3.7
942	1.923	4.7
952	1.976	3.6
903	1.865	1.7
913	1.871	4.5
923	1.889	6.4
933	1.919	6.8
904	1.920	14.6
914	1.926	4.5
924	1.943	8.3
905	1.986	3.7
915	1.992	1.3

* Reflection not recorded.

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Appendix I.

Molecular Orbital Description of Dimethylcorticrocein.

Introduction.

It is now well known that the intimate description of a chemical bond is essentially electronic, but Heisenberg[1] has shown that our knowledge of so minute a particle can never be as precise as a classical treatment requires. Wave mechanics, which is based on Schrödinger's[2] wave equation, provides a solution to this problem. The equation itself can only be completely solved for some rather special cases, so that when dealing with molecules we must use approximations. Of these the two chief ones are the valence bond and molecular orbital (usually abbreviated to m.o.) methods. We shall deal with the latter exclusively.

In the m. o. treatment we consider that each electron moves in an orbital which is essentially polycentric and which is governed by a set of quantum numbers. Molecules can thus be built up by feeding electrons into the allowed orbitals. Most of these electrons can be localised but some, which are called mobile or π , and which occur in conjugated and aromatic systems, have orbitals extending over several atoms.

When we deal with conjugated compounds it is usual to consider only the π electrons and the simplest way to obtain their m. o.'s is by taking linear combinations of the contributing atomic orbitals.[3, 4.] Hence the complete π electron wave-function for a chain containing r atoms, each contributing one π electron from an atomic orbital ψ_r , is,

$$\psi = \sum_r c_r \psi_r ,$$

where the coefficients c_r are chosen so as to minimise the energy.

We now introduce an approximate Hamiltonian H for each π electron which neglects all the other π electrons. The wave equation for one π electron then becomes,

$$H \psi = E \psi$$

The Variation Principle[5] can now be applied to give us r secular equations, each of which has the form,

$$\sum_S (H_{rs} - S_{rs} E) c_s = 0,$$

where s also enumerates the atoms in the chain, and where

$$H_{rs} = \int \psi_r H \psi_s \, d\tau \text{ and } S_{rs} = \int \psi_r \psi_s \, d\tau$$

We can simplify these equations by assuming that;

(1) $H_{rs} = 0$ when $r \neq s$ and r and s are not immediate neighbours.

(2) for the same kinds of atoms all the H_{rr} and all the H_{rs} are equal.

(3) $S_{rs} = 0$ when $r \neq s$ and that all the atomic orbitals are separately normalised, i.e. $S_{rr} = 1$.

When the secular equations are solved we obtain r values for the energy E which represent the r possible energy levels of a π electron in the molecule. Similarly there are r sets of values of C_r which correspond to these energy levels and each set must be normalised so that,

$$\sum_r c_r^2 = 1.$$

The coefficients also have the property of orthogonality, i.e.

$$\sum_r c_{rj} c_{rk} = 0,$$

where j and k are different energy levels.

Using these C_r values we can obtain important information about the molecule and for this we consider all the occupied orbitals. The familiar interpretation of ψ^2 is electron density, so that we define the π electron charge on the rth atom by,

$$q_r = \sum_{i=1}^{j} n_i \left(c_r^i\right)^2$$

where n_i = number of electrons in orbital i and there are j energy levels. Similar reasoning leads to the mobile bond order being defined as,

$$p_{rs} = \sum_{i=1}^{j} n_i c_r^i c_s^i$$

The total bond order is 1 + p_{rs} since there is always a σ bond which is supposed to be of order 1.

Bond lengths can be implied from bond orders if we use an empirical curve for correlation with certain standard compounds. The curve used in this work for carbon-carbon bonds is due to Coulson[6] and is given in Figure AI. The accuracy is about ± 0.03Å.[7] No equally satisfactory eruve exists for oxygen-carbon bonds, but one can be constructed[8] and is also given in Figure AI. These bond orders can also be used to deduce the free valence (N_r) of the rth atom from,

$$N_r = N_{max.} - \sum_s p_{rs}$$

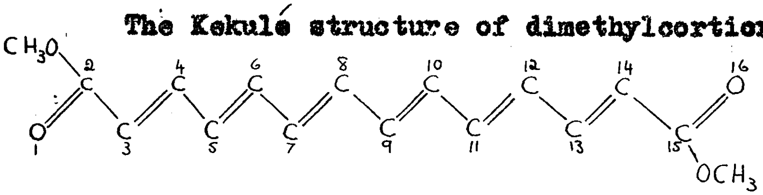
For trigonally hybridised carbon N_{max} is given by the square root of the number of similarly hybridised carbons to which it is attached.

Lastly it can be said that from calculations made along these general lines the beginnings of a theory of chemical reactivity are appearing.[10,11,12,13].

Calculations.

This work is based on the theories set out by Coulson in his book "Valence",[14] and by B. and A. Pullman[15] in "Les Théories Électronique de la Chimie Organique". The mathematical treatment of the determinants was developed by Goodwin and Vand.[16]

The Kekulé structure of dimethylcorticrocein is:



In the calculations the lone pair of electrons on the methoxy oxygen has been neglected since, from chemical properties, they are less mobile than the other π electrons.

It is clear that we may now deal with the molecule according to the methods set out in the introduction. For carbon we put all the $H_{rr} = E_0$ and all the $H_{rs} = \beta$, but since oxygen is more electronegative it will claim a greater share of the π electrons, so that we put $H_{11} = H_{16,16} = E_0 + \beta$ and $H_{12} = H_{15,16} = 2\beta$.

We now have for the sixteen secular equations,

$$\left.\begin{array}{l} c_1(\overline{E_0+\beta}-E) + 2c_2\beta = 0 \\ 2c_1\beta + c_2(E_0-E) + c_3\beta = 0 \\ c_2\beta + c_3(E_0-E) + c_4\beta = 0 \\ \cdots\cdots\cdots \\ 2c_{15}\beta + c_{16}(\overline{E_0+\beta}-E) = 0 \end{array}\right\} \text{— } \underline{I}$$

If the c's are to be non-trivial the determinant of their coefficients must be zero. This gives us,

$$\begin{vmatrix}
x+1 & 2 \\
2 & x & 1 \\
& 1 & x & 1 \\
& & 1 & x & 1 \\
& & & 1 & x & 1 \\
& & & & 1 & x & 1 \\
& & & & & 1 & x & 1 \\
& & & & & & 1 & x & 1 \\
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& & & & & & & & & & & 1 & x & 1 \\
& & & & & & & & & & & & 1 & x & 1 \\
& & & & & & & & & & & & & 1 & x & 2 \\
& & & & & & & & & & & & & & 2 & x+1
\end{vmatrix} = 0 \text{ --- II}$$

By the well known property determinants, that it is permissable to add any linear combination of lines or columns to any other without altering the value, II is convertible to III.

$$\begin{vmatrix}
x+1 & 2 \\
2 & x & 1 \\
-2P_1 & -P_2 & & 1 \\
2P_2 & P_3 & & & 1 \\
-2P_3 & -P_4 & & & & 1 \\
2P_4 & P_5 & & & & & 1 \\
-2P_5 & -P_6 & & & & & & 1 \\
2P_6 & P_7 & & & & & & & 1 \\
& & & & & & & 1 & & & & & & & P_7 & 2P_6 \\
& & & & & & & & 1 & & & & & & -P_6 & -2P_5 \\
& & & & & & & & & 1 & & & & & P_5 & 2P_4 \\
& & & & & & & & & & 1 & & & & -P_4 & -2P_3 \\
& & & & & & & & & & & 1 & & & P_3 & 2P_2 \\
& & & & & & & & & & & & 1 & & -P_2 & -2P_1 \\
& & & & & & & & & & & & & 1 & x & 2 \\
& & & & & & & & & & & & & & 2 & x+1
\end{vmatrix} = 0 \text{ --- III}$$

P_n represents a continuant of the nth order. This is a special form of determinant, e.g.

$$P_n = \begin{vmatrix} x & 1 & \cdots & & \\ 1 & x & 1 & & \\ \vdots & & \ddots & & \vdots \\ & & 1 & x & 1 \\ & & \cdots & 1 & x \end{vmatrix} n.$$

The values of these continuants are given by,

$$P_n = P_1 P_{n-1} - P_{n-2}$$

If we now use the central symmetry of the determinant III we can immediately factorise it into two eighth order determinants, of of which (S) will give, on solution, values of C_r so that $C_r = C_{17-r}$, and the other (A) will give C_r values where $C_r = -C_{17-r}$. These two determinants can be finally reduced to,

$$S = P_8 + 2P_7 - 2P_6 - 3P_5 = 0, \text{ and}$$

$$A = P_8 + P_7 - 3P_6 = 0$$

The roots of A and S which lie between ± 2 can be readily found if we employ the relationship,

$$P_n = \frac{\sin(n+1)\alpha}{\sin\alpha}$$

where $x = 2\cos\alpha$.

This expression can be evaluated using normal Fourier methods. The remaining roots were found by systematic trial and error since it is unusual for the roots to exceed ± 3 when this type of compound is being dealt with. All the roots were refined using Taylor's theorem. Their values are given in Table AI.

Table AI.

Number of Root.	Value (= x).	Factor used.	Number of Root.	Value (= x).	Factor used.
16	2.417	A	8	-0.293	A
15	2.060	S	7	-0.727	S
14	1.884	A	6	-1.129	A
13	1.662	S	5	-1.480	S
12	1.366	A	4	-1.755	A
11	1.000	S	3	-1.935	S
10	0.593	A	2	-2.737	A
9	0.158	S	1	-2.737	S

These values, when we apply the normalisation and orthogonality conditions, lead in turn to the values of C_r which are in Table A II. The values for only one half the molecule are given, the others being related as stated previously. Only the coefficients for the eight lowest levels have been evaluated since, in the ground state, the rest will be unoccupied.

Table A II.

Root	Factor.	Atoms. 1	2	3	4	5	6	7	8
1	S	0.509	0.442	0.192	0.083	0.037	0.015	0.006	0
2	A	0.509	0.442	0.192	0.083	0.037	0.015	0.006	0
3	S	0.065	0.030	-0.070	-0.167	-0.253	-0.322	-0.371	-0.396
4	A	0.112	0.042	-0.150	-0.305	-0.386	-0.372	-0.267	-0.097
5	S	0.142	0.034	-0.234	-0.380	-0.328	-0.106	0.171	0.352
6	A	0.161	0.010	-0.310	-0.361	-0.097	0.251	0.381	0.179
7	S	0.172	-0.024	-0.361	-0.239	0.187	0.375	0.085	-0.313
8	A	0.180	-0.064	-0.379	-0.047	0.365	0.154	-0.320	-0.247

We may also use the roots to calculate the total energy of the π electrons which is $16E_0 + 25.586\beta$. The difference between this energy and the energy of the Kekulé structure is 5.586β, which represents the resonance energy of the molecule and is comparable with the values for phenanthrene or anthracene.[10.]

The bond orders etc. which were calculated using the coefficients of Table AII are given in Table A III. In Figure A II the same values are given in the form of a conventional molecular diagram.

Table A III.

(1) charge distribution and free valence.

	Atom. 1	2	3	4	5	6	7	8
charges	1.286	0.798	1.054	0.936	1.000	0.962	0.984	0.972
resultant charges	-0.286	+0.202	-0.054	+0.064	0	+0.038	+0.016	+0.028
free valence	-	-	0.256	0.096	0.158	0.128	0.148	0.142

Table A III.

(2) bond orders and lengths.

	Bond.							
	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9
bond order	1.896	1.386	1.790	1.528	1.728	1.558	1.708	1.564
bond length	1.22	1.45	1.37	1.42	1.38	1.41	1.39	1.41

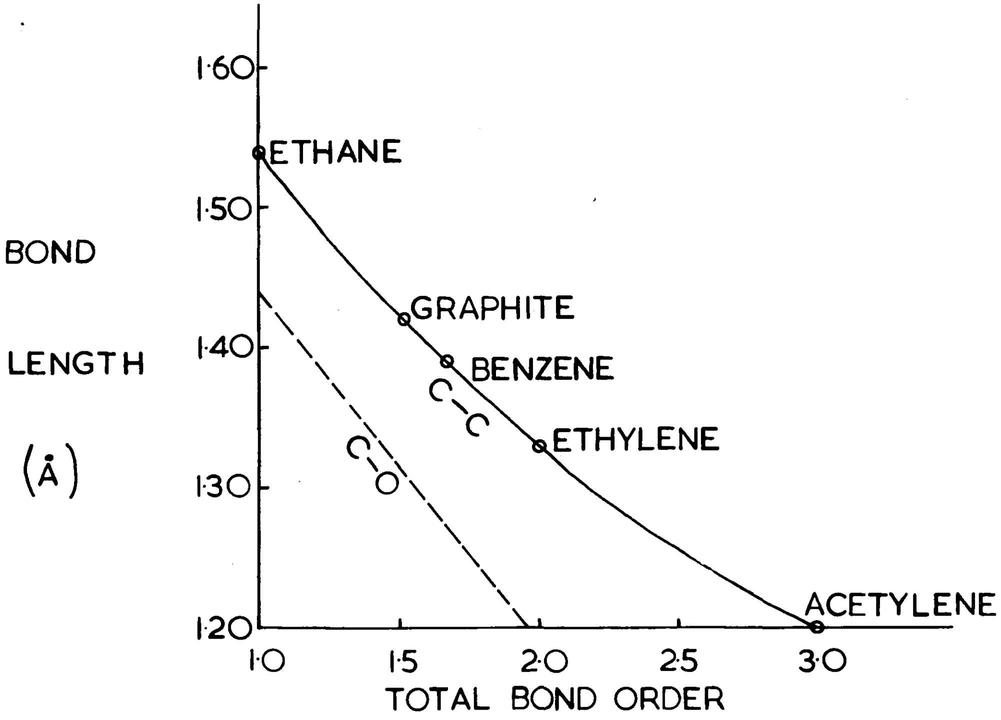
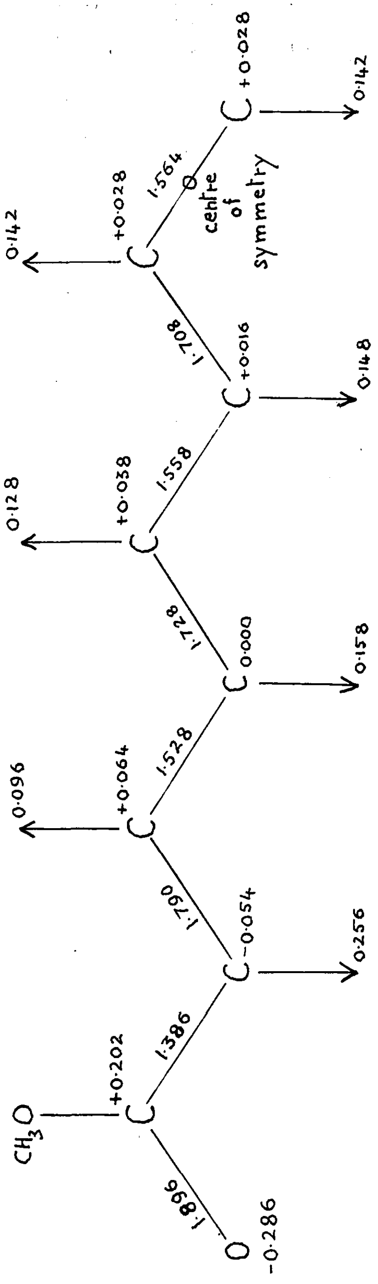


Figure A I.

Order-length curves used for carbon-carbon and carbon-oxygen bonds.

Figure A II.

Molecular Diagram for Dimethylcorticrocin.



Discussion.

It is unfortunate that no experimental bond lengths are are available for comparison with our calculations. However the bond orders can be compared with those of the corresponding hydrocarbon as Coulson[6] has obtained a general formula for these compounds.* Our compound shows a greater degree of alternation between the "single" and "double" bonds but the difference~~s~~ ~~are~~ is only large for the 2-3 ~~and 8-9 bonds~~ bond where ~~they~~ it amounts to about $\frac{1}{3}$ ~~and $\frac{1}{8}$~~ of the mobile order. ~~respectively.~~

Predictions of reactivity can also be made which show the carbon (3) to be the most reactive except towards anionic radicals which will favour the central atoms. No reactions have yet been reported for dimethylcortierocin, but this is in line with general chemical considerations.

* see leaf opposite

IN LINE 5 AFTER

for these compounds.

ADD

Coulson's formula is,

$$p_r = \frac{1}{2n+1}\left\{\text{cosec.}\frac{\pi}{4n+2} + (-1)^{r-1}\text{cosec.}\,(2r+1)\frac{\pi}{4n+2}\right\}$$

where p_r is the mobile bond order of the rth bond and n is the number of carbon atoms.

The total bond orders which are calculated by this method are:-

1·851, 1·476, 1·730, 1·564, 1·697, 1·585, 1·683, and 1·595

where the sequence is the same as that given in the molecular diagram.

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which will favour the central atoms. No reactions have yet been reported for dimethylcorticrocin, but this is in line with general chemical considerations.

* see leaf opposite

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Appendix II.

Re-Determination of the Film Absorbtion Factor.[1]

Previous workers in this department have found that this factor does not change appreciably for different batches of any one make of film. However it was decided to check up on this by redetermining the factor for CuK$_\alpha$ radiation (the factor varying with the wavelength).

Monochromatic radiation was obtained by reflecting Ni filtered CuK$_\alpha$ from a large calcite crystal, which gives a very intense (200) reflection, and a short exposure oscillation photograph was taken with a pack of four films. A series of wedges of known intensity gradation were also exposed on a separate film and all the films were developed together. The relative intensities of the spots on the different films were then found using a photometer calibrated by means of the wedges.

The film employed was Ilford Industrial G, each sheet of which was kept wrapped in its black paper covering, and which was found to have an absorbtion factor of 3.22. This value agrees, within the limits of the probably experimental error, with the value of 3.3 which had been employed previously.

This work was carried out in collaboration with G.A. Sim and we are indebted to Dr. S.T.R.S. Mitchell for the use of his photometer.

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