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The Application of the Fourier-Transform Method to the Analysis of the Structure of Triphenylene, $C_{18}H_{12}$

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The Fourier-transform method of Ewald and Knott has been successfully applied to determine the approximate crystal structure of triphenylene, $C_{18}H_{12}$. Since the molecules are asymmetric and do not lie at special positions in the unit cell, the treatment as developed here is more general than any hitherto attempted. It is suggested that the method may be found useful in making the preliminary estimate of a crystal structure composed of planar molecules.

Introduction

In many organic crystals the atoms are grouped together to form molecules of more or less accurately known dimensions and configuration, and it would evidently be advantageous to be able to treat the molecule as the unit in the preliminary stages of a crystal analysis when an approximate structure is being sought; for the position and orientation of a molecule of known configuration are determined by six parameters only, and these alone need be handled, instead of the very much larger number fixing the positions of the individual atoms.

The amplitude of the wave scattered by a molecule may be represented in reciprocal space, as Hettich (1935) and Ewald (1935) have pointed out. When considered in this way, the molecular scattering factor is called the Fourier transform of the molecule, and Knott (1940) has shown how to represent the transform of a planar molecule as a contour map and has illustrated its application by taking the case of naphthalene, a known structure. The only instance of the application of this method to an unknown structure appears to be the work of Waser & Lu (1944) on biphenylene. No details are given, but, like naphthalene, the molecule has a centre of symmetry in the idealized model used in calculating the transform, which is consequently real; moreover, the absence of certain types of reflexion (e.g. $hk0$ appears only with $h=3n$) suggests immediately that the molecules lie at special positions in the unit cell, and this simplifies the procedure.

In this paper an account is given of the successful use of the Fourier-transform method to determine the approximate structure of triphenylene (Klug, 1950). In this structure the molecules have no centre of symmetry, and lie in general positions in the unit cell, and it provides a more general example of the application of the method than any given previously.

The Fourier transform of a single molecule

It will be convenient at this point to summarize the properties of the molecular structure factor in the form in which they will be required.

We consider first the scattering factor of a single molecule, a typical atom of which, of atomic scattering factor f_j, is fixed relative to a convenient origin by a vector $\mathbf{r}_j$. The amplitude scattered by the molecule is proportional to

$$F(\mathrm{S}/\lambda)=\sum_j f_j \exp\frac{2\pi i}{\lambda}(\mathbf{S}\,.\,\mathbf{r}_j), \tag{1}$$

where $\mathbf{S}=\mathbf{s}-\mathbf{s}_0$, $\mathbf{s}$ and $\mathbf{s}_0$ being the unit vectors in the direction of incidence and scattering. If we denote the vector $\mathbf{S}/\lambda$ by $\boldsymbol{\rho}$, we may write

$$F(\boldsymbol{\rho})=\sum_j f_j \exp 2\pi i(\boldsymbol{\rho}\,.\,\mathbf{r}_j). \tag{2}$$

We can thus plot $F(\boldsymbol{\rho})$ in the space defined by the vector $\boldsymbol{\rho}$ drawn from the origin, and from the distribution so obtained determine the amplitude scattered by the molecule when it is in the position determined by the vectors $\mathbf{r}_j$; for $\boldsymbol{\rho}$ is determined by the conditions of incidence and scattering, and the amplitude scattered under these conditions is given by the value of $F(\boldsymbol{\rho})$ at the extremity of the vector $\boldsymbol{\rho}$.

The vectors $\boldsymbol{\rho}$ and $\mathbf{r}_j$ occur in $F(\boldsymbol{\rho})$ only in the form of the scalar product, and it is therefore immaterial what co-ordinate axes we may choose relative to which to express their components. If, however, the molecule forms the unit of structure of a crystal lattice, the natural choice of axes will be the crystal axes for $\mathbf{r}_j$ and the corresponding reciprocal axes for $\boldsymbol{\rho}$. $F(\boldsymbol{\rho})$ is then considered as a distribution in the reciprocal space and is called the Fourier transform of the molecule. A spectrum is produced only when $\boldsymbol{\rho}$ is a vector in the reciprocal lattice, i.e. when the components of $\boldsymbol{\rho}$ parallel to the reciprocal axes are an integral number h, k, l of times the primitive translations a^*, b^*, c^* of the reciprocal lattice. If then the reciprocal lattice is supposed drawn with the appropriate orientation relative to the distribution $F(\boldsymbol{\rho})$, the value of F at the points of the lattice give the contributions of the molecule to the ordinary structure factor $F(hkl)$.

It should be noted that the Fourier transform of a molecule is a property of the geometry of the molecule itself and does not primarily depend on its relation to

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a crystal structure. In the numerical calculation of the transform, the crystal axes may therefore not be the most convenient ones to use.

Some properties of the transform

The structure factor f_j is also a function of ρ. We shall here assume it to be real, and spherically symmetrical about the origin. It will have its maximum value for $\rho=0$, and will decrease with increasing $|\rho|$.

Equation (2) may be written

$$F(\rho)=\sum_j f_j \cos 2\pi(\rho\,.\,\mathbf{r}_j)+i\sum_j f_j \sin 2\pi(\rho\,.\,\mathbf{r}_j). \quad (3)$$

Neither term in (3) is truly periodic, because of the factor f_j, but if we consider only molecules in which all the atoms are alike, and of scattering factor f, we may write

$$T(\rho)=\frac{F(\rho)}{f(\rho)}=\sum_j \cos 2\pi(\rho\,.\,\mathbf{r}_j)+i\sum_j \sin 2\pi(\rho\,.\,\mathbf{r}_j) \quad (4)$$

$$=A(\rho)+iB(\rho). \quad (5)$$

Evidently $\rho\,.\,\mathbf{r}_j$ is constant over planes in the reciprocal space which are perpendicular to $\mathbf{r}_j$. Each term in (4) represents a plane sinusoidal distribution in the ρ-space with wave-length $1/|\mathbf{r}_j|$, with the wave-normal parallel to $\mathbf{r}_j$. There is one such distribution in the real part $A(\rho)$ of $T(\rho)$, and one in the imaginary part $B(\rho)$, for each atom in the molecule. By the addition of these wave distributions the real and imaginary parts of the transform can be built up. The real distribution $A(\rho)$ is centro-symmetrical with respect to the origin, and the imaginary part anti-symmetrical, since

$$B(\rho)=-B(-\rho).$$

The modulus $|T(\rho)|$ is of course centro-symmetrical.

The transform of a planar molecule

The distributions $A(\rho)$ and $B(\rho)$ are of course three-dimensional, and cannot easily be shown diagrammatically. For a plane molecule, however, they take a simple form. If the origin of co-ordinates lies in the plane of the molecule, the wave-normals of all the constituent sinusoidal distributions lie in this plane, and the resultant distributions are cylindrical in character, and have the same value along any line normal to the plane of the molecule. The distributions have this property whatever origin may be chosen, but the natural choice of an origin in the molecular plane makes it immediately evident.

The transform of triphenylene

For the purpose of calculating the transform, the molecule of triphenylene was assumed to be plane, and to consist of regular hexagons of carbon atoms with an interatomic spacing 1·40 A. The molecule has no centre of symmetry, so that both real and imaginary parts of the transform must be used. To calculate the transform, axes of x and y are chosen in the plane of the molecule as shown in the inset of Fig. 2, the origin being at the centre of the molecule. The co-ordinates of the jth atom are (x_j, y_j, z_j), but z_j is always zero. The reciprocal vector ρ is referred to axes coincident with those of x, y, z, its components being written (X, Y, Z). The transform of the molecule is then

$$T(X, Y, Z)$$
$$=\sum_j \cos 2\pi(x_j X+y_j Y)+i\sum_j \sin 2\pi(x_j X+y_j Y). \quad (6)$$

T is independent of Z, and from (6) the real and imaginary parts of the transform can be calculated and plotted as contour diagrams giving any section perpendicular to Z and parallel to the plane of the molecule. Such sections are shown in Fig. 2 (*a*) and (*b*). With the axes so chosen x_j and y_j are always multiples of 0·70 and 1·21 A. respectively, and the transform is periodic in the XY plane; but this is not a general property of such transforms if no simple relationship between the individual atomic co-ordinates exists. The true transform for triphenylene in fact is not simply periodic, for the molecule has not the idealized regular form assumed in the preliminary calculations, although it approaches it.

The Fourier transform of a unit cell

The unit cell of triphenylene contains four molecules, related by the symmetry elements of the space group $P2_12_12_1$. The transform for the unit cell is obtained by adding together those of the individual molecules, each in its correct orientation and with its correct phase factor, and the resulting expression would be very cumbersome. We can, however, determine the transform applicable to those spectra for which one index is zero relatively easily.

For this purpose, it is convenient to express the transform in terms of co-ordinates referred to the crystal axes and their reciprocal axes. If (u, v, w) are the co-ordinates of an atom in the molecule, expressed as fractions of the edges of the unit cell, and (ξ, η, ζ) are those of a point in the reciprocal space, referred to the reciprocal axes and expressed as multiples of the edges of the reciprocal-lattice cell, the transform may be written

$$T(\xi, \eta, \zeta)_{\text{mol.}}=\Sigma \exp 2\pi i(\xi u+\eta v+\zeta w), \quad (7)$$

where the sum is over all the atoms of the molecule.

Suppose now we wish to determine the $hk0$ structure factors. We need the section of T in the plane $\zeta=0$, i.e. $T(\xi, \eta, 0)$. The values of the w co-ordinates are then immaterial, and in considering the symmetry of the cell we may think of the atoms as projected on the plane (001). Let us choose as origin a point at which one of the twofold screw axes intersects the plane of projection, and let (u_c, v_c, w_c) be the fractional co-ordinates, referred to the crystal axes, of the centre of the molecule used as origin in calculating the transform. Let (u_j, v_j, w_j) be the fractional co-ordinates of the jth atom, referred to axes parallel to the crystal axes but with the molecular centre as origin. Then $(u_c+u_j, v_c+v_j, w_c+w_j)$ are the co-ordinates relative to the crystal axis chosen. The screw axis through this origin produces a corresponding atom with co-ordinates $-(u_c+u_j)$, $-(v_c+v_j)$, $(w_c+w_j+\frac{1}{2})$. The contribution of the pair of molecules related by this screw axis to the transform is therefore, for the plane $\zeta=0$,

$$\begin{aligned} T_1(\xi,\eta,0) &= 2\sum_j \cos 2\pi\{\xi(u_c+u_j)+\eta(v_c+v_j)\} \\ &= 2\sum_j \cos 2\pi\{(\xi u_j+\eta v_j)+(\xi u_c+\eta v_c)\} \qquad (8) \\ &= 2\{A(\xi,\eta,0)\cos 2\pi(\xi u_c+\eta v_c) \\ &\qquad -B(\xi,\eta,0)\sin 2\pi(\xi u_c+\eta v_c)\} \\ &= 2\,|\,T(\xi,\eta,0)\,|_{\text{mol.}}\cos 2\pi\{\xi u_c+\eta v_c+\alpha(\xi,\eta)\}. \end{aligned} \tag{9}$$

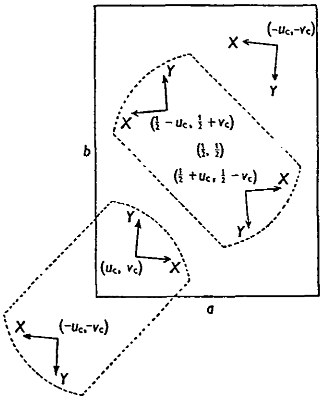

Fig. 1. The projection of the unit cell of triphenylene on the *a b* face showing how it may be regarded as made up of two molecule pairs situated at (0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$) respectively.

In these equations A and B have the significance of equation (5), and are the real and imaginary parts of the transform of a single molecule, referred, however, to the fractional reciprocal co-ordinates;

$$|\,T\,|_{\text{mol.}}=\sqrt{(A^2+B^2)}; \tag{10}$$

and the phase angle α is given by

$$2\pi\alpha(\xi,\eta)=\arctan\{B(\xi,\eta,0)/A(\xi,\eta,0)\}. \tag{11}$$

So far as the projection on the plane (001) is concerned, the co-ordinates of any atom in the other pair of molecules in the unit cell are derived from those of the corresponding atom of the first pair by reversing the sign of v_j and v_c and adding $\frac{1}{2}$ to both u_c and v_c. This is immediately evident from Fig. 1. The reversal of the sign of the v co-ordinate in equations (8) and (9) is equivalent to reversing the sign of η. We may therefore write at once from (9), for the contribution to the transform of the second molecule pair,

$$\begin{aligned} T_2(\xi,\eta,0) &= 2\,|\,T(\xi,\bar{\eta},0)\,|_{\text{mol.}} \\ &\quad \times\cos 2\pi\{\xi u_c+\eta v_c+\tfrac{1}{2}(\xi+\eta)+\alpha(\xi,\bar{\eta})\}. \end{aligned} \tag{12}$$

The total transform may be obtained by adding (9) and (12).

Let us consider only the reciprocal-lattice rows $(h,0,0)$ and $(0,k,0)$. Putting $\xi=h$ and $\eta=0$ in (9) and (12), and taking the sum, we obtain

$$\begin{aligned} T(h00)_{\text{cell}} &= 2\,|\,T(h00)\,|_{\text{mol.}} \\ &\quad \times[\cos 2\pi\{hu_c+\alpha(h,0)\}+\cos 2\pi\{hu_c+\alpha(h,0)+\tfrac{1}{2}h\}]. \end{aligned}$$

When h is odd this expression vanishes, which is one of the space-group conditions, and for h even

$$T(h00)_{\text{cell}}=4\,|\,T(h00)\,|_{\text{mol.}}\cos 2\pi\{hu_c+\alpha(h,0)\}. \tag{13}$$

Similarly, since

$$|\,T(0k0)\,|_{\text{mol.}}=|\,T(0\bar{k}0)\,|_{\text{mol.}} \quad\text{and}\quad \alpha(0,\bar{k})=-\alpha(0,k),$$

$$T(0k0)_{\text{cell}}=4\,|T(0k0)\,|_{\text{mol.}}\cos 2\pi\{kv_c+\alpha(0,k)\}, \tag{14}$$

if k is even, but vanishes if k is odd.

An exactly similar relation will hold for $T(00l)_{\text{cell}}$.

The derivation of the crystal structure of triphenylene with the aid of the molecular transform

We have seen how the Fourier transform of the unit cell of the triphenylene crystal can be built up by superposing the transforms of the four molecules that it contains, and how for any point in the plane $\zeta=0$, it can easily be expressed in terms of the transform of a single molecule. The expression takes a particularly simple form, given in equations (13) and (14), for reciprocal-lattice points lying along the reciprocal axes themselves.

Suppose now a certain orientation of the axes ξ, η, ζ to have been chosen relative to the molecular transforms calculated in terms of the axes X, Y. For each point $(h,0,0)$ and $(0,k,0)$, along the axes ξ and η, which are identical with the reciprocal axes a^* and b^*, we read the values of the real and imaginary parts, A and B, of the transform, and from these form the value of $|\,T\,|_{\text{mol.}}$. This value of $|\,T\,|$, multiplied by the appropriate phase factor for the point concerned, given in equations (13) and (14), should, for each point of the rows, be equal to the corresponding value of $\frac{1}{4}\,|\,F_{\text{obs.}}\,|$ divided by the appropriate value of the atomic scattering factor, i.e. $\frac{1}{4}\,|\,T\,|_{\text{cell}}$. The process of deriving the crystal structure from the transform consists in varying the orientation of the reciprocal axes relative to the transform until agreement is reached.

The measurements of the magnetic anisotropy of the triphenylene crystal (Banerjee & Guha, 1937) indicate that the normals to the molecular planes are inclined at 51° to the c axis, and equally inclined at about 57° to the a and b axes. The inclination of the plane of the molecule to the crystal axes is thus known, but there is still a parameter determining the orientation of the molecule in its own plane, as well as the three parameters u_c, v_c, w_c, fixing the centre of the molecule, to be determined. The projection of a reciprocal net on to the plane of the molecule, and hence on to the $X\,Y$ plane of its transform, is easily found. In Fig. 2 the projection of the reciprocal axes a^* and b^* is plotted on the same scale as the contour maps of the real and imaginary parts, A and B, of the Fourier transform, and with the same origin. Since all $h00$ and $0k0$ spectra of odd index are absent according to space-group requirements, only reciprocal points $(h, 0, 0)$ and $(0, k, 0)$ with even indices are indicated in the figure. The reciprocal axes, the angle between which is of course fixed by the inclination assumed for the molecular plane, must be rotated relative to the transform into a position such that an equation of the form of (13) or (14) can be fulfilled for each lattice point. This can be done only by trial and error, and, since the real and imaginary parts must be considered together, the problem of finding both the correct orientation and the correct values of u_c or v_c appearing in the phase factors appears at first sight to be very difficult.

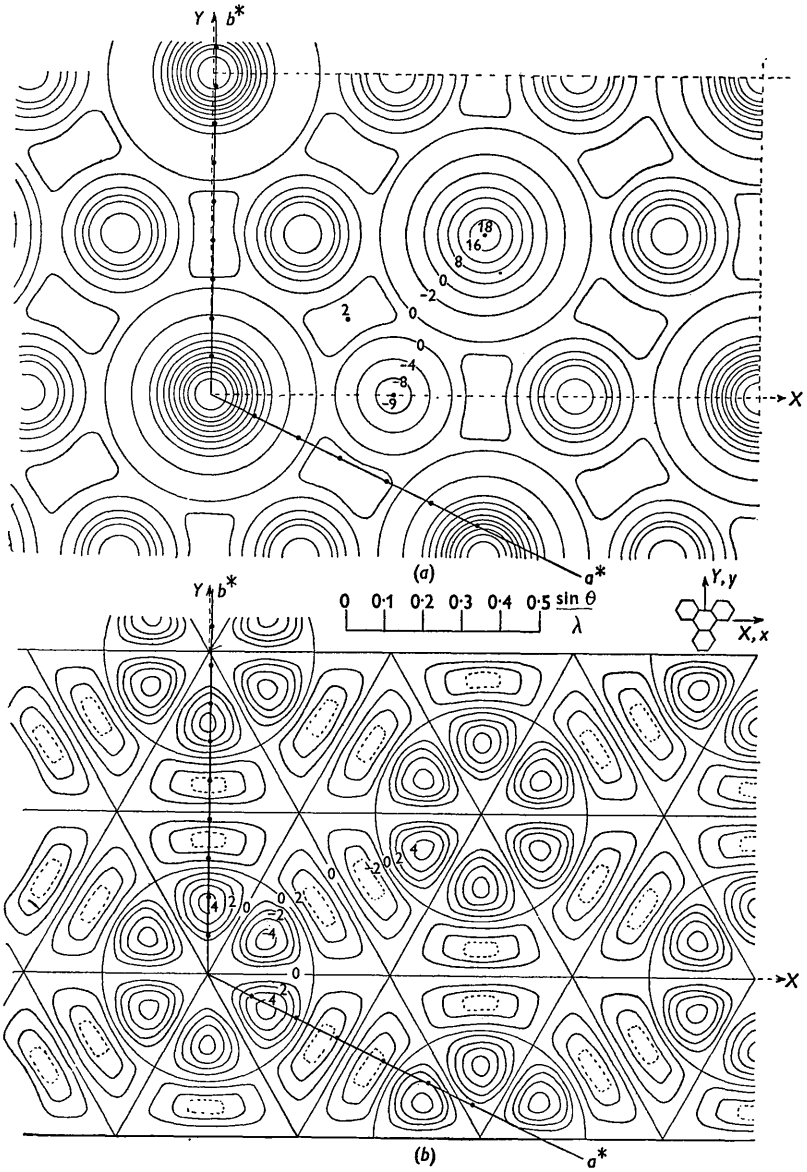

Fig. 2. (a) Contour map of $A(\xi, \eta, 0)$, the real part of the Fourier transform of triphenylene. For clarity in numbering, some contour lines have been omitted from parts of the diagram. (b) Contour map of $B(\xi, \eta, 0)$, the imaginary part.

The projections of the a^* and b^* axes are shown in both contour maps, but only the reciprocal-lattice points of even index are indicated, since the spectra of odd order on these axes are in any case absent. The unit cell of the transform is indicated by the broken lines in (a).

There are, however, several clues. It may be seen from Fig. 2 that, owing to the symmetry of the real part of the transform, the values of $A(200)$, $A(400)$ and $A(020)$, $A(040)$, $A(060)$ do not depend on the orientation of the axes. Only the variation of the imaginary parts need be considered in these cases, and unsatisfactory molecular orientations can easily be rejected. Consider, for example, the point $(0, 4, 0)$. The observed value of $\frac{1}{4}|T(040)|_{\text{cell}}$ is 3·8 and from the contour diagram $A(040) = -1{\cdot}85$. Now the greatest possible value of

$\frac{1}{4}|T|_{\text{cell}}$ obtainable from the transform is $|T|_{\text{mol.}}$ or $\sqrt{(A^2+B^2)}$. Hence the least value of $B(040)$ necessary to account for the observed value of $\frac{1}{4}|T|_{\text{cell}}$ is given by $\sqrt{(3{\cdot}8^2-1{\cdot}85^2)}=3{\cdot}3$. Thus, in Fig. 2 (*b*), the lattice point $(0, 4, 0)$ must lie at a position in the contour map which will give a value of B greater than 3·3.

Similar considerations applied to the spectra mentioned fix the orientation of the reciprocal axes within fairly narrow limits. Other spectra which are particularly useful for this purpose are those that are of high order but still comparatively strong (e.g. 0.18.0 and 12.0.0); in such cases the value of $\sqrt{(A^2+B^2)}$ may be very sensitive to slight changes in orientation. Furthermore, since the maximum value of A, namely 18, is so much greater than that of B, namely $4\frac{1}{2}$, the orientation may in some cases be largely decided by considering the real part of the transform only.

By studying the possible variations in the values of $\sqrt{(A^2+B^2)}$ for the individual $h00$ and $0k0$ spectra, the orientation may be determined with some accuracy. The final position adopted is shown in Fig. 2, b^* making an angle of about 1° with Y; but it should be noted that, owing to the trigonal symmetry of the transform, there are two other equivalent positions.

The molecular parameters u_c, v_c have now to be determined. To find v_c we consider first the point (0,2,0). The observed value of $\frac{1}{4}|T(020)|_{\text{cell}}$ is 2·8. From Fig. 2, $A(020)=+7{\cdot}4$, $B(020)=+1{\cdot}6$, giving $2\pi\alpha=\arctan(1{\cdot}6/7{\cdot}4)=2\pi\times0{\cdot}035$. Then, from equation (14),

$$|2{\cdot}8|=\sqrt{(7{\cdot}4^2+1{\cdot}6^2)}\cos 2\pi\{2v_c+0{\cdot}035\},$$

whence $2v_c+0{\cdot}035=0{\cdot}19,\ 0{\cdot}31,\ 0{\cdot}69$ or $0{\cdot}81$,

or $v_c=+0{\cdot}077,\ -0{\cdot}114,\ +0{\cdot}136$ or $0{\cdot}326$.

In the same way,

$\frac{1}{4}|T(040)|_{\text{cell}}=3{\cdot}8,\quad A(040)=1{\cdot}85,\quad B(040)=+4{\cdot}2,$ giving

$2\pi\alpha=-2\pi\times0{\cdot}182$ and $|3{\cdot}8|=4{\cdot}6\cos 2\pi(4v_c-0{\cdot}182)$, whence we obtain

$$v_c=+0{\cdot}069,\ +0{\cdot}146,\ -0{\cdot}056.$$

The value of v_c thus lies either near $+0{\cdot}07$ or $+0{\cdot}140$, and the former may be discarded as leading to a physically impossible structure. In any event, the ambiguity is decided when $0k0$ spectra of higher order are considered. The mean value of v_c obtained by considering all relevant spectra is $v_c=+0{\cdot}140$.

By a similar procedure, the details of which need not be given, the value $u_c=+0{\cdot}175$ was obtained. The w_c parameter could not be derived very accurately, since only three $00l$ spectra, all of which are weak, appear. It appeared, however that w_c was small, and lay between 0·02 and 0·05. The effect of slight changes in orientation was considered, but no improvement on that shown in Fig. 2 and on the corresponding molecular parameters could be obtained. The molecular position determined in this way was completely confirmed by a Fourier synthesis, the details of which are given elsewhere (Klug, 1950).

Although the spread about their means of the individual values of u_c and v_c, obtained is about $\pm0{\cdot}006$, this is not unduly large when it is considered that the transform was calculated for an idealized molecule, whereas it was afterwards found that the molecule is by no means regular, and that variations of as much as 0·07 A. from the assumed interatomic spacing of 1·40 A. occur. A good estimate of the molecular position is in fact obtained, because the final values of u_c and v_c are found by taking the mean of the values obtained for a good number of axial reflexions.

Discussion

The example given in this paper suggests that the Fourier transform method may be found useful in the preliminary analysis of a structure composed of planar molecules, especially if one or more parameters are known—for example, the inclination of the molecular plane, as in this case. It should, however, be noted that, even had no magnetic data been available for triphenylene, the approximate inclination could have been determined very easily from the ratio of the short c spacing, 5·28 A., to the usual interplanar distance, about 3·6 A., between parallel hydrocarbon molecules. Once the transform of triphenylene had been drawn, it took only a few hours to determine the molecular position and orientation, and the atomic co-ordinates so derived led at once to a Fourier projection on the ab plane which showed quite clearly the position of the atoms.

In the other examples to which the method has been applied, naphthalene and biphenylene, the application of the method is simplified because the presence of a centre of symmetry in the molecule makes the Fourier transform essentially real, and the molecules lie at special positions. The application described in this paper shows that it is possible to use the method for asymmetric molecules which are not situated at special positions in the unit cell. In the case of molecules containing an inherent centre of symmetry, which is not used in building the crystal structure (e.g. pyrene, Robertson (1947)), the complexity of the method would lie between the special and general cases mentioned above; for, in such a case, the transform though real must be combined with a phase factor depending on the position of the molecular centre, and the equation corresponding to (13) would be

$$\tfrac{1}{4}|T(h00)|_{\text{cell}}=|T(h00)|_{\text{mol.}}\cos 2\pi h u_c.$$

Finally, it should be noted that since this work was completed Booth (1948, p. 35) has devised a type of molecular structure factor to determine the parameters of translation of a molecule. The method involves the calculation of certain quantities A and B, which can be seen to be analogous to the real and imaginary parts of a Fourier transform. This must, however, be done separately for each spectrum, so that it is not as useful as the Fourier transform in the case of planar molecules where contour maps can be constructed.

Furthermore, Booth's method presupposes a knowledge of the orientation which is not generally completely available. Since it does not involve plotting contour diagrams, it might, however, prove advantageous in the case of non-planar molecules.

I wish to thank Prof. R. W. James for many helpful discussions throughout the course of the work, and particularly for his valued advice in the formulation of the theoretical part of this paper. To the South African Council of Scientific and Industrial Research I am indebted for a research grant, during the tenure of which this work was done.

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The Phases and Magnitudes of the Structure Factors*

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Inequalities among the coefficients of a Fourier series representing the electron density in a crystal are derived on the basis that the series represents a positive function. The procedure is formulated for obtaining all inequalities which are based on this characteristic of positiveness, and some of the simpler ones are listed. No symmetry properties are required for deriving the inequalities, but they may be readily introduced into the inequality relationships. It is indicated that application of the linear transformation theory on hermitian forms may prove fruitful in future investigation.

An extensive and fundamental system of inequalities exists among the coefficients of a Fourier series which represents a positive function. The structure factors are the coefficients in the Fourier-series representation of the positive electron density distribution function for crystals. It is the purpose of this paper to derive the fundamental system of inequalities among the structure factors and express them in a useful form.†

By making use of the symmetry characteristics which are found in crystals and the Schwarz inequality, Harker & Kasper (1948) have derived certain useful inequalities among the structure factors. An extension of this work has been made by Gillis (1948), who has applied some additional inequalities of formal mathematical analysis. In both cases it was necessary to resort to symmetry characteristics and certain standard inequalities in analysis. Implicit in their investigations though was the assumption that their distribution function was positive. In recent work on the structure of atoms‡ we have found that the electron distribution about atoms is accurately determined by a limited amount of experimental data since the distribution function is positive. This characteristic of positiveness will be seen to be alone sufficient to yield a system of inequalities which limits the phases and magnitudes of the structure factors for crystals.

Symmetry considerations are not basic to the development of the theory. However, it will be shown how symmetry relations may be introduced into the final results.

Theory

The Fourier coefficient, F_{hkl}, is defined in terms of the electron density distribution function for a crystal, $\rho(x,y,z)$, as follows:

$$F_{hkl}=V\int_0^1\int_0^1\int_0^1 \rho(x,y,z) \times \exp\left[-2\pi i(hx+ky+lz)\right]dx\,dy\,dz, \quad (1)$$

where V is the volume of the unit cell. We construct from expression (1) useful hermitian forms which will be shown to be non-negative. The forms obtained from (1) are

$$\mathop{\sum_{hkl}\sum_{h'k'l'}}_{1}^{m} X_{hkl}\overline{X}_{h'k'l'}F_{h-h',\,k-k',\,l-l'} = V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\mathop{\sum_{hkl}\sum_{h'k'l'}}_{1}^{m} X_{hkl}\overline{X}_{h'k'l'} \times \exp\{-2\pi i[(h-h')\,x+(k-k')\,y+(l-l')\,z]\}\,dx\,dy\,dz, \quad (m=1,2,\ldots), \quad (2)$$

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† A system of inequalities for the one-dimensional case has been found by Achyeser & Krein (1934) in their studies of the one-dimensional trigonometric moment problem.

‡ To be published (*Phys. Rev.*, February 1950). Presented at ASXRED Meeting, Columbus, Ohio, December 1948.