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On the determination of intermolecular vectors in molecular crystals by a modified Patterson function. By E. GIGLIO, A. M. LIQUORI and A. RIPAMONTI, *Istituto di Chimica Generale dell'Università di Bari, Italy*

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The localization of the molecules in the unit cell after their orientation has been approximately established is one of the main difficulties involved in the application of the Fourier-transform method in the preliminary stages of a structure determination. If the Fourier transform $T_M(\mathbf{S})$ of each molecule at

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (1)$$

is supposed to be known to a certain degree of accuracy, the problem reduces to determine the \mathbf{R}_M vectors appearing in the structure amplitude expressed as

$$F(\mathbf{S}) = \sum_M T_M(\mathbf{S}) \exp \{2\pi i \mathbf{S} \cdot \mathbf{R}_M\}, \quad (2)$$

where

$$T_M(\mathbf{S}) = \sum_n f_n \cdot \exp \{2\pi i \mathbf{S} \cdot \mathbf{r}_n\} \quad (3)$$

$$\mathbf{R}_M = X_M \mathbf{a} + Y_M \mathbf{b} + Z_M \mathbf{c} \quad (4)$$

are vectors from the origin of the unit cell to a reference point in the M th molecule, and

$$\mathbf{r}_n = x_n \mathbf{a} + y_n \mathbf{b} + z_n \mathbf{c} \quad (5)$$

are vectors from the reference points in the molecule to the n th atom.

In the special case when all the molecules have the same orientation either in space or in projection, (2) may be written as

$$F(\mathbf{S}) = T(\mathbf{S}) \cdot A(\mathbf{S}), \quad (6)$$

where

$$A(\mathbf{S}) = \sum_M \exp \{2\pi i \mathbf{S} \cdot \mathbf{R}_M\}. \quad (7)$$

The \mathbf{R}_M vectors may then be obtained (Booth, 1948) as those quantities which satisfy relation (6). On the basis of relation (6), Taylor (1954) has developed a method for determining the \mathbf{R} 's which may also be applied to cases where the molecules have not necessarily the same orientation. However, Taylor's method, though interest-

ing, has several limitations in its practical application, the most restrictive one being due to the inaccuracy with which the quantities $A(\mathbf{S})$ may be obtained.

A modification of the Booth-Taylor method, applicable to centrosymmetric molecules, has been suggested by Liquori & Ripamonti (1956) which overcomes the above difficulty. However, the solutions are not always unique, especially when the number of independent molecules is larger than two. A similar method has been more recently proposed by Taylor (1957).

It is obvious that in view of the poor accuracy of the $A(\mathbf{S})$ values, the efficiency of a method of determining the \mathbf{R}_M vectors should increase with increasing the number of $A(\mathbf{S})$ which can be used. The automatic averaging which would result should in part reduce both the number of false solutions and the inaccuracy of the true solutions. The above consideration suggests that a suitable modified Patterson function would lend itself to this purpose. In fact, it is a common observation that the Patterson projection of a structure containing groups of atoms arranged in centro-symmetric regular assemblies in the unit cell does contain maxima corresponding to vectors between centers of such assemblies (Patterson, 1949). However, it is usually difficult to recognize these maxima when the unit cell contains a large number of atoms.

It may be shown that it is possible to enhance the maxima corresponding to intermolecular vectors with respect to those corresponding to interatomic vectors by a suitable modification of the vector functions.

An idealized structure will be considered here consisting of identical atoms and located at the centers of the molecules. If the Fourier transform of the molecule is calculated taking its center as origin, the electron-density distribution of the idealized structure is:

$$\rho(\mathbf{R}) = \frac{1}{V} \sum_{\mathbf{S}} G(\mathbf{S}) \exp \{2\pi i \mathbf{S} \cdot \mathbf{R}\}, \quad (8)$$

where

$$G(\mathbf{S}) = f \cdot \sum_M \exp \{2\pi i \mathbf{S} \cdot \mathbf{R}_M\}. \quad (9)$$

The vector function $P(\mathbf{q})$ for this idealized structure

$$P(\mathbf{q}) = V \int \varrho(\mathbf{R}) \cdot \varrho(\mathbf{R} + \mathbf{q}) d\mathbf{R} \quad (10)$$

becomes

$$P(\mathbf{q}) = \frac{1}{V} \sum_{\mathbf{S}} |G(\mathbf{S})|^2 \cdot \exp \{2\pi i \mathbf{S} \cdot \mathbf{q}\}. \quad (11)$$

This modified Patterson function will give the vector distribution corresponding to the structure which has been considered and, therefore, will contain $M(M-1)$ maxima relating to the M molecular centers.

Since the practical utility of such a modified Patterson function is limited to projections, it is easy to see that for centrosymmetric molecules it may be applied both to $p2$ and pgg plane groups. For plane groups $p2$ the coefficients of (11) are

$$G^2(h, k) = f^2(F^2(h, k)/T^2(h, k)), \quad (12)$$

and for plane groups pgg :

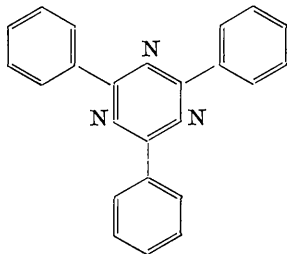
$$G^2(h, k) = f^2(F^2(h, k)/[2T_1(h, k) + 2T_2(h, k)]^2). \quad (13)$$

$2T_1(h, k)$ and $2T_2(h, k)$ being the Fourier transform (sampled at reciprocal-lattice points h, k) of the pairs of molecules with different orientations.

The most prominent maxima of a Patterson projection having as coefficients the observed intensities normalized with respect to the square of the Fourier transform of the molecules sampled at reciprocal-lattice points should therefore be related to the positions of the molecular centers.

The application of the above method to the $h0l$ projection of the structure of triphenyl-triazine, space groups $P2_1/c$, $Z = 4$ (Giglio & Ripamonti, 1958) is illustrated below.

The chemical formula of this compound is



The molecule consists of atoms arranged in four coplanar or nearly coplanar rings with approximately hexagonal symmetry. Taking therefore the hexagonal ring as a unit, the whole structure was considered to consist of 16 atoms located at the centers of the rings. The orientation of the hexagonal rings was easily deduced by inspection of the $h0l$ weighted reciprocal-lattice section, and the Fourier transform of a benzene ring with this orientation was sampled at reciprocal-lattice points ($h0l$); see Fig. 1. The observed structure amplitudes were divided by $T(h0l)$'s and the squares of these quantities were used as coefficients of a Fourier series. A plot of the function is shown in Fig. 2, where it may be observed that the maxima occur at the expected positions with a satis-

factory accuracy. In Fig. 3, the Patterson function calculated using the $F^2(h0l)$ as coefficients is shown for comparison. As expected, the inter-ring peaks, which are

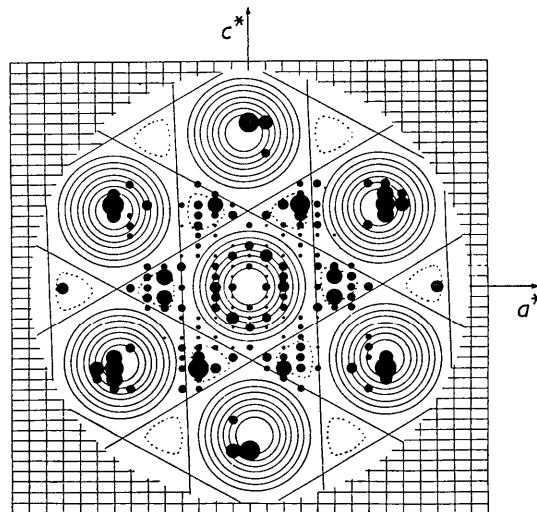


Fig. 1. $h0l$ weighted equatorial section with the Fourier transform of a benzene ring.

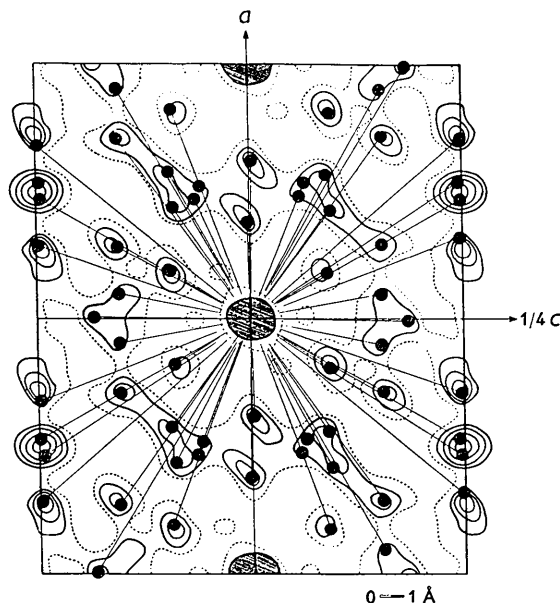


Fig. 2. Modified Patterson projection on 010 with inter-ring vectors superimposed.

not easily recognizable in Fig. 3, become the only peaks of Fig. 2.

The satisfactory results obtained in this single case suggest that the use of this modified Patterson function might be of help in the application of the Fourier-transform method to molecules with partially known structure. For instance, let us suppose that a molecule is known to contain a centrosymmetric group such as a benzene ring which contains a large fraction of the atoms. It would then be possible to recognize from the weighted

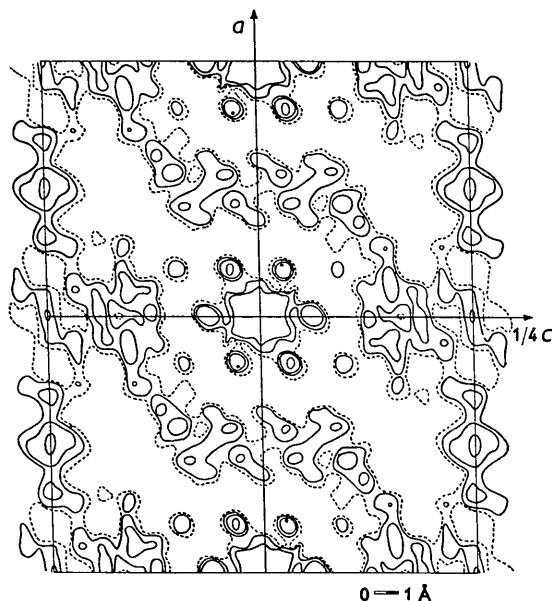


Fig. 3. Patterson projection on 010.

reciprocal-lattice section the orientation of its transform. Normalization of the observed intensities with respect to

the square of the Fourier transform of such a group might allow its approximate location in the unit cell by means of the modified Patterson function.

It may be pointed out that it is an important advantage of the above method that a knowledge of the absolute scale is not required, although, incidentally the possibility of putting the $F(S)$'s on absolute scale is clearly implied in this method.

It is also possible to use an artificial temperature factor which will reduce both the effects of series termination and of errors in the coefficients without an appreciable loss of detail since the intermolecular vectors are large and their number is small.

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Atomic scattering factors for wolfram. By EDGAR L. EICHORN, *Applied Mathematics Department, Electro Data Division of Burroughs, Pasadena, California, U.S.A.*

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Integration of the selfconsistent wave field of wolfram, computed on the M.I.T. analog computer in 1936

Table 1. *Atomic scattering factors for wolfram*

cm.10 ⁻⁸ sin θ/λ	Selfconsistent field without exchange ($Z = 74$, 14 shells)				
	0.00	0.02	0.04	0.06	0.08
0.0	74.00	73.77	73.04	71.92	70.59
0.1	69.07	67.56	66.04	64.52	63.05
0.2	61.58	60.14	58.72	57.33	55.95
0.3	54.59	53.27	51.97	50.71	49.47
0.4	48.27	47.12	45.99	44.91	43.86
0.5	42.83	41.83	40.89	39.93	39.05
0.6	38.12	37.28	36.43	35.62	34.83
0.7	34.06	33.30	32.56	31.87	31.14
0.8	30.46	29.82	29.19	28.56	27.95
0.9	27.36	26.79	26.24	25.69	25.18
1.0	24.68	24.20	23.73	23.32	22.87
1.1	22.45	22.05	21.70	21.32	20.98
1.2	20.62	20.30	20.00	19.69	19.41
1.3	19.15	18.88	18.63	18.38	18.14
1.4	17.91	17.70	17.49	17.28	17.09
1.5	16.91	16.71	16.57	16.40	16.22
1.6	16.07	15.93	15.78	15.63	15.48
1.7	15.36	15.23	15.09	14.98	14.84
1.8	14.73	—	—	—	—

(Manning & Millman, 1936), has now been carried out by a general wave field integration routine programmed for a fast new ferrite core storage computer, the Burroughs type 220. The algorithms utilized are the same as set out in a previous paper describing the computation of atomic form factors for the monovalent molybdenum ion on the Burroughs type 205 machine (Eichhorn, 1957). The same fine mesh in $\sigma = \sin \theta/\lambda$ was applied. The results are shown in Table 1.

The present curve (*ELLE*) was compared to the scattering curve of wolfram listed in the original edition of the Internationale Tabellen, part II (*TF*) and derived from a Thomas-Fermi model. The comparison was then extended to the scattering values obtained for wolfram by application of the same model taking into account spin energy exchange (*TFD*), which have been listed recently (Thomas & Umeda, 1957).

The *TF* curve is lower than the *ELLE* curve with a maximum discrepancy of almost 6% up to $\sigma = 0.85$; the two curves then intersect and the *TF* curve is then above the *ELLE* curve, with a maximum difference of approximately 4%. That is to say that the *ELLE* curve appears to be a 'sharpened' version of the *TF* curve. The *TFD* curve has the same qualitative deviations from the new scattering curve, but the percentwise discrepancies are much less, and in some points probably not