déterminé leurs paramètres et groupes spatiaux par des diagrammes d'oscillation, de rotation et de Weissenberg. Les mesures de densité ont été faites par flottation dans des solutions de nitrate d'argent.

Monochlorodurène

Par évaporation lente de solution dans l'éthanol à 20 °C, nous avons obtenu des plaques allongées suivant la direction [010]. Le système est monoclinique:

$$a = 15{,}89 \pm 0{,}05, \quad b = 5{,}80 \pm 0{,}02, \quad c = 11{,}17 \pm 0{,}04 \text{ Å}; \quad \beta = 109°7' \pm 30'$$

Densité mesurée: 1,15 Densité calculée: 1,153
Groupe spatial $P2_1/a$ $Z = 4$.

Monobromodurène

Forme β — Par évaporation d'une solution d'éthanol à 45 °C, nous avons obtenu des cristaux en forme de plaques allongées suivant la direction [010], ces cristaux scellés dans un tube capillaire restent sous cette forme à l'état métastable à 20 °C; le système est monoclinique:

$$a = 16{,}07 \pm 0{,}05, \quad b = 5{,}80 \pm 0{,}02, \quad c = 11{,}39 \pm 0{,}04 \text{ Å}, \quad \beta = 110°45' \pm 30'$$

Densité mesurée: 1,42 Densité calculée: 1,426
Groupe spatial $P2_1/a$ $Z = 4$.

Forme α — L'évaporation lente des solutions dans l'éthanol à 20 °C fournit des cristaux sous forme d'aiguilles dont l'axe est dans la direction [010]. La système est orthorhombique et à 20 °C:

$$a = 14{,}62 \pm 0{,}05, \quad b = 5{,}43 \pm 0{,}02, \quad c = 12{,}05 \pm 0{,}04 \text{ Å}$$

Densité mesurée: 1,47 Densité calculée: 1,478
Groupe spatial $P2_12_12_1$ $Z = 4$;

à 40 °C il se transforme en forme β.

Acta Cryst. (1964). **17**, 781

Dispersion corrections and crystal structure refinements*.

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(*Received* 9 *December* 1963 *and in revised form* 16 *January* 1964)

Patterson (1963) has recently considered the treatment of the effects of anomalous dispersion in X-ray crystal structure refinements. He indicates that there are many ways of taking these effects into account and that he holds no particular brief with the way he has chosen, namely to correct the *observed* structure amplitudes for both least-squares and Fourier refinements. We feel that such a correction when used in the least-squares refinement has disadvantages, and we advocate instead the inclusion of the dispersion effects in the *calculated* structure factors.

The notation is that of Patterson. Let there be one element in the structure that shows dispersive effects; the generalization to several elements is obvious. Let this element have a geometrical structure factor $H_d + iK_d$ and atomic scattering factor $f_d + \Delta f_d' + i\Delta f_d''$. Let the total contributions of the nondispersive elements to the structure factor be $A_n + iB_n$. Further define

$$\begin{aligned} A &= A_n + f_d H_d = A_n + A_d \\ B &= B_n + f_d K_d = B_n + B_d\,. \end{aligned}$$

Thus A and B are the nondispersive structure factor components for the whole structure. Let + indicate the structure factor for the plane (hkl) and − that for $(\bar{h}\bar{k}\bar{l})$. Then we have

$$F_c = F_{\pm} = (A + \Delta f_d' H_d - \sigma \Delta f_d'' K_d) + i(\sigma B + \sigma \Delta f_d' K_d + \Delta f_d'' H_d) \quad (1)$$

where σ is $+1$ for F_+ and -1 for F_-. Patterson defines an 'experimental' value of $|F|_o$, which we designate G_o, in the following way:

$$G_o^2 = \tfrac{1}{2}(|F_+|_o^2 + |F_-|_o^2) - 2\delta_1(AA_d + BB_d) - (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2) \quad (2)$$

where $\delta_1 = \Delta f_d'/f_d$ and $\delta_2 = \Delta f_d''/f_d$ and where $|F_+|_o^2$ and $|F_-|_o^2$ are the observed values of $|F_+|^2$ and $|F_-|^2$. Patterson suggests that the simplest procedure is to use this 'experimental' G_o instead of $|F|_o$ both in the least-squares refinement and as a coefficient in the Fourier series to obtain an 'observed' electron density map. In the latter application the appropriate phase angle α is taken to be that which is calculated in the absence of dispersive effects, namely $\tan \alpha = A/B$. The disadvantages of this approach are as follows: (1) As Patterson points out, it is necessary in the final stages of refinement to recalculate G_o after each cycle of least-squares. In effect the assumptions concerning the model are distributed between G_o and F_c. (2) In order to apply the method of equation (2) to a non-centrosymmetric crystal both $|F_+|_o^2$ and $|F_-|_o^2$ must be observed; if they are both observed, then it is appropriate to include them separately in the observational equations (perhaps with different weights) rather than to average them first.

A straightforward approach to the problem which avoids these difficulties is to base the analysis directly on the usual $|F|_o$ and on $|F_c|$ of equation (1)†. In this way all of the observations can be included with proper

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* Research performed under the auspices of the U.S. Atomic Energy Commission.

† Such a procedure, which has been employed here for some time, can be carried out by making minor modifications to existing least-squares programs, such as the Busing–Levy ORFLS program.

weights in the least-squares analysis. One can even carry out the analysis with only part of the data, *e.g.* only $|F_+|_o$ for a non-centrosymmetric crystal. In this approach the values of $|F|_o$, except for possible rescaling, remain constant throughout the calculations and are unaffected by assumptions about the model. This we feel is a convenience. Furthermore, since one of the principal objects of publishing data is to enable others to check or reinterpret the work, we feel that the $|F|_o$ values, since they are less apt to include calculational errors, should be published rather than the G_o values.

In application to non-centrosymmetric crystals this method assumes that the absolute configuration is known. If it is not, it can be determined by carrying out the refinement for both configurations and then comparing the resultant R factors (Hamilton, 1961). In this way the absolute configuration is conveniently determined without the necessity of additional experiments with different radiations in order to compare (hkl), $(\bar{h}\bar{k}\bar{l})$ pairs.

Let us now turn to the Fourier synthesis. We feel, along with Patterson and others, that this should represent the electron density and thus be independent of the wavelength of the radiation used in the experiment (and hence independent of anomalous scattering effects). If we require that the expected values of the real and imaginary components of F_o be those of F_c, if we assume that $|F|_o$ is an unbiased estimate of $|F|_c$,* and if we require that the expected value of ϱ_o be ϱ_c, then the appropriate electron density function is

$$\varrho_o(xyz) = V^{-1} \sum_{+,-} |F|_o \left\{ \frac{A}{|F|_c} \cos\varphi + \frac{B}{|F|_c} \sin\varphi \right\} \quad (3)$$

where $\varphi = 2\pi(hx+ky+lz)$. Equation (3) can be expanded to yield

$$\varrho_o(xyz) = V^{-1} \sum_{+} |F_+|_o \left\{ \frac{A}{|F_+|} \cos\varphi + \frac{B}{|F_+|} \sin\varphi \right\} + V^{-1} \sum_{-} |F_-|_o \left\{ \frac{A}{|F_-|} \cos\varphi + \frac{B}{|F_-|} \sin\varphi \right\}. \quad (4)$$

For a non-centrosymmetric crystal it is necessary only to establish the absolute configuration. Thereafter either of the sums in (4), when doubled, is an unbiased representation of the electron density, and there is no necessity, as in Patterson's formulation, to measure the intensities for all planes (hkl) and $(\bar{h}\bar{k}\bar{l})$. Of course a density function based on twice as many observations might be more accurate.

Note that in our formulation, if both the + and the − terms are observed, then the quantity corresponding to Patterson's G_o which is to be phased by $\alpha = \tan^{-1}(A/B)$ is†

$$\tfrac{1}{2}\sqrt{(A^2+B^2)} \left\{ \frac{|F_+|_o}{|F_+|} + \frac{|F_-|_o}{|F_-|} \right\}.$$

Thus in our formulation an unbiased representation of the electron density requires that the expected values of $|F_+|_o$ and $|F_-|_o$ be $|F_+|$ and $|F_-|$.

Patterson's formulation requires that the expected value of $\sqrt{(\frac{1}{2}|F_+|_o^2 + \frac{1}{2}|F_-|_o^2 - \frac{1}{2}|F_+|^2 - \frac{1}{2}|F_-|^2 + A^2 + B^2)}$ be equal to $\sqrt{(A^2+B^2)}$. If there are random errors in the data, then these estimates will be biased slightly in different ways. This, together with the fact that Patterson averages before taking the square root, will cause the two approaches to give different numerical results. These differences are unimportant as long as $\sigma(F^2) < < F^2$.

We conclude by noting that equations (3) and (4) are general: a difference Fourier synthesis is formulated in the same way with $|F|_o$ replaced by $|F|_o - |F|_c$. For a centrosymmetric crystal the density function becomes

$$\varrho_o(xyz) = 2V^{-1} \sum_{+} |F|_o [A/\sqrt{((A + \Delta f'_d H_d)^2 + (\Delta f''_d H_d)^2)}] \cos\varphi. \quad (5)$$

We would like to express our appreciation to A. L. Patterson for allowing us to see a preprint of his manuscript.

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* This is not generally true, since one usually carries out measurements so as to obtain $|F|^2{}_o$ as an unbiased estimate of $|F|^2{}_c$ for the correct structure. Then an unbiased estimate of $|F|_c$ is given approximately by the formula

$$|F|_o[1 + \sigma^2(|F|_o)/(2|F|^2{}_o] .$$

To the extent that the term in brackets differs from unity the electron density derived from $|F|_o$ will be a biased representation of the electron density based on $|F|_c$.

† Templeton (1955) cited this quantity as one of the possible approximations to the correct coefficients.