On Centrosymmetric Molecules in Non-Centrosymmetric Space Groups

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Re-determination of the space group of 4:4'-dinitrodiphenyl has confirmed its assignment to *Pc*. Thus the occurrence of centrosymmetric molecules (to within the accuracy of a structure determination) in non-centrosymetric space groups has now been demonstrated for two compounds: 4:4'-dinitrodiphenyl and the monoclinic form of 1:2–5:6-dibenzanthracene (Robertson & White). The intensity distributions from hypercentrosymmetric molecules in non-centrosymmetric space groups have been investigated theoretically and the theoretical results compared with experiment. Further evidence of the marked effect that non-crystallographic molecular symmetry has on the intensity distributions is provided by these results. Consequently, caution is essential when using the statistical method for the detection of crystallographic centres of symmetry when the molecules possess high symmetry or pseudo-symmetry.

Introduction

It is common experience that centrosymmetric crystals may contain either centrosymmetric† or non-centrosymmetric molecules. Although there is no theoretical reason why centrosymmetric molecules should not also sometimes crystallize in non-centrosymmetric crystals, this appears to be a rare occurrence. A literature survey, discussed in more detail below, has shown that there is only one confirmed example of this situation: the monoclinic modification‡ of 1:2–5:6-dibenzanthracene (I), which has been reported to crystallize in space group *P2₁* (Iball & Robertson, 1933; Robertson & White, 1956).

Another possible example is 4:4'-dinitrodiphenyl (II), which has been reported to have space group *Pc* (van Niekerk, 1943). As this assignment has been questioned (Bunn, 1945), we have re-determined the space group of this compound. During this work an attempt was made to use the intensity distributions to distinguish between possible space groups (Wilson, 1949; Howells, Phillips & Rogers, 1950) but with ambiguous results. It was therefore decided to investigate theoretically the intensity distributions expected from hypercentrosymmetric molecules (Lipson & Woolfson, 1952; Rogers & Wilson, 1953), crystallizing in non-centrosymmetric crystals. Thus the results described in this paper fall into two main parts: in the first the re-determination of the space group of 4:4'-dinitrodiphenyl is reported, while in the second the theoretical intensity distributions for hyper-

centrosymmetric molecules in non-centrosymmetric crystals are deduced and compared with the available experimental results.

Determination of the space group of 4:4'-dinitrodiphenyl

Previous work

The space group of 4:4'-dinitrodiphenyl was first determined by van Niekerk (1943) from a series of overlapping oscillation photographs. The only extinction observed was *h0l* absent for *l* odd, indicating either *P2/c* or *Pc*. It was assumed that the latter was correct and a structure analysis was carried out on this basis. Bunn (1945) later pointed out that the atomic co-ordinates found in the structure analysis were not very different from those for *P2₁/c*, and suggested that this might be the true space group.

X-ray photography

Long needles of 4:4'-dinitrodiphenyl (from British Drug Houses (Laboratory Chemicals Group), Poole, England) were obtained from amyl acetate; large flat plates were obtained from tetralin. X-ray photographs showed the two forms to be identical. The needles show {011} faces and the plates {001} faces. Weissenberg photographs were taken of a crystal mounted about the [100] (needle) axis with Cu *Kα* (Ni-filtered) radiation (zero- and first-layer photographs) and Fe *Kα* (Mn-filtered) radiation (zero layer only). The cell dimensions obtained from these photographs were in good agreement with those previously reported. The only systematic absence found was *h0l* absent for *l* odd. The 010, 030 and 050 reflexions were present on both zero-layer photographs, in addition to even orders. The appearance of the 0*k*0, *k* odd, reflexions was quite normal and there was no reason to suppose that they were due to multiple reflexions (see Bland (1954) and Murty (1955) for examples of crystals where

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† When non-crystallographic symmetry is attributed to a molecule in this paper, it should be understood that this symmetry can only be demonstrated unequivocally by a structure analysis and will apply only to within the limits of accuracy of the analysis.

‡ We shall refer to this as the *β*-modification. There is also an orthorhombic polymorph, space group *Pcab*, 4 molecules per unit cell (Robertson & White (1947)).

space-group determination has been hindered by the presence of multiple reflexions). This result eliminated $P2_1/c$ as a possible space group.

Tests for pyro-electricity

Tests for pyro-electricity were applied to decide between space groups Pc and $P2/c$. Of the simple qualitative tests described by Wooster (1938) only one was successful: in this test the crystals were placed on a metal plate which was then cooled in liquid air. The $4:4'$-dinitrodiphenyl crystals stuck firmly to the metal plate whereas diphenyl crystals, used as a control, fell off at once. Despite this success, it was felt that a confirmatory electrical measurement was desirable. The usual form of this test (see, for example, Wood & McCale (1940)) was modified as follows: the crystal was gripped between two electrode leads of a dismantled radio tube, while a stream of liquid air was directed at it. The tube base remote from the crystal was kept warm and dry by a stream of hot air in order to prevent condensation of moisture and resultant short-circuiting of the crystal. The electrode leads were connected to a conventional electrometer-tube circuit, a Ferranti B.M. 4A tube being used.

In order to be assured that the circuit was working satisfactorily, crystals of tourmaline, pentaerythritol and diphenyl were first tested. The first two substances gave large deflexions on the microammeter when the crystals were cooled down, and deflexions of opposite sense when they were allowed to warm up to room temperature. These deflexions occurred in the opposite senses when the crystals were reversed between the electrodes. No deflexions were obtained when diphenyl crystals were used. Deflexions of the same order of magnitude as for pentaerythritol were found for the $4:4'$-dinitrodiphenyl crystals tested. The most satisfactory results were obtained for the flat plates, with the electrodes along the [001] axis.

These results show that $4:4'$-dinitrodiphenyl crystals are polar. It follows that the space group must be Pc, in agreement with van Niekerk's result.

Literature survey

The molecules in β-$1:2$–$5:6$-dibenzanthracene have been shown by structure analysis to be centrosymmetric within the limits of accuracy of the analysis (Robertson & White, 1956) and thus this is at present the only reasonably certain example of a crystal in which centrosymmetric molecules crystallize in a non-centrosymmetric space group. The structure analysis of $4:4'$-dinitrodiphenyl was carried out on the assumption that the molecule was centrosymmetric, and the agreement among observed and calculated structure factors ($R(0kl) = 33\%$, $R(h0l) = 44\%$ for the first trial structure) supports, but does not prove, the correctness of this assumption.

Thus $4:4'$-dinitrodiphenyl is a possible second ex

ample. We have surveyed the literature (Donnay & Nowacki, 1954; Hertel, 1955) for other possible examples of this situation and have found only three.

The first of these is mercury-n-ethyl mercaptan (III) (Wells, 1937). Although the crystals gave negative results for the pyroelectric test, the space group Cc was preferred to $C2/c$ because of packing considerations. A structure analysis gave the positions of the Hg and S atoms, while the carbon positions were inferred on the assumption that the molecule was centrosymmetric.

Another possible example is difluorenylidene (IV), which crystallizes in two orthorhombic forms, one (α) centrosymmetric ($Pcan$; Fenimore, 1948) and the other (β) non-centrosymmetric ($P2_12_12_1$; Harnik, Herbstein, Schmidt & Hirshfeld, 1954). The molecules in the α-form have been shown to be centrosymmetric (Fenimore, 1948, Nyburg, 1954) by structure analysis. If the molecular configuration remains the same in the β-form, then β-difluorenylidene must be added to our list.

A final possibility is $4:4'$-dimethoxy-α, β-diethylstilbene (V). However, a decision must be suspended here as there are conflicting reports on the space group, which was reported by Giacomello & Bianchi (1941) as $P2_1$, and by Carlisle & Crowfoot (1941) as $P2_1/n$.

The intensity distributions from hypercentrosymmetric molecules in non-centrosymmetric crystals

Theoretical

Although the effect of non-crystallographic molecular symmetry on the intensity distributions is now well recognized (Lipson & Woolfson, 1952; Rogers & Wilson, 1953) the particular situation in which hypercentrosymmetric molecules occur in a non-centrosymmetric crystal does not appear to have been discussed theoretically. This situation is analysed here, the methods used being those previously outlined by Wilson, and by Rogers & Wilson. The theoretical curves obtained are then compared with the available experimental data.

We consider here a non-centrosymmetric cell with two crystallographic units*. We choose an origin in the unit cell such that the vectors to the molecular centres of symmetry of hypercentrosymmetric molecules I and II are d_1 and $-d_1$ (see Fig. 2, where the space group Pc is used as an example). Consider molecule I. One half of the molecule is taken to be composed of 2^{n-2} centrosymmetric motifs (each with m atoms), which are related by a sequence of $(n-2)$ centres of symmetry. With the inclusion of the centre of the motif, there are $(n-1)$ independent centres in one half of the molecule at vector distances (d_1+d_2), $(d_1+d_2+d_3)$, ..., $(d_1+d_2+...+d_n)$ from the origin

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* By 'crystallographic unit' we imply what is often called the 'asymmetric unit'. The latter term is obviously inappropriate here.
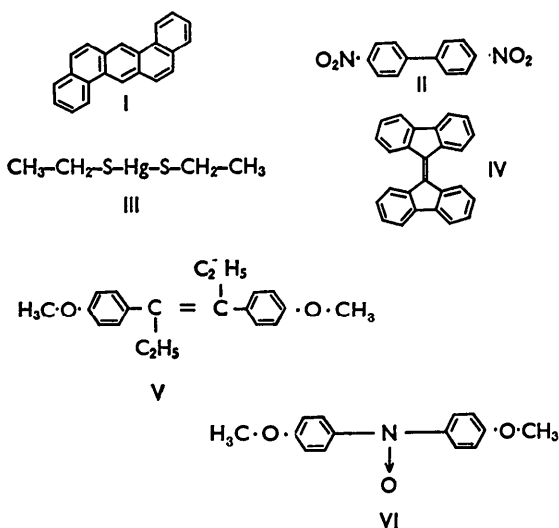
Fig. 1. Molecular formulae of (I) 1:2–5:6-dibenzanthracene; (II) 4:4'-dinitrodiphenyl; (III) mercury-n-ethyl mercaptan; (IV) difluorenylidene; (V) 4:4'-dimethoxy-α,β-diethylstilbene; (VI) di-p-anisyl nitric oxide.
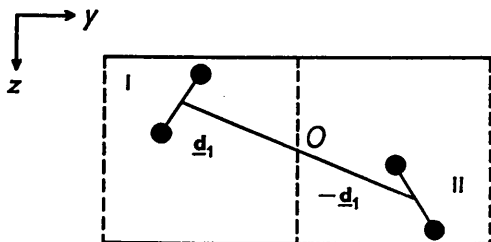

Fig. 2. Arrangement of hypercentrosymmetric molecules in space group Pc. The origin O is taken on the glide plane so that the vectors from O to the molecular centres of symmetry are $\mathbf{d_1}$ and $-\mathbf{d_1}$. No attempt has been made to represent the true symmetry of the half-molecules.

of the unit cell. Since none of these centres coincides with the molecular centre, there are n independent centres in the molecule. As a result of the operation of the successive symmetry centres on the motifs, the centres of the motifs in the molecule lie at vector distances $\mathbf{D}_j (j = 1, \ldots, 2^{n-1})$ from the molecular centre, where the $\mathbf{D}_j$ vectors are made up as follows: first the sum of the $\mathbf{d}_k (k = 2, \ldots, n)$ vectors all taken positively, then all possible sums of the $\mathbf{d}_k$ vectors with all but one taken positively, and so on, until finally all are taken negatively. Of the $2^{n-1}\mathbf{D}_j$ vectors, only 2^{n-2} are independent because of the operation of the molecular centre of symmetry. The contribution of the symmetry-related atoms in one molecule to the structure factor may now be written as

$$\Phi_i^{\mathrm{I}} = \exp\,[2\pi i\mathbf{S}.\mathbf{d_1}]\sum_{j=1}^{j=2^{n-2}} 2\cos 2\pi\mathbf{S}.\mathbf{D}_j$$
$$\times (2f_i\cos 2\pi\mathbf{S}.\mathbf{q}_i)(i = 1, \ldots, \tfrac{1}{2}m)\,, \quad (1)$$

where $\mathbf{q}_i$ is the vector from the centre of the motif

to the ith atom, and $\mathbf{S}$ is the position vector in reciprocal space.

Using the relationship between a sum and product of cosines (see, for example, Hobson, 1928), equation (1) can be rewritten

$$\Phi_i^{\mathrm{I}} = \exp\,[2\pi i\mathbf{S}.\mathbf{d_1}](2f_i\cos 2\pi\mathbf{S}.\mathbf{q}_i)$$
$$\times (2^{n-1}\cos \psi_2 \cos \psi_3\ldots\cos \psi_n)\,, \quad (2)$$

where $\psi_k = 2\pi\mathbf{S}.\mathbf{d}_k$.

The contribution of the corresponding set of atoms in the second molecule will have a similar form except that the vectors $\mathbf{D}_j$, $\mathbf{d}_k$ and $\mathbf{q}_i$ must be replaced by vectors $\mathbf{E}_j$, $\mathbf{e}_k$ and $\mathbf{r}_i$, which are similarly defined and have the same absolute magnitudes but different directions:

$$\Phi_i^{\mathrm{II}} = \exp\,[-2\pi i\mathbf{S}.\mathbf{d_1}](2f_i\cos 2\pi\mathbf{S}.\mathbf{r}_i)$$
$$\times (2^{n-1}\cos \mu_2 \cos \mu_3\ldots\cos \mu_n)\,, \quad (3)$$

where $\mu_k = 2\pi\mathbf{S}.\mathbf{e}_k$.

The real and imaginary parts of the contribution to the structure factor of a set of atoms related by the symmetries of molecule and unit cell now follow as

$$\xi_i = 2^{n-1}\cos 2\pi\mathbf{S}.\mathbf{d_1}[2f_i\cos 2\pi\mathbf{S}.\mathbf{q}_i\cos \psi_2 \cos \psi_3 \ldots$$
$$\times \cos \psi_n + 2f_i\cos 2\pi\mathbf{S}.\mathbf{r}_i\cos \mu_2\cos \mu_3\ldots\cos \mu_n]\,, \quad (4)$$

$$\eta_i = 2^{n-1}\sin 2\pi\mathbf{S}.\mathbf{d_1}[2f_i\cos 2\pi\mathbf{S}.\mathbf{q}_i\cos \psi_2 \cos \psi_3 \ldots$$
$$\times \cos \psi_n - 2f_i\cos 2\pi\mathbf{S}.\mathbf{r}_i\cos \mu_2\cos \mu_3\ldots\cos \mu_n]\,. \quad (5)$$

The structure factor for the unit cell is

$$F = \sum_{i=1}^{i=\frac{1}{2}m} (\xi_i+i\eta_i) = F_R+iF_I\,. \quad (6)$$

Following Wilson (1949), we now apply the central limit theorem (Cramer, 1937), which states that the sum of a sufficiently large number N of random variables with mean values x_j and variances α_j^2 is normally distributed about

$$X = \sum_{j=1}^{N} x_j$$

with variance

$$A^2 = \sum_{j=1}^{N} \alpha_j^2\,,$$

whatever the distribution functions of the individual random variables. Thus we have

$$\langle\xi_i\rangle = 0 \qquad \text{for } |\mathbf{S}| \text{ large enough,} \quad (7)$$

$$\langle\eta_i\rangle = 0\,, \quad (8)$$

$$\langle\xi_i^2\rangle = 2^{2n}\cos^2 \delta.f_i^2[\langle\cos^2 2\pi\mathbf{S}.\mathbf{q}_i\rangle \cos^2 \psi_2 \ldots \cos^2 \psi_n$$
$$+\langle\cos^2 2\pi\mathbf{S}.\mathbf{r}_i\rangle\cos^2 \mu_2 \ldots\cos^2 \mu_n$$
$$+2\langle\cos 2\pi\mathbf{S}.\mathbf{q}_i\cos 2\pi\mathbf{S}.\mathbf{r}_i\rangle$$
$$\times\cos \psi_2 \ldots\cos \psi_n \cos \mu_2 \ldots\cos \mu_n]\,, \quad (9)$$
$$\delta = 2\pi\mathbf{S}.\mathbf{d_1}\,.$$

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If the two molecules in the cell are independent, then the final term in equation (9) will vanish. In the following we assume independence of the molecules; the approximations involved here and at later stages will be discussed more fully at the end of this section.

We now write

$$\langle \xi_i^2 \rangle = 2^{2n-1} f_i^2 \cos^2 \delta \, [\cos^2 \psi_2 \ldots \cos^2 \psi_n \\ + \cos^2 \mu_2 \ldots \cos^2 \mu_n] , \quad (10)$$

$$\langle \eta_i^2 \rangle = 2^{2n-1} f_i^2 \sin^2 \delta \, [\cos^2 \psi_2 \ldots \cos^2 \psi_n \\ + \cos^2 \mu_2 \ldots \cos^2 \mu_n] , \quad (11)$$

$$A_n^2 = \sum_{i=1}^{i=\frac{1}{2}m} \langle \xi_i^2 \rangle = 2^{n-2} \Sigma \cos^2 \delta \, [\cos^2 \psi_2 \ldots \cos^2 \psi_n \\ + \cos^2 \mu_2 \ldots \cos^2 \mu_n] , \quad (12)$$

$$B_n^2 = \sum_{i=1}^{i=\frac{1}{2}m} \langle \eta_i^2 \rangle = 2^{n-2} \Sigma \sin^2 \delta \, [\cos^2 \psi_2 \ldots \cos^2 \psi_n \\ + \cos^2 \mu_2 \ldots \cos^2 \mu_n] , \quad (13)$$

where

$$\Sigma = \sum_{i=1}^{i=N} f_i^2 .$$

N is the total number of atoms in the unit cell.

The distribution functions for the real and imaginary parts of the structure factor follow at once from the central limit theorem:

$$_aP_{n,2}(F_R) dF_R | \delta, \psi_2 \ldots \psi_n, \mu_2 \ldots \mu_n$$

$$= \frac{\exp \left[-F_R^2 / 2^{n-1} \Sigma \cos^2 \delta \right.}{\left. \times (\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n) \right] dF_R}{(2^{n-1} \pi \Sigma)^{\frac{1}{2}} |\cos \delta|} , \quad (14)$$
$$\times (\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n)^{\frac{1}{2}}$$

$$_aP_{n,2}(F_I) dF_I | \delta, \psi_2 \ldots \psi_n, \mu_2 \ldots \mu_n$$

$$= \frac{\exp \left[-F_I^2 / 2^{n-1} \Sigma \sin^2 \delta \right.}{\left. \times (\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n) \right] dF_I}{(2^{n-1} \pi \Sigma)^{\frac{1}{2}} |\sin \delta|} , \quad (15)$$
$$\times (\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n)^{\frac{1}{2}}$$

(The nomenclature of the intensity distribution functions is discussed in the following section.)

These distribution functions can be re-cast in terms of $z = I/\Sigma$, where $F_R = \sqrt{I} . \cos \varphi$ and $F_I = \sqrt{I} . \sin \varphi$, φ being the phase angle of the structure factor. After integrating over φ and averaging over all values of $\delta, \psi_2 \ldots \psi_n, \mu_2 \ldots \mu_n$ between 0 and 2π, the general expression for the probability distribution can be written

$$_aP_{n,2}(z) dz$$

$$= \frac{2^{n+2}}{\pi^{2n}} \int_{q=0}^{\pi/2} \int_{\delta=0}^{\pi/2} \int_{\psi_2=0}^{\pi/2} \cdots \int_{\psi_n=0}^{\pi/2} \int_{\mu_2=0}^{\pi/2} \cdots \int_{\mu_n=0}^{\pi/2}$$

$$\frac{\operatorname{cosec} 2\delta}{\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n}$$

$$\times \exp \left[-\frac{z}{2^{n-1}} \frac{\cos^2 \varphi \sec^2 \delta + \sin^2 \varphi \operatorname{cosec}^2 \delta}{\cos^2 \psi_2 \ldots \cos^2 \psi_n + \cos^2 \mu_2 \ldots \cos^2 \mu_n} \right]$$

$$\times d\varphi \, d\delta \, d\psi_2 \ldots d\psi_n d\mu_2 \ldots d\mu_n dz . \quad (16)$$

For $n = 1$ the distribution function becomes

$$_aP_{1,2}(z) dz$$

$$= \frac{2}{\pi} \int_0^{\pi/2} \frac{\exp \left(-z/\sin^2 2\delta \right)}{\sin 2\delta} I_0 \left(\frac{z \cos 2\delta}{\sin^2 2\delta} \right) d\delta \, dz , \quad (17)$$

where $I_0(u)$ is the modified Bessel function of the first kind and zero order. For comparison of experimental results with theoretical predictions, it is preferable to use the cumulative probability distribution

$$N(z) = \int_0^z P(z) dz$$

(Howells et al., 1950):

$$_aN_{1,2}(z)$$

$$= \frac{2}{\pi} \int_0^z \int_0^{\pi/2} \frac{\exp \left(-z/\sin^2 2\delta \right)}{\sin 2\delta} I_0 \left(\frac{z \cos 2\delta}{\sin^2 2\delta} \right) d\delta \, dz . \quad (18)$$

We also require expressions for $_aP_{2,2}(z)$ and $_aN_{2,2}(z)$. Use of equation (16) has, however, led to intractable multiple integrals. With a view to the application of the results, we have calculated these distributions for the simplified special case where d_2 and e_2 are parallel, thus making $\psi_2 = \mu_2$; the symbols for these special functions are bracketed to distinguish them from the general functions. The expressions for $[_aP_{2,2}(z)]$ and $[_aN_{2,2}(z)]$ are:

$$[_aP_{2,2}(z)] dz$$

$$= \frac{2\sqrt{2}}{\pi^{5/2}} \int_0^{\pi/2} \int_0^{\pi/2} \frac{\exp \left[-z \left(\frac{1-\cos 2\delta \cos 2\varphi}{2 \sin^2 2\delta} \right) \right]}{[z(1-\cos 2\delta \cos 2\varphi)]^{\frac{1}{2}}} d\delta \, d\varphi \, dz , \quad (19)$$

$$[_aN_{2,2}(z)]$$

$$= \left(\frac{2}{\pi} \right)^2 \int_0^{\pi/2} \int_0^{\pi/2} \frac{\sin 2\delta}{1-\cos 2\delta \cos 2\varphi}$$

$$\times \operatorname{erf} \left[\frac{z(1-\cos 2\delta \cos 2\varphi)}{2 \sin^2 2\delta} \right]^{\frac{1}{2}} d\delta \, d\varphi , \quad (20)$$

where

$$\operatorname{erf} u = \frac{2}{\sqrt{\pi}} \int_0^u \exp \left[-x^2 \right] dx .$$

It is interesting to note that both the probability distributions (17) and (19) are infinite for $z = 0$. The hypercentrosymmetric distributions for centrosymmetric crystals are infinite at $z = 0$ for $n \geq 2$ (Rogers & Wilson, 1953).

We have not been able to integrate the expressions (18) and (20) analytically but have computed values of $_aN_{1,2}(z)$ and $[_aN_{2,2}(z)]$ for a number of values of z by numerical integration. The results are listed in Table 1 and given graphically in Fig. 4. In the derivation of these results, the following assumptions were made: (a) the two molecules in the unit cell were assumed to be independent (derivation of equations (10) and (11)); (b) the real and imaginary parts of

Table 1. *Values of* $_aN_{1,2}(z)$ *and* $[_aN_{2,2}(z)]$.

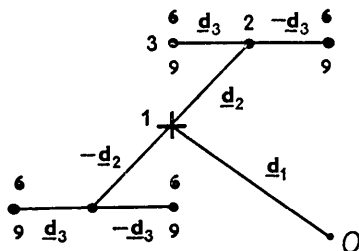| z	$_aN_{1,2}(z)$	$[_aN_{2,2}(z)]$
0	0	0
0·1	0·149	0·291
0·2	0·250	0·393
0·4	0·406	0·521
0·6	0·520	—
0·7	—	0·636
0·8	0·609	—
1·0	0·681	0·712

Fig. 3. Hypercentrosymmetric arrangement with $n = 3$. O is the origin of the unit cell (see Fig. 2). The molecular centre of symmetry is indicated by a cross, while the non-crystallographic local centres are indicated by dots. The three independent centres in the molecule can be taken at 1, 2 and 3.
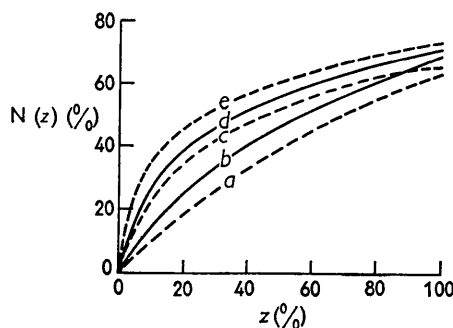

Fig. 4. The cumulative probability-distribution curves $N(z)$ for (a) acentric, (c) centric, (e) 1-centro: 1-centric, (b) 1-centro: 2-acentric and (d) 2-centro: 2-acentric (special case) distributions.

the structure factor were assumed to be independent (derivation of (16) from (14) and (15)).

These assumptions have been avoided in a comprehensive analysis of the distribution functions for all space groups for molecules without symmetry (Karle & Hauptman, 1953; Hauptman & Karle, 1953). These authors have shown that the distribution functions originally derived by Wilson are first approximations to the true distribution functions. Comparison of Wilson's distribution functions with experiment has shown that the approximate theory is adequate for most applications. As the present derivation of equations (16) and (18) involves approximations similar to those used by Wilson, the accuracy of these equations should be adequate for our present purposes. This will also be true of equation (20) when the assumption of parallel $\mathbf{d}_2$ and $\mathbf{e}_2$ vectors under which it was derived holds.

The relative disposition of the distribution curves in Fig. 4 can be explained by using some results obtained by Wilson (1956) for crystals containing more than one pair of centrosymmetrically-related (and hence parallel) hypercentrosymmetric crystallographic units. The pairs of hypercentrosymmetric crystallographic units in the unit cell must be related by elements of symmetry other than centres, and consequently the fringe system of a particular pair of parallel crystallographic units will be partially obliterated by the unrelated, additive fringe systems of the other pairs. Wilson concluded that, to a crude first approximation, the distribution appropriate to a unit cell with p pairs of n-centrosymmetric crystallographic units would be the centric distribution increased by one-pth of the difference between the n-centric and centric distributions. In non-centrosymmetric crystals the n-centrosymmetric crystallographic units, taken singly, are related by elements of symmetry other than centres. By analogy with Wilson's result we should expect that the distribution function for a unit cell containing s n-centrosymmetric crystallographic units would be the acentric distribution increased by one-sth of the difference between the n-centric and acentric distributions. In agreement with this, the curve for $_aN_{1,2}(z)$ lies approximately midway between the curves for the ordinary acentric and centric distributions (see Fig. 4). The $[_aN_{2,2}(z)]$ curve lies somewhat higher than midway between the acentric and bicentric curves; presumably this is because the special assumption under which $[_aN_{2,2}(z)]$ was calculated involved the introduction of additional non-crystallographic symmetry. The general $_aN_{2,2}(z)$ curve would be expected to lie below that for the special case.

Nomenclature

The number of possible distributions has now become so large that the nomenclature used by Rogers & Wilson (1953) is no longer adequate. It is necessary to label a distribution function with respect to

(a) the symmetry of the crystallographic unit,

(b) the number of crystallographic units in the unit cell,

(c) the crystallographic symmetry, which can be either centrosymmetric or non-centrosymmetric.

We suggest that the distributions for hypercentrosymmetric molecules in centrosymmetric space groups should be called n-centro:p-centric distributions, where n is the number of independent centres of symmetry in the crystallographic unit, and p is the number of pairs of centrosymmetrically-related crystallographic units in the unit cell (special allowance may be necessary for projections). The suggested name for the distributions from hypercentrosymmetric molecules in non-centrosymmetric space groups is n-centro:s-acentric where s is the number of crystallographic units in the unit cell. The probability distributions would be symbolized by $_cP_{n,p}(z)$ and $_aP_{n,s}(z)$

Table 2. *Proposed new symbolism*

Crystal symmetry	Number of crystallographic units in unit cell	Symmetry of the crystallographic unit	Nomenclature of intensity distributions		
			Old name	New name	New symbol
$\bar{1}$	One pair p pairs	None	Centric	Centric	$_cP_0(z)$
	One pair	n-centrosymmetric	$(n+1)$-centric	n-centro: 1-centric	$_cP_{n,1}(z)$
	p pairs	n-centrosymmetric	p-th sesquicentric	n-centro: p-centric	$_cP_{n,p}(z)$
1	One unit s units	None	Acentric	Acentric	$_aP_0(z)$
	One unit	n-centrosymmetric	—	n-centro: 1-acentric	$_aP_{n,1}(z)$
	s units	n-centrosymmetric	—	n-centro: s-acentric	$_aP_{n,s}(z)$

respectively, while the symbols for the cumulative probability distributions would have N instead of P. The prefixes c and a have been preferred to $\bar{1}$ and 1 in order to reduce the number of figures in the symbols; in addition if it is desired to distinguish the intensity distributions from different space groups then c (or a) could be replaced by the number of the space group given in the *International Tables*. In Table 2 we list the old and suggested new symbols for a number of distribution functions. Because the proposed nomenclature and symbols are somewhat cumbersome, the older notation should be used when this can be done without risk of ambiguity.

Comparison of experimental and theoretical cumulative probability distributions

The $N(z)$ curves for the $(0kl)$ zone (56 reflexions) of 4:4′-dinitrodiphenyl and the $(0kl)$ (47 reflexions) and $(h0l)$ (186 reflexions) zones of β-1:2–5:6-dibenzanthracene were calculated in the usual way. The intensity data were obtained from van Niekerk's thesis (1942) and Robertson & White's (1956) paper.

The $N(z)$ curve for the $(0kl)$ zone of 4:4′-dinitrodiphenyl is shown in Fig. 5(a). The experimental curve is similar to that given by Lipson & Woolfson (1952) for the $(0kl)$ zone of di-p-anisyl nitric oxide (VI) (Fig. 5(b)). In both instances the projections are non-centrosymmetric, while either the molecule has a centre (4:4′-dinitrodiphenyl) or may be considered as composed of two approximately centrosymmetric parts (di-p-anisyl nitric oxide). The experimental points for these two crystals are in reasonable agreement with the 1-centro:2-acentric distribution $_aN_{1,2}(z)$.

The $N(z)$ curve for the $(0kl)$ zone of β-1:2–5:6-dibenzanthracene is shown in Fig. 5(c). The experimental points here are in good agreement with the 2-centro:2-acentric curve $[_aN_{2,2}(z)]$. It should be noted that the crystal structure of β-1:2–5:6-dibenzanthracene is such that the two molecules in the unit cell are approximately parallel. The $(0kl)$ projection in the space group $P2_1$ is, of course non-centrosymmetric and the distribution would be expected to be acentric. Nevertheless the distribution found is close to the centric distribution.

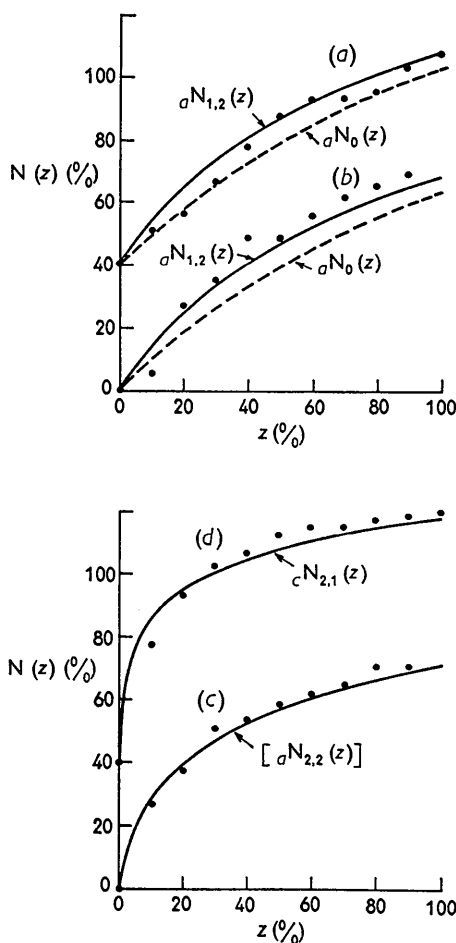Finally we consider the $N(z)$ curve for the $(h0l)$ zone of β-1:2–5:6-dibenzanthracene (Fig. 5(d)). The

Fig. 5. (a, b) The experimental $N(z)$ points for (a) the $(0kl)$ zone of 4:4′-dinitrodiphenyl and (b) the $(0kl)$ zone of di-p-anisyl nitric oxide (Lipson & Woolfson, 1952) compared with the 1-centro: 2-acentric $_aN_{1,2}(z)$ curve (full lines) and the acentric $_aN_0(z)$ curve (broken lines). The upper set of curves has been moved up the $N(z)$ axis by 40%. (c) The experimental $N(z)$ points for the $(0kl)$ zone of β-1:2–5:6-dibenzanthracene compared with the 2-centro: 2-acentric $[_aN_{2,2}(z)]$ curve. (d) The experimental $N(z)$ points for the $(h0l)$ zone of β-1:2–5:6-dibenzanthracene compared with the 2-centro: 1-centric $_cN_{2,1}(z)$ curve. The curve has been moved up the $N(z)$ axis by 40%.

experimental points here fit the 2-centro:1-centric distribution curve rather better than that for the

1-centro:1-centric distribution. This, and the results for the (0*kl*) zone, are in good agreement with expectations based on the molecular structure, for the molecule can be considered as composed of two centrosymmetric 'naphthalene' groupings, related by the molecular centre, and two atoms in the 9, 10 positions, also related by the molecular centre. For a zone without a crystallographic centre of symmetry, the intensity distribution contributed by the two 'naphthalene' groupings would be 2-centro:2-acentric and that by the two atoms 1-centro:2-acentric. For a zone with a crystallographic centre of symmetry which does not coincide with the molecular centre, the 'naphthalene' groupings contribute a 2-centro:1-centric distribution and the two extra atoms a 1-centro:1-centric distribution. These predictions agree well with the experimental results.

It should be emphasized that the molecular symmetry need not be exact for it to influence the form of the distribution function; all that is necessary is that capacity to scatter X-rays should be approximately symmetrically distributed in the molecule. An example of a pseudo-symmetric molecule with a changed $N(z)$ curve is di-*p*-anisyl nitric oxide, mentioned above.

Conclusions

The results described in this paper bear out the theoretical prediction that it is not impossible for centrosymmetric molecules to crystallize in non-centrosymmetric crystals.

The influence of non-crystallographic molecular symmetry or pseudo-symmetry on the intensity distributions has been shown to be considerable. For the (0*kl*) zone of β-1:2–5:6-dibenzanthracene this influence is large enough to convert what would ordinarily be an acentric distribution into one that is close to a centric distribution. Thus caution is necessary when using the intensity distributions to test for crystallographic symmetry in crystals with non-crystallographic molecular symmetry or pseudo-symmetry. Conversely the intensity distributions may provide information about molecular symmetry under favourable conditions.

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