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Analysis of the Diffuse X-ray Scattering from Substitutionally Disordered Molecular Crystals: Monoclinic 9-Bromo-10-methylanthracene

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Abstract

Model calculations of random and correlation distributions of diffuse X-ray scattering are used to determine the correlations between molecular sites of a substitutionally disordered molecular crystal. The correlation coefficients are varied until qualitative agreement is obtained between the calculated diffuse scattering and that measured using Weissenberg film techniques. This procedure was used to determine the correlation coefficients of the monoclinic form of 9-bromo-10-methylanthracene, $C_{15}H_{11}Br$. The four nearest-neighbour correlations were found to be $a = 0.4$ (0.1), $b = 0.20$ (0.05), $c = 0.0$ (0.05) and $d = 0.05$ (0.03), respectively. These values imply that the probability of bromine–methyl contacts between neighbouring molecules is greater than that for a random distribution of molecules and that the probabilities of bromine–bromine and methyl–methyl contacts are smaller than for the random distribution.

Introduction

The diffuse intensities of X-rays which are scattered by a disordered molecular crystal contain information about the correlations between the displacements of pairs of nuclei and, in the case of substitutional disorder, information about the pair distribution function of the crystal (Guinier, 1963; Amorós & Amorós, 1968; De Ridder, 1978; Fouret, 1979).

The monoclinic form of 9-bromo-10-methylanthracene is one example of a class of substituted anthracene crystals which is substitutionally disordered. The orthorhombic form is also disordered and is the subject of a separate study (Welberry, Jones & Epstein, 1982). Each site of the crystal may be occupied by one of two types of molecule, labelled *A* and *B*, respectively. *A* and *B* differ only in the positions of the bromine and methyl substituents and, in effect, represent two orientations of the same molecule, related by a twofold rotation about the long axis of the anthracene frame. Within the resolution of the measured Bragg diffraction data, the anthracene frame is ordered, but the bromine and methyl substituents at the 9- and 10-positions are disordered. For the monoclinic form 64.3% of the sites are occupied by molecules of type *A*, with the Br substituent at the 9-position, and 35.7% of the sites are occupied by molecules of type *B*, with the CH_3 substituent at the 9-position (Jones & Welberry, 1980). The average crystal structure has space group $P2_1/c$ with four molecules per unit cell.

From the diffuse intensities of X-rays scattered by such a disordered crystal the *A–A*, *A–B*, *B–A* and *B–B* pair distribution functions may be obtained. As the degree of substitutional disorder in the crystalline phase is independent of temperature (*i.e.* no exchange occurs between molecules of different types), these pair distributions reflect the intermolecular interactions which have occurred during crystal growth.

A preliminary analysis of the diffuse intensities in the

$h0l$ and $0kl$ sections of reciprocal space for the monoclinic form of 9-bromo-10-methylanthracene has been reported by Welberry & Jones (1980). By comparing the diffuse intensities observed using Weissenberg film methods with those produced by optical simulations, a correlation coefficient of +0.6 was obtained between nearest-neighbour molecular sites.

The purpose of this paper is to demonstrate that the diffuse scattering from substitutionally disordered molecular crystals may be analysed using simple model calculations to determine the correlation coefficients between pairs of molecular sites.

X-ray scattering from a disordered molecular crystal

The total intensity of X-rays scattered by a crystal is (Born, 1942–43)

$$I_{\text{tot}}(\mathbf{S}) = \sum_i W_i \langle i | |F_{\text{cryst}}(\mathbf{S}; \mathbf{Q})|^2 | i \rangle, \quad (1)$$

where W_i is the probability that the crystal is in the vibrational state $|i\rangle$ and $F_{\text{cryst}}(\mathbf{S}; \mathbf{Q})$ is the crystal structure factor for the set of nuclear positions represented by \mathbf{Q} . The magnitude of the scattering vector \mathbf{S} is $4\pi \sin \theta/\lambda$.

For a two-component disordered crystal,

$$\begin{aligned} |F_{\text{cryst}}(\mathbf{S}; \mathbf{Q})|^2 = & N \sum_n^{\text{cell}} [F_n(\mathbf{S}; \mathbf{Q})]_{\text{av}} \exp(i\mathbf{S} \cdot \mathbf{R}_n)^2 \\ & + Nm_A m_B \sum_n^{\text{cell}} \sum_m^{\text{cell}} C_{nm}^{AB} \exp(i\mathbf{S} \cdot \mathbf{R}_{nm}) \\ & \times \Delta F_n(\mathbf{S}; \mathbf{Q}) \Delta F_m^*(\mathbf{S}; \mathbf{Q}). \end{aligned} \quad (2)$$

Equation (2) is analogous to corresponding expressions for a binary metal alloy (Cowley, 1950; Warren, Averbach & Roberts, 1951; Guinier, 1963). N is the number of unit cells; $[F_n]_{\text{av}} = m_A F_n^{(A)} + m_B F_n^{(B)}$ where m_A is the probability that the molecule at a particular site is of type A and $F_n^{(A)}$ is the structure factor for an A -type molecule at site n , specified by the vector \mathbf{R}_n ; $\mathbf{R}_{nm} = \mathbf{R}_n - \mathbf{R}_m$; $\Delta F_n = F_n^{(A)} - F_n^{(B)}$; and C_{nm}^{AB} is a correlation coefficient or short-range-order parameter defined by

$$\begin{aligned} C_{nm}^{AB} &= (1 - p_{nm}^{AB}/m_A) = (t_{nm}^{AA} - m_A^2)/m_A m_B \\ C_{nn}^{AB} &= 1. \end{aligned} \quad (3)$$

In (3), p_{nm}^{AB} is the conditional probability that site n is occupied by a molecule of type A given that site m is occupied by a molecule of type B . The joint probability t_{nm}^{AB} that site n is occupied by a molecule of type A and site m is occupied by a molecule of type B is related to p_{nm}^{AB} by

$$t_{nm}^{AB} = p_{nm}^{AB} m_B. \quad (4)$$

When there is no correlation between the types of molecules occupying sites n and m , $t_{nm}^{AB} = m_A m_B$ and $C_{nm}^{AB} = 0$.

Following Born (1942–43), the vibrational average of (2) may be obtained by expressing the molecular structure factors in terms of pseudoatom scattering factors and invoking the rigid pseudoatom (Epstein & Stewart, 1979) and harmonic approximations. The vibrational average of the first term of (2) is then

$$I_1(\mathbf{S}) = I_{\text{Bragg}}(\mathbf{S}) + I_{\text{TDS}}(\mathbf{S}). \quad (5)$$

In equation (5),

$$\begin{aligned} I_{\text{Bragg}}(\mathbf{S}) = & N |m_A \sum_n^{\text{cell}} \sum_\alpha f_{n\alpha}^{(A)}(\mathbf{S}) T_{n\alpha}^{(A)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{n\alpha}^{(A)}) \\ & + m_B \sum_n^{\text{cell}} \sum_\beta f_{n\beta}^{(B)}(\mathbf{S}) T_{n\beta}^{(B)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{n\beta}^{(B)})|^2 \end{aligned} \quad (6)$$

corresponds to the Bragg scattering from an ordered molecular crystal with each site occupied by an 'average' molecule with structure factor $[F_n(\mathbf{S}; \mathbf{Q})]_{\text{av}}$; $f_{n\alpha}^{(A)}(\mathbf{S})$ is the scattering factor for pseudoatom α of a molecule of type A at site n ; $\dot{\mathbf{R}}_{n\alpha}$ is the vector from the origin to the equilibrium position of the corresponding nucleus; and $T_{n\alpha}^{(A)}(\mathbf{S}) = \exp(-i\mathbf{S} \cdot \mathbf{U}_{n\alpha}^{(A)}/2)$ is the usual Debye–Waller factor. $I_{\text{TDS}}(\mathbf{S})$ is diffuse scattering resulting from correlated motions of pairs of nuclei (thermal diffuse scattering).

The vibrational average of the second term of (2) is

$$I_2(\mathbf{S}) = I_{\text{diff}}(\mathbf{S}) + I_{\text{TDS}}'(\mathbf{S}), \quad (7)$$

where

$$\begin{aligned} I_{\text{diff}}(\mathbf{S}) = & Nm_A m_B \sum_n^{\text{cell}} \sum_m^{\text{cell}} C_{nm}^{AB} \\ & \times \left[\sum_\alpha f_{n\alpha}^{(A)}(\mathbf{S}) T_{n\alpha}^{(A)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{n\alpha}^{(A)}) \right. \\ & \left. - \sum_\beta f_{n\beta}^{(B)}(\mathbf{S}) T_{n\beta}^{(B)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{n\beta}^{(B)}) \right] \\ & \times \left[\sum_\alpha f_{m\alpha}^{(A)}(\mathbf{S}) T_{m\alpha}^{(A)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{m\alpha}^{(A)}) \right. \\ & \left. - \sum_\beta f_{m\beta}^{(B)}(\mathbf{S}) T_{m\beta}^{(B)}(\mathbf{S}) \exp(i\mathbf{S} \cdot \dot{\mathbf{R}}_{m\beta}^{(B)}) \right]^* \end{aligned} \quad (8)$$

In (7), $I_{\text{TDS}}'(\mathbf{S})$ is an additional contribution to thermal diffuse scattering.

The diffuse scattering represented by (8) is the primary interest of the present study. For each molecular site n of the unit cell, the contribution to $I_{\text{diff}}(\mathbf{S})$ consists of two types of terms. The first term occurs for $m = n$ and involves internuclear vectors between pseudoatoms belonging to the molecule at site

n . The resulting diffuse scattering is labelled as the *random intensity* since these are the only contributions to $I_{\text{diff}}(\mathbf{S})$ for a crystal in which the distribution of A -type and B -type molecules is random. The random intensity is positive-definite everywhere in reciprocal space and is zero at the origin of reciprocal space when type- A molecules and type- B molecules are isoelectronic. The second type of term includes contributions from all distinct pairs of molecular sites n and m for which C_{nm}^{AB} is significantly different from zero. These contributions involve internuclear vectors between pseudoatoms belonging to different molecular sites. For each pair of sites n and m (and the symmetry-related pairs) the contribution to $I_{\text{diff}}(\mathbf{S})$ is referred to as the *correlation distribution*. If $C_{nm}^{AB} \neq 0$, the m th molecular site belongs to the *correlation neighbourhood* of site n . The correlation distributions are also zero at the origin of reciprocal space when A -type and B -type molecules are isoelectronic.

Note that although the correlation distribution from each member of the neighbourhood of site n may be negative in some regions of reciprocal space, the sum of the random intensity plus all correlation distributions must be positive-definite everywhere in reciprocal space.

Analysis of the diffuse scattering from monoclinic 9-bromo-10-methylanthracene

Observed intensities

Scattered intensities were recorded using Weissenberg film methods, then processed using an Optronics P-1700 Photomation system to remove the distortion of reciprocal space and to correct for background scattering (Welberry & Jones, 1980). The resulting intensities for the $h0l$, $hk0$ and $0kl$ sections of reciprocal space are shown in Figs. 2(a), 3(a) and 4(a), respectively. Each section of reciprocal space is enclosed by the locus of points for which $\sin \theta/\lambda \approx 0.5 \text{ \AA}^{-1}$. With the long exposure times of ~ 3 d and the enhancement procedures used (Welberry & Jones, 1980), broad regions of diffuse scattering are visible, together with the sharp maxima at the reciprocal-lattice positions due to the Bragg scattering.

Details of the model for diffuse scattering

$I_{\text{diff}}(\mathbf{S})$, $I_{\text{TDS}}(\mathbf{S})$ and $I'_{\text{TDS}}(\mathbf{S})$ all contribute to the diffuse scattering shown in Figs. 2(a), 3(a) and 4(a). The contributions from $I'_{\text{TDS}}(\mathbf{S})$ are expected to be small and may be sensibly neglected. Contributions from $I_{\text{TDS}}(\mathbf{S})$ are expected to be most important at or near the Bragg peaks and may also be important at more general points in reciprocal space at large values of $\sin \theta/\lambda$ (Born, 1942–43; Annaka & Amorós, 1960). Though the importance of $I_{\text{TDS}}(\mathbf{S})$ is recognized, no

effort has been made in the present work to separate the contributions due to thermal diffuse scattering from those due to substitutional disorder. The data shown here were recorded at room temperature. The contributions from thermal diffuse scattering may be minimized by carrying out the experiment at low temperatures. Alternatively, $I_{\text{TDS}}(\mathbf{S})$ may be calculated from first principles. Such a calculation relies on the use of a suitable model for the vibrational motion of the disordered molecular crystal.

In the present work the dominant contribution to the observed diffuse scattering was therefore assumed to be from substitutional disorder. The procedure used for this analysis was to calculate $I_{\text{diff}}(\mathbf{S})$ from (8) and determine the set of correlation coefficients for which the best qualitative agreement was obtained between calculated and observed diffuse intensity distributions.

The fractional site occupancies m_A and m_B used for these calculations were those reported from the least-squares analysis of the average structure factors obtained from the Bragg intensities measured independently by diffractometer (Jones & Welberry, 1980). From these data no differences between the pseudoatoms of the anthracene frame of type- A molecules and the corresponding pseudoatoms of type- B molecules could be resolved. The anthracene frame was therefore considered to be ordered and does not contribute to $I_{\text{diff}}(\mathbf{S})$. The diffuse scattering was modelled by considering only the disorder of the bromine and methyl substituents. In addition, the equilibrium positions of the bromine nucleus of a type- A molecule and the methyl carbon nucleus of a type- B molecule could not be distinguished in the analysis of the Bragg data. Similarly the equilibrium position of the methyl carbon nucleus of a type- A molecule could not be resolved from that of the bromine nucleus of a type- B molecule. For the calculations of diffuse scattering, idealized positions of the bromine and carbon substituents were used, rather than these average positions. The idealized positions were based on previously determined Br–C(aromatic) and C(methyl)–C(aromatic) internuclear distances discussed by Jones & Welberry (1980) and are given in Table 1.

The vibrational tensors obtained for the methyl carbon and bromine substituents from the analysis of

Table 1. Idealized positions (fractional coordinates) for bromine and methyl-carbon substituents for monoclinic 9-bromo-10-methylanthracene

Molecule type	Nucleus	x	y	z
A	Br	0.2524	0.5773	0.8252
	C	–0.2881	0.1941	0.9469
B	C	0.2178	0.5531	0.8330
	Br	–0.3225	0.1695	0.9546

the Bragg data are site-specific parameters. The effects of the unresolved differences between the carbon and bromine positions would be to increase these vibrational parameters. However, this increase may be partially offset by the neglect of thermal diffuse scattering at the positions of the Bragg peaks. Because of the uncertainty in the true vibrational parameters, equivalent isotropic vibrational parameters, $\frac{1}{3}(U_{11} + U_{22} + U_{33})$, were used for the calculations of $I_{\text{diff}}(\mathbf{S})$. The equivalent isotropic vibrational parameters for the 9-substituent and the 10-substituent were 0.0605 \AA^2 and 0.0654 \AA^2 , respectively.

The bromine and methyl carbon pseudoatoms were assumed to be isolated spherically-averaged atoms. The scattering factors used were those given by the analytical approximations of Table 2.2B, in *International Tables for X-ray Crystallography* (1974). The scattering from the hydrogen pseudoatoms of the methyl substituent was neglected.

Correlation neighbourhoods

The molecular sites were labelled by five-digit designation codes, the first three digits specifying unit-cell translations along the crystallographic axes **a**, **b** and **c**, respectively, and the last two digits specifying a particular symmetry operation. The site labelled 55501 referred to the site with coordinates x, y, z in the origin unit cell. The corresponding sites at $\bar{x}, \bar{y}, \bar{z}$, $x, y + \frac{1}{2}, z + \frac{1}{2}$ and $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ for the space group $P2_1/c$ were labelled 55502, 55503 and 55504, respectively. The site labelled 56501 was at $x, y + 1, z$.

From preliminary calculations of the random intensity and correlation distributions, the correlation distributions for neighbouring sites related to 55501 by

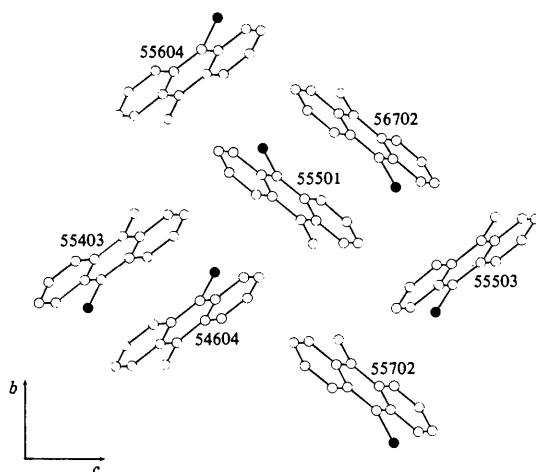


Fig. 1. The *a*-axis projection of monoclinic 9-bromo-10-methylanthracene showing the six nearest neighbours of the molecular site labelled 55501. All molecules shown are of type *A*. Bromines are represented by full circles.

Table 2. Site designation codes, correlation coefficients and internuclear distances (for *A*-*A* pairs) of the nearest neighbours of site 55501 for monoclinic 9-bromo-10-methylanthracene

Site designation code	Correlation coefficient	Vector type	Internuclear distance (Å)
56702	<i>a</i>	C-Br	3.86
		Br-C	3.86
55604	<i>b</i>	Br-C	3.97
		Br-Br	6.66
54604	<i>b</i>	C-Br	3.97
55702	<i>c</i>	Br-Br	6.66
		C-C	6.18
55503	<i>d</i>	C-C	6.99
		C-Br	7.05
55403	<i>d</i>	C-C	6.99
		Br-C	7.05

cell translations along the *a* axis appeared to be of little importance in describing the observed diffuse intensity distributions. These sites were therefore not included in the correlation neighbourhood of 55501. The remaining six nearest neighbours of 55501 are shown in Fig. 1 for an ordered structure of type-*A* molecules. The designation codes and correlation coefficients for these neighbours are given in Table 2, together with the vector types and internuclear distances for the ordered structure of type-*A* molecules. As the relevant set of internuclear vectors between sites 55501 and 55604 is identical to that between sites 55501 and 54604, the correlation distributions for these neighbours were indistinguishable. Each neighbour was assigned the same correlation coefficient *b*. Similarly, neighbours 55503 and 55403 were assigned the same correlation coefficient *d*.

Coefficients for the remainder of the correlation neighbourhood were assumed to be products of these primary coefficients. This is equivalent to the assumption that the directions along which correlations are propagated obey the statistics of a non-stationary Markov chain (Isaacson & Madsen, 1976) and is implicit in the work of Wilson (1949) used by Flack (1970) and Glazer (1970) in their analyses of disorder from measurements of the breadth of diffuse intensity maxima. For example, the correlation coefficient for the sites 55501 and 56503 is *a* × the correlation coefficient for the pair of sites 56702 and 56503. As this latter pair of sites is symmetrically equivalent to the pair of sites 55501 and 54604 which have correlation coefficient *b*, the correlation coefficient for sites 55501 and 56503 was assigned the value *a* × *b*. The designation codes and coefficients for the correlation neighbourhood of site 55501 are given in Table 3. The corresponding neighbourhoods for the remaining sites in the unit cell were generated from this neighbourhood by symmetry.

Table 3. Designation codes and coefficients for the correlation neighbourhood of site 55501

Designation code	Correlation coefficient	Designation code	Correlation coefficient	Designation code	Correlation coefficient
56702	<i>a</i>	54501	<i>b</i> ²	57702	<i>ab</i> ²
55604	<i>b</i>	55704	<i>ad</i>	56802	<i>ad</i> ²
54604	<i>b</i>	54704	<i>ad</i>	56604	<i>b</i> ³
55702	<i>c</i>	56602	<i>bd</i>	53604	<i>b</i> ³
55403	<i>d</i>	55602	<i>bd</i>	55504	<i>bd</i> ²
55503	<i>d</i>	55601	<i>d</i> ²	54504	<i>bd</i> ²
56503	<i>ab</i>	55401	<i>d</i> ²	55603	<i>d</i> ³
56403	<i>ab</i>	54403	<i>bc</i>	55303	<i>d</i> ³
56501	<i>b</i> ²	54503	<i>bc</i>		

Details of the analysis

The random intensity in the *h*0*l* section of reciprocal space for the monoclinic form of 9-bromo-10-methylanthracene is shown in Fig. 2(b). The origin of the parallel bands of diffuse intensity may be understood by examining the expression for the random intensity when average positions are assumed for both the 9- and 10-substituents and the vibrational parameters are set equal to zero. From (8),

$$I_r(\mathbf{S}) = 2Nm_A m_B |f_{Br}(\mathbf{S}) - f_C(\mathbf{S})|^2 \sum_n^{\text{cell}} [1 - \cos(\mathbf{S} \cdot \mathbf{R}_n)] \quad (9)$$

where \mathbf{R}_n is the intramolecular vector between the bromine and methyl carbon substituents at site *n*. For \mathbf{S} belonging to the *h*0*l* section, only the projection of \mathbf{R}_n onto the (010) plane is important. Since these projections are parallel or anti-parallel for all sites in the unit cell, the random intensity in the *h*0*l* section consists of only one fringe pattern. Neither the use of idealized positions rather than average positions nor the introduction of non-zero vibrational parameters significantly alters the form of this fringe pattern.

If the effects of thermal diffuse scattering are neglected, the differences between the random intensity distribution of Fig. 2(b) and the observed diffuse intensities of Fig. 2(a) are due to the effects of correlations between pairs of molecular sites.

The *h*0*l* sections of the three distinct correlation distributions for the nearest neighbours of Table 2, calculated for correlation coefficients of +0.6, are shown in Figs. 2(c)–2(e). Note that the correlation distribution for 55702 is indistinguishable from that of 56702 in this section of reciprocal space. In other sections the two distributions are different.

The correlation distributions in the *h*0*l* section have the same broad fringe pattern as the random distributions but are further modulated by fringe patterns characteristic of intermolecular vectors. This is best demonstrated by examining the expression for the correlation distribution assuming average positions and

zero vibrational amplitudes. The contributions to $I_{\text{diff}}(\mathbf{S})$ of (8) for $m \neq n$ are then

$$8Nm_A m_B |f_{Br}(\mathbf{S}) - f_C(\mathbf{S})|^2 \sum_n^{\text{cell}} \sin(\frac{1}{2}\mathbf{S} \cdot \mathbf{R}_n) \times \sum_m C_{nm}^{AB} \cos[\frac{1}{2}\mathbf{S} \cdot (\mathbf{R}'_{nm} + \mathbf{R}''_{nm})] \sin(\frac{1}{2}\mathbf{S} \cdot \mathbf{R}_m) \quad (10)$$

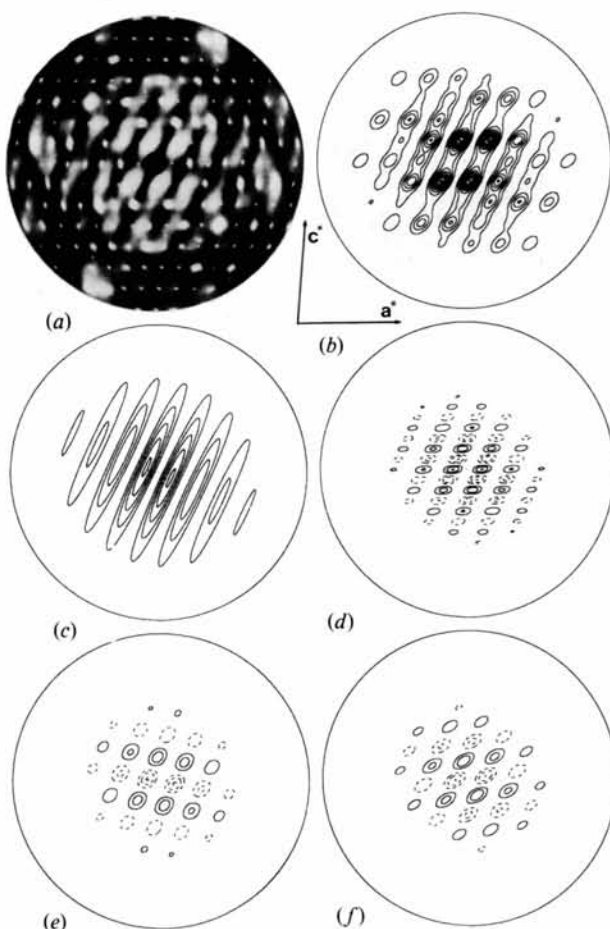


Fig. 2. Diffuse scattering distributions in the *h*0*l* section for monoclinic 9-bromo-10-methylanthracene. (a) Observed distribution. (b) Random intensity calculated from equation (8) for $m = n$. Correlation distributions for the neighbours of Table 2: (c) 56702, (d) 55604, (e) 55503. (f) Final calculated distribution. All contour levels shown are in steps of 25 arbitrary intensity units. Negative contours are dashed lines. Positive contours are continuous lines.

where the *intramolecular* vectors \mathbf{R}_n and \mathbf{R}_m are defined as in (9) and \mathbf{R}'_{nm} and \mathbf{R}''_{nm} are *intermolecular* vectors between nuclei of distinct molecular sites. As the projections onto the (010) plane of all vectors \mathbf{R}_n and \mathbf{R}_m are parallel or anti-parallel, the form of (10) for the $h0l$ section is

$$4Nm_A m_B |f_{Br}(\mathbf{S}) - f_C(\mathbf{S})|^2 \sum_n^{\text{cell}} [1 - \cos(\mathbf{S} \cdot \mathbf{R}_n)] \times \sum_m \epsilon_{nm} C_{nm}^{AB} \cos[\frac{1}{2}\mathbf{S} \cdot (\mathbf{R}'_{nm} + \mathbf{R}''_{nm})], \quad (11)$$

where ϵ_{nm} is ± 1 depending on whether the projections of \mathbf{R}_n and \mathbf{R}_m are parallel or anti-parallel. For neighbours with small intermolecular vectors \mathbf{R}'_{nm} and \mathbf{R}''_{nm} , the fringe pattern of the random distribution is modulated by additional fringes which are widely spaced. For neighbours with large internuclear vectors, the corresponding modulating fringes are closely

spaced. This is illustrated by the correlation distributions for 56702 and 55503 shown in Figs. 2(c) and (e), respectively.

For the positive correlation coefficients used to calculate the distributions shown in Figs. 2(c)–(e), positive regions add intensity to the random distribution; negative regions remove intensity. Negative correlation coefficients would re-distribute intensity in the opposite sense.

Note that distinct correlation distributions may be weighted by more than one correlation coefficient. As discussed previously, the $h0l$ section of the 56702 distribution is weighted by both a and c . An additional weighting of ab^2 is required since in this section of reciprocal space the correlation distribution of 57702 is also indistinguishable from that of 56702. The weights of distinct correlation distributions for the various sections of reciprocal space may be obtained from Table 3.

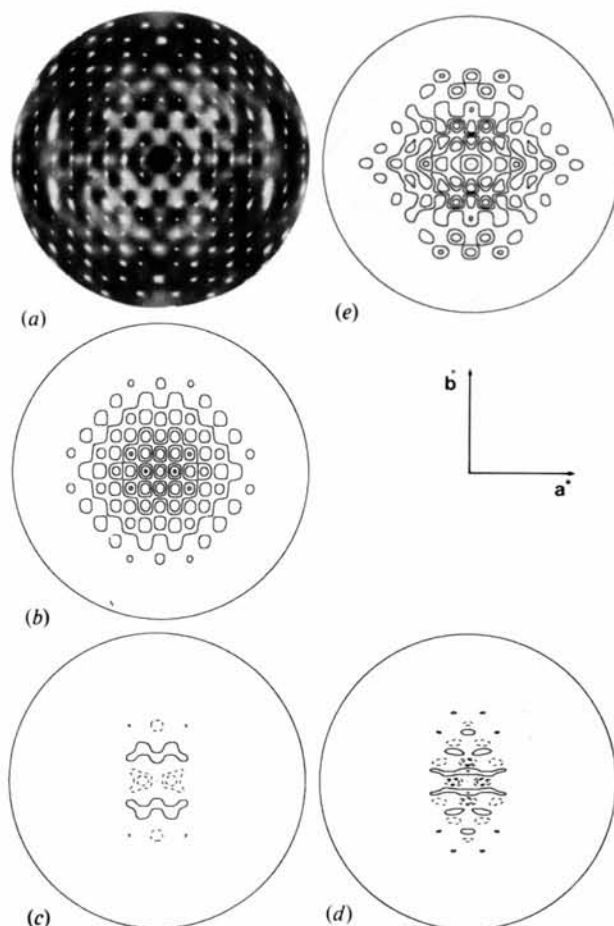


Fig. 3. Diffuse scattering distributions in the $hk0$ section for monoclinic 9-bromo-10-methylantracene. (a) Observed distribution. (b) Random intensity calculated from equation (8) for $m = n$. Correlation distributions for the neighbours of Table 2: (c) 56702. (d) 55702. (e) Final calculated distribution. Contours are as for Fig. 2.

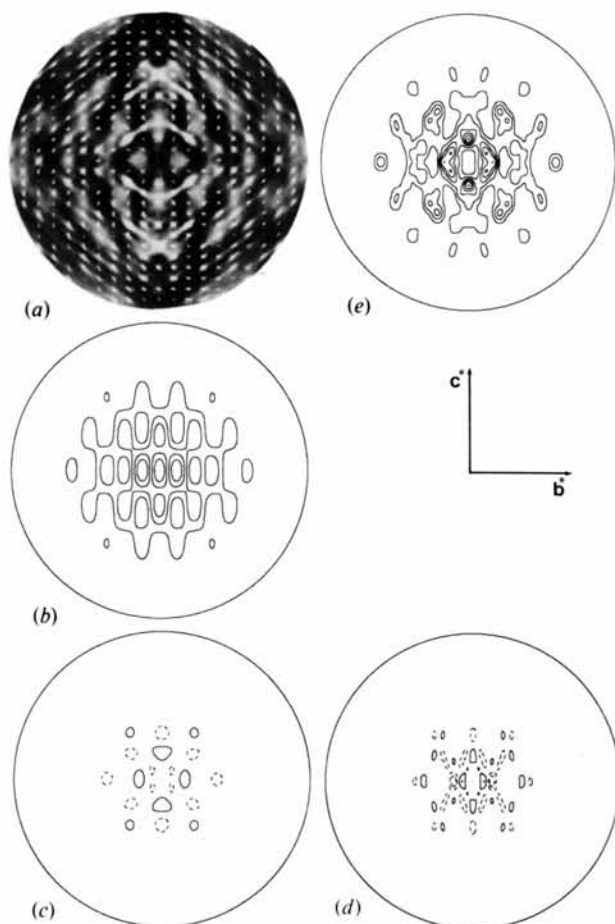


Fig. 4. Diffuse scattering distributions in the $0kl$ section for monoclinic 9-bromo-10-methylantracene. (a) Observed distribution. (b) Random intensity calculated from equation (8) for $m = n$. Correlation distributions for the neighbours of Table 2: (c) 56702. (d) 55702. (e) Final calculated distribution. Contours are as for Fig. 2.

For the $h0l$ section, $I_{\text{diff}}(\mathbf{S})$ was calculated from the superposition of random plus distinct correlation distributions. The values of a , b , c , and d were varied until the best qualitative agreement was obtained between the observed and calculated diffuse intensity distributions. From the analysis of this section, the values obtained for these primary correlations were $(a + c) = 0.4$ (0.1), $b = 0.20$ (0.05) and $d = 0.05$ (0.03). The estimated errors in parentheses are crude estimates based on the half-width of the step size used for the scans over these variables. Values for a and c could not be separately determined from this section since the weights of the most important correlation distributions involved the sum $a + c$ (see Table 3). The distribution of diffuse intensity calculated using these values is shown in Fig. 2(f). Diffuse intensity which appears in the observed distribution of Fig. 2(a) in the immediate vicinity of the Bragg peaks and at large values of $\sin \theta/\lambda$ is attributed to thermal diffuse scattering which has not been included in the present calculations. The agreement otherwise between the two distributions is considered to be satisfactory.

Separate values for the a and c primary correlation coefficients could be resolved from the analysis of the diffuse scattering in the $hk0$ section. The random intensity distribution is shown in Fig. 3(b). The correlation distributions for 56702 and 55702, calculated for correlation coefficients of +0.6, are shown in Figs. 3(c) and (d), respectively. Fixing the values of b and $d = 0.20$ and 0.05 , respectively, the values of a and c were varied subject to the condition that $a + c = 0.4$. The best agreement between the calculated and observed diffuse intensity distribution was obtained for $a = 0.4$ and $c = 0.0$. The distribution calculated with these values of the primary correlation coefficients is

Table 4. Joint probabilities calculated for the neighbours of site 55501 listed in Table 2 and the corresponding values calculated for a random distribution of molecules

Correlation coefficient	t^{AA}	t^{AB}	t^{BA}	t^{BB}
0.0	0.413	0.230	0.230	0.127
(random)				
$a = 0.4$ (56702)	0.50 (2)*	0.14 (2)	0.14 (2)	0.22 (2)
$b = 0.2$ (55604)	0.46 (1)	0.18 (1)	0.18 (1)	0.18 (1)
$c = 0.0$ (55702)	0.41 (1)	0.23 (1)	0.23 (1)	0.13 (1)
$d = 0.05$ (55503)	0.425 (7)	0.218 (7)	0.218 (7)	0.139 (7)

* Errors in parentheses are in the last digit and are obtained from the error estimates of the correlation coefficients.

shown in Fig. 3(e) and is in good qualitative agreement with the observed distribution of Fig. 3(a).

Similar values for a and c were obtained from the analysis of the diffuse scattering in the $0kl$ section. The random and correlation distributions for 56702 and 55702 for this section are shown in Figs. 4(b), (c) and (d), respectively. The diffuse intensity distribution calculated with $a = 0.4$ and $c = 0.0$ is shown in Fig. 4(e). Note that the streaks of diffuse intensity between intense Bragg peaks of Fig. 4(a) are attributed to displacement disorder, of either static or dynamic origin (Welberry & Jones, 1980).

From these analyses, the estimated errors in the values of a and c were ± 0.1 and ± 0.05 , respectively. The values for the primary correlation coefficients were therefore determined to be $a = 0.4$ (0.1), $b = 0.20$ (0.05), $c = 0.0$ (0.05) and $d = 0.05$ (0.03).

Discussion

Using the values of a , b , c and d which have been determined, the joint probabilities and conditional probabilities of (4) may be calculated. These latter probabilities define the pair distribution for the molecular crystal and are related to the correlation coefficients by (3).

The joint probabilities t_{nm}^{AA} , t_{nm}^{AB} , t_{nm}^{BA} and t_{nm}^{BB} involving site 55501 and the neighbouring sites of Table 2 are given in Table 4, together with the corresponding values for a random distribution of molecules. For the pairs of sites 55501 and 56702, the joint probability that both sites are occupied by molecules of type A is significantly greater than that for the random case. Similarly the joint probability that both sites are occupied by molecules of type B is also greater than that for a random distribution, while the joint probability that one site is occupied by a molecule of type A and the other by a molecule of type B is significantly smaller than for the random case. When both sites are occupied by type- A molecules, the shortest inter-nuclear vectors between substituent groups are Br-C vectors (see Table 2). The correlation between these sites therefore ensures that this type of intermolecular interaction occurs more frequently than for a random distribution of molecules. When one site is occupied by a molecule of type A and the other by a molecule of type B , the shortest vectors between substituent groups are C-C and Br-Br vectors. The correlation between these sites therefore also ensures that these types of interactions occur less frequently than for the random case. Similar conclusions for nearest-neighbour sites resulted from the analysis of the diffuse scattering from the orthorhombic form of 9-bromo-10-methylanthracene (Welberry, Jones & Epstein, 1982).

Summary and concluding remarks

Using simple model calculations, the diffuse intensities of X-rays scattered from the substitutionally disordered monoclinic form of 9-bromo-10-methylanthracene have been analysed. Qualitative agreement between observed and calculated diffuse intensity distributions was obtained using four primary correlation coefficients. Correlation coefficients between other molecular sites were assumed to be products of these coefficients.

The correlation coefficients obtained from this analysis showed that correlations between molecular sites increased the number of short-range bromine-methyl contacts and decreased the number of bromine-bromine and methyl-methyl contacts relative to the random distribution of molecules over the molecular sites.

The procedures used for this analysis are completely general and are readily implemented. They complement optical-simulation techniques since the latter are necessarily restricted to analyses of only zero-layer intensity distributions.

The present method is semi-quantitative in that only qualitative features of the observed diffuse intensity distributions have been reproduced. More quantitative procedures must rely on the separation of thermal diffuse scattering (neglected in the present study) from the diffuse scattering resulting from substitutional disorder. Such a separation would then allow correlation coefficients to be determined *via* a least-squares analysis of the measured diffuse intensities. Studies in these directions are proceeding.

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Treatment of Equations of Constraint in Least-Squares Refinement

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Abstract

With a least-squares program organization, as described by Busing [*Acta Cryst.* (1971), A27, 683–684], the constraints have to be put into a form where

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the dependent parameters are expressed by the independent ones and, possibly, by further constants. Difficulties may arise if (1) several linear or non-linear constraints refer simultaneously to several parameters, and (2) if the constraints are not linear and cannot be

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