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Comments on Allegra's paper »A simplified formula for the calculation of the X-ray intensity diffracted by a monodimensionally disordered structure«.

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The intensity of X-rays diffracted by a one-dimensionally disordered crystal was given, in a matrix form, first by Hendricks & Teller (1942) and also by Kakinoki & Komura (1952) as follows:

$$I = N \text{ spur } \mathbf{VF} + \sum_{n=1}^{N-1} (N-n) \text{ spur } \mathbf{VFQ}^n + \text{conj.}\,, \tag{1}$$

where:

N is the total number of layers;
$(\mathbf{VF})_{ts} = w_s V_s V_t^*$;
$(\mathbf{Q})_{st} = P_{st} \exp(-i\varphi_s)$;
φ_s is the phase shift due to the layer of sth kind;
V_s is the layer form factor of the layer of sth kind;
w_s is the probability of finding the layer of sth kind;
P_{st} is the probability of finding the layer of tth kind after that of sth kind;
conj. means the complex conjugate of the second term in (1).

Allegra (1961) recently reported a new method of carrying out the summation in (1) regardless of whether the matrix $\mathbf{Q}$ could be diagonalized by the similarity operation $\mathbf{OQO}^{-1}$ or not. His formula is rewritten by using our notation as

$$I_{\text{av.}} = \text{spur } \mathbf{VF}(\mathbf{1}-\mathbf{Q})^{-1} + \text{conj.} - \text{spur } \mathbf{VF}, \tag{2}$$

where N in (1) is taken as infinite. The same result has already been given by us (Kakinoki & Komura, 1952) leaving N as finite:

$$\begin{aligned} I = N\{&\text{spur } \mathbf{VF} + \text{spur } \mathbf{VFQ}(\mathbf{1}-\mathbf{Q})^{-1} + \text{conj.}\} \\ &+ \text{spur } \mathbf{VF}(\mathbf{Q}^{N+1} - \mathbf{Q})(\mathbf{1}-\mathbf{Q})^{-2} + \text{conj.} \end{aligned} \tag{3}$$

The first three terms (called diffuse term) are found to be the same with (2) in which $I_{\text{av.}}$ means the average intensity per layer while I in (1) is the average per crystallite with N layers. The rest of (3) (called higher term) contributes to the intensity when N is very small or when the structure tends to regular one.

In our study calculation of the intensity equation (1) has further progressed even when the matrix $\mathbf{Q}$ cannot be diagonalized. The idea is to use a Jordan's normal form reduced from any type of matrix $\mathbf{Q}$ by the similarity transformation. Let us take a simple example in which the eigenvalues of $3 \times 3\mathbf{Q}$ matrix are all equal and the normal form is expressed by

$$\mathbf{OQO}^{-1} = \mathbf{Q}_0 = \begin{pmatrix} x_1 & 1 & 0 \\ 0 & x_1 & 1 \\ 0 & 0 & x_1 \end{pmatrix} \tag{4}$$

In this case spur $\mathbf{VFQ}^n$ can be written in a form as

$$\text{spur } \mathbf{VFQ}^n = c_1^{(0)} x_1^n + c_1^{(1)} n x_1^{n-1} + c_1^{(2)} \tfrac{1}{2} n(n-1) x_1^{n-2}, \tag{5}$$

and then (1) (neglecting higher term) can be expressed by

$$I = N\left\{\frac{c_1^{(0)}}{(1-x_1)} + \frac{c_1^{(1)}}{(1-x_1)^2} + \frac{c_1^{(2)}}{(1-x_1)^3} + \text{conj.} - \text{spur } \mathbf{VF}\right\}. \tag{6}$$

$c_1^{(0)}, c_1^{(1)}, c_1^{(2)}$ in (6) are the solutions of simultaneous equations obtained from (5) by putting $n = 0$, 1 and 2. There is no need, in this calculation, to evaluate $\mathbf{O}$, $\mathbf{O}^{-1}$ and $\mathbf{OVFO}^{-1}$.

Further simplification can be made without obtaining eigenvalues and c_ν's. If we use the relations between roots and coefficients in

$$\det(x\mathbf{1} - \mathbf{Q}) = \sum_{n=0}^{S} a_n x^{S-n}\,, \tag{7}$$

and other relations such as

$$\begin{aligned} J_n &= \text{spur } \mathbf{VFQ}^n \\ &= \sum_\nu \sum_{p_\nu} c_\nu^{(p_\nu)} \frac{n(n-1)\ldots(n-p_\nu+1)}{p_\nu!} x_\nu^{n-p_\nu}\,. \end{aligned} \tag{8}$$

I in (1) can be expressed in a general form as

$$\begin{aligned} I &= ND + H\,, \\ D &= D' + \text{conj.} - J_0, \quad H \text{ is the higher term,} \\ D' &= \sum_{n=1}^{S-1} \sum_{m=0}^{n} a_{n-m} J_m \Big/ \sum_{n=0}^{S} a_n\,. \end{aligned} \tag{9}$$

This equation is found to be valid for any type of $\mathbf{Q}$. The general derivation and discussion of this result will be given in this Journal in a near future.

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The molecular dimensions of 2:3-dihydro-2:3-methylene-1:4-naphthaquinone: a comparison of the results of two- and three-dimensional analysis.

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The compound, $C_{11}H_8O_2$, with the chemical constitution implied in Fig. 1, crystallizes in the space group $P2_1/m$ with two molecules in a cell of dimensions,

$$a = 6{\cdot}98,\ b = 10{\cdot}55,\ c = 5{\cdot}46\ \text{Å};\ \beta = 94{\cdot}5°.$$

For a non-planar molecule, it is remarkable in having nearly all its atoms effectively resolved in all three principal projections; along the comparatively long b-axis this is possible because the molecule is bisected by the mirror-plane so that pairs of atoms precisely coincide in this projection. The structure therefore seemed well suited for analysis by two-dimensional methods, and such a study has been reported in some detail (Grant & Speakman, 1958). Standard deviations for the bond-lengths were then assessed at 0·015 Å for C–O, and at 0·018–0·030 for C–C.

Subsequently we have been able to apply three-dimensional refinement, using the DEUCE programs devised by Rollett (1961). The coordinate-shifts were considerable. Though they exceeded three times the previously estimated standard deviations only for C(4), their overall effect on the bond-lengths was radical: for instance, they invalidated a supposed parallelism between the bond-lengths in the naphthalenic part of the molecule and those in naphthalene itself. This experience illustrates the risk of placing reliance on projections, even when they seem well-resolved. The unsophisticated criterion of resolution—namely that the atoms have separated electron-density maxima—is no doubt inadequate.

Table 1. *Atomic coordinates, with respect to an origin located at a centre of symmetry*

x, y, and z are fractional, the decimal point to the left being omitted; X', Y and Z' are in Å and with respect to orthogonal axes, X' being parallel to x and Y to y

(To avoid inconsistencies due to rounding-off, more figures appear in the last three columns than are significant)

Atom	x	y	z	X'	Y	Z'
O	3284	0016	2734	2·1752	0·0159	1·4878
C(1)	0512	1837	8322	0·0006	1·9381	4·5295
C(2)	1564	1197	6681	0·8044	1·2619	3·6371
C(3)	2651	1837	5017	1·6353	1·9373	2·7316
C(4)	3674	1112	3188	2·4282	1·1731	1·7363
C(5)	5191	1779	1934	3·5403	1·8764	1·0521
C(6)	6651	2500	3533	4·4903	2·6375	1·9210
H(1)	−043	136	968	−0·712	1·432	5·273
H(2)	158	023	672	0·818	0·237	3·658
H(5)	582	127	043	4·045	1·339	0·237
H(6)	617	250	522	4·084	2·638	2·841
H(6′)	770	250	297	5·248	2·638	1·617

Table 2. *Thermal parameters* × 10^2 (see text)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
O	3·64	1·24	6·06	−0·82	0·73	−0·14
C(1)	2·40	1·76	4·45	−0·07	−0·24	0·10
C(2)	2·98	1·30	4·63	0·55	0·59	0·08
C(3)	2·76	1·16	4·01	0·41	−0·02	0·17
C(4)	3·39	1·24	4·22	0·02	0·44	−0·22
C(5)	2·44	1·26	4·72	−0·30	0·11	−0·24
C(6)	3·35	1·52	5·80	—	−0·69	—
H's (All)	2·98	1·30	4·87	—	0·59	—

(These values, for H, correspond to an isotropic Debye-factor, $B = 4{\cdot}0$ Å^2.)

The refinement was based on 611 independent reflexions, some 70% of those accessible to Cu $K\alpha$-radiation, and it consisted of six cycles of least-squares during which R for the observed terms fell from 22·2% to 13·8%. Inclusion of the hydrogen atoms after three cycles improved the agreement, though the refinement of their positional parameters is questionable and that of their thermal parameters negligible. The final coordinates are listed in Table 1. The revised bond-lengths and angles are shown in Fig. 1, where for comparison the original bond-lengths are given in parentheses. Table 2 lists anisotropic thermal parameters, b_{ij} being the constants in the expression,

$$2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{31}lh)} .$$

Standard deviations, $\sigma(r)$, assessed from the least-squares residuals, are 0·004 Å for oxygen and 0·006 Å (average) for carbon atoms; these correspond to 0·007 for C–O (which depends substantially only on the y-coordinates), to 0·010 for the C–C bonds that lie across the mirror-plane, and to 0·008 Å for the other C–C bonds. For bond-angles the deviations are about 0·6°. Though the comparison is inexact, as new and rescaled experimental data are involved, we compared the R-values for the three principal zones with those obtained in the two-dimensional analysis: for $hk0$, $h0l$ and $0kl$ respectively they are 12·6, 12·8 and 13·3% against the original 13·0, 11·3 and 12·2%. For these partial data, the more exact analysis yields an agreement that is slightly less impressive.

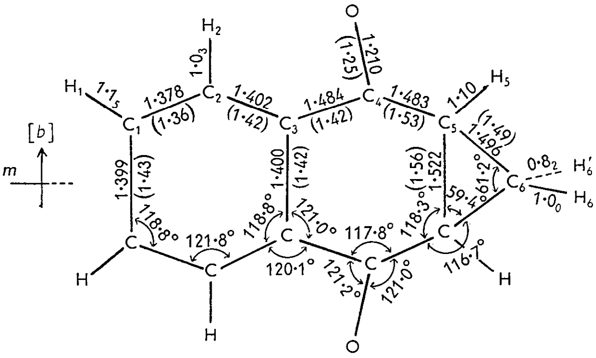

Fig. 1. Numbering of atoms and molecular dimensions. The bond-lengths (Å) found in the earlier, two-dimensional analysis are shown in parentheses. C(6), H(6) and H(6′) are in special positions on the mirror-plane perpendicular to b.

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