

listed in Table 6. The structural details thus depend on complex factors, probably including the role played by unpaired  $d$  electrons in the central metal ion.

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## The Crystal Structure of *trans*-9-Isopropyl-10-methyl-9,10-dihydroanthracene\*

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The crystal structure of *trans*-9-isopropyl-10-methyl-9,10-dihydroanthracene,  $C_{18}H_{20}$ , has been determined by the application of known molecular geometry, symmetry, Patterson map and structure factor calculations. Three-dimensional data were collected on a Datex-automated General Electric diffractometer with Ni-filtered Cu  $K\alpha$  radiation to a maximum value of  $2\theta$  of  $120^\circ$  ( $d_{min} = 0.9\text{ \AA}$ ). The crystals are tetragonal, space group  $I4_1md$ , with  $a = b = 23.1811$  (5) and  $c = 5.2156$  (7)  $\text{\AA}$ , and with eight molecules per unit cell. Each molecule lies on a mirror plane resulting in one half molecule per asymmetric unit. The data were collected as if the crystal were monoclinic; and the resulting four sets of equivalent data have been compared by the use of normal-probability plots. The coordinates of all atoms in the molecule, the isotropic temperature factors for the hydrogen atoms, and the anisotropic temperature factors for the carbon atoms were refined by the method of least squares. The final  $R$  index is 0.028. The structure is compared with that previously determined for *cis*-9-methyl-10-ethyl-9,10-dihydroanthracene [Bordner, Stanford & Zieger (1973), *Acta Cryst.* **B29**, 313–318].

### Introduction

This compound, 9-isopropyl-10-methyl-9,10-dihydroanthracene,  $C_{18}H_{20}$ , was prepared by Zieger & Gelbaum (1972) during a study of the alkylation of 10-alkyl-9,10-dihydroanthracenyl-lithiums with alkyl iodides. The structural assignments for *cis* and *trans* stereoisomers were determined by means of n.m.r. nuclear Overhauser enhancement experiments. This structure determination was undertaken to confirm this assignment.

### Experimental

The crystal used in this investigation was cut, from a longer crystalline needle of the presumed *trans*-isomer

supplied by Zieger & Gelbaum, to a size of  $0.2 \times 0.3 \times 0.5$  mm and was sealed in a thin-walled capillary to prevent slow decomposition in air. Precession and Weissenberg photographs of the crystal showed tetragonal symmetry and absence of  $hkl$  reflections with  $h+k+l$  odd and  $hhl$  reflections with  $2h+l \neq 4n$ , indicating that the space group was  $I4_1md$  or  $I42d$ . The unit-cell parameters were determined from the  $2\theta$  values for 24 reflections measured on a Datex-automated General Electric diffractometer with Ni-filtered Cu  $K\alpha$  radiation [ $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ ]. The resulting values for the unit-cell dimensions are:  $a = b = 23.1811$  (5),  $c = 5.2167$  (7)  $\text{\AA}$ . The calculated density of the crystal, assuming eight molecules per unit cell, is  $1.12 \text{ g cm}^{-3}$ .

Intensity data were collected by the  $\theta$ - $2\theta$  scan method on the diffractometer with Ni-filtered Cu  $K\alpha$  radiation. The scan speed was one degree in  $2\theta$  per min and background counts of 30 s were collected at

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mined by examining the Patterson function. With this information it was now possible to calculate structure factors for fifteen values (at intervals of 0.025) for the  $y$  coordinate of C(1), with the constraint that the molecule must avoid the twofold axes at  $y=0$  and  $y=\frac{1}{2}$ . A fixed isotropic temperature factor of  $3.6 \text{ \AA}^2$  was used for all atoms; and only the atoms of the anthracene system and only those reflections with  $\sin^2 \theta/\lambda^2 \leq 0.15$  (214 reflections) were included. The lowest  $R$  index was obtained for  $y[\text{C}(1)]=0.227$ .

### Refinement of the structure

All calculations were carried out on an IBM 370/155 computer with subprograms operating under the CRYM system [a modification of the CRYRM system for the IBM 7094 computer (Duchamp, 1964)]. The atomic scattering factor for C was taken from *International Tables for X-ray Crystallography* (1962), and for H from Stewart, Davidson & Simpson (1965). The

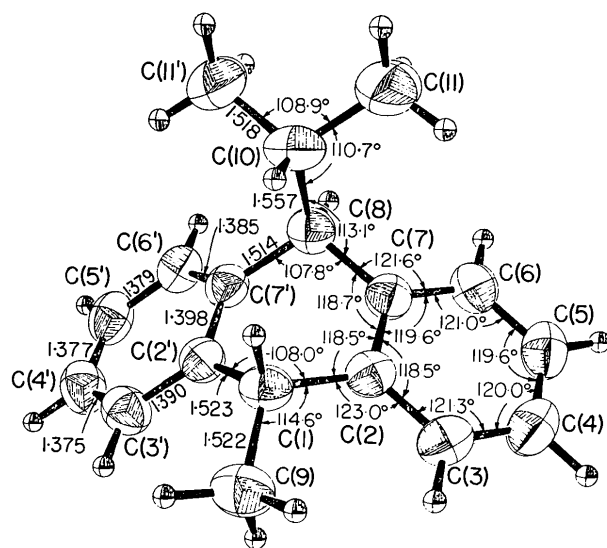


Fig. 2. Bond distances and angles for the carbon atoms of the molecule.

least-squares routine minimized the quantity  $\sum w(F_o^2 - F_c^2)^2$ . The weights,  $w$ , were set equal to  $1/\sigma^2(F_o^2)$ . The variance of the intensity was calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2,$$

where  $S$  is the total counts collected during the scan,  $B_1$  and  $B_2$  are the numbers of counts collected for each background,  $\alpha$  is the ratio of scan time to total background time, and  $d$  is an empirical constant taken to be 0.02.

After several cycles of least-squares refinement of the positions, as determined above, for the atoms of the anthracene systems, a Fourier map revealed the positions of the remaining carbon atoms, those of the *trans*-related methyl and isopropyl groups. Coordinates of those hydrogen atoms at C(1), C(3), C(4), C(5), C(6), C(8) and C(10), whose positions are fixed by the geometry of the molecule, were calculated. Following several additional cycles of least-squares, difference Fourier maps were calculated in the planes where the remaining methyl hydrogen atoms should be located. Their coordinates were easily found in these plane sections. In the final stages of refinement the positional parameters for all atoms were included in one matrix; and the temperature factors, anisotropic for carbon atoms and isotropic for the hydrogens, the scale factor and a secondary extinction factor were included in a second matrix. The expression used for the secondary extinction correction is  $F_{\text{corrected}}^2 = (F_{\text{cal}})^2/[1 + g\beta(F_{\text{cal}})^2]$  (Larson, 1967); and the final value obtained for  $g$  is  $4.6(2) \times 10^{-6}$ . The final  $R$  index,  $\sum ||F_o| - |F_c||/\sum |F_o|$ , is 0.028; the weighted  $R$  index,  $\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4$ , is 0.002; the 'goodness-of-fit',  $[\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$  (where  $m$  is the number of observations and  $s$  is the number of parameters being refined), is 2.3. The observed and calculated structure factors,  $F_o$  and  $F_c$ , and the phase angles,  $\phi$ , are listed in Table 1.

The final coordinates and anisotropic temperature factors for the carbon atoms and their standard deviations, calculated from the least-squares residuals, are given in Table 2. The coordinates and isotropic temperature factors for the hydrogen atoms and their standard deviations are given in Table 3. The shifts calculated for the parameters in the final cycle of least-

Table 2. Carbon atom parameters and their standard deviations

The values have been multiplied by  $10^5$ . The temperature factor is in the form

$$T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	$x$	$y$	$z$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
C(1)	0	23251 (11)	18800	216 (6)	153 (5)	3180 (122)	0	0	-34 (43)
C(2)	5314 (7)	24003 (7)	1972 (68)	185 (4)	162 (4)	3142 (84)	-1 (6)	-177 (31)	-227 (32)
C(3)	10123 (9)	20440 (8)	3635 (72)	226 (4)	191 (4)	3934 (96)	56 (7)	-136 (37)	-126 (37)
C(4)	14712 (8)	21054 (9)	-12848 (71)	195 (5)	245 (5)	4949 (118)	85 (9)	-176 (38)	-454 (41)
C(5)	14596 (9)	25261 (10)	-31482 (69)	174 (4)	274 (5)	4607 (110)	-24 (8)	173 (38)	-515 (41)
C(6)	9914 (9)	28908 (9)	-33141 (69)	192 (4)	221 (5)	3774 (92)	-56 (7)	-40 (32)	-42 (36)
C(7)	5275 (7)	28354 (7)	-16580 (66)	170 (4)	168 (4)	3375 (90)	-23 (6)	-84 (32)	-180 (32)
C(8)	0	32168 (11)	-18837 (77)	197 (6)	180 (5)	3061 (128)	0	0	177 (45)
C(9)	0	17807 (15)	35088 (89)	293 (8)	204 (7)	4358 (157)	0	0	345 (54)
C(10)	0	37266 (11)	597 (98)	296 (8)	150 (6)	4819 (174)	0	0	-60 (51)
C(11)	5326 (13)	40990 (12)	-2930 (102)	270 (6)	224 (5)	13017 (256)	-34 (10)	-553 (65)	-1185 (64)

squares were all less than one fifth of the standard deviations.

Table 3. *Hydrogen atom parameters and their standard deviations*

The values for the coordinates have been multiplied by  $10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(12)	0	2663 (9)	3041 (53)	3.5 (0.5)
H(13)	1026 (7)	1743 (7)	1729 (39)	4.1 (0.4)
H(14)	1813 (8)	1842 (7)	-1166 (43)	5.7 (0.5)
H(15)	1772 (8)	2571 (8)	-4386 (48)	5.6 (0.5)
H(16)	979 (7)	3189 (7)	-4681 (41)	4.4 (0.4)
H(17)	0	3392 (9)	-3614 (57)	3.9 (0.6)
H(18)	0	3545 (11)	1779 (65)	5.4 (0.7)
H(19)	0	1434 (11)	2286 (58)	5.0 (0.7)
H(20)	381 (8)	1758 (9)	4594 (47)	6.8 (0.6)
H(21)	531 (10)	4423 (12)	857 (46)	8.5 (0.7)
H(22)	888 (10)	3867 (11)	-143 (73)	10.2 (0.7)
H(23)	507 (15)	4238 (15)	-2220 (83)	13.7 (1.1)

### Description of the structure

The bond distances and angles involving the carbon atoms are shown in Fig. 2. Distances and angles involving hydrogen atoms are listed in Table 4. The standard deviations in the atomic coordinates (Tables 2 and 3) correspond to positional uncertainties of approximately 0.003 Å for the carbon atoms and 0.03 Å for the hydrogen atoms. The standard deviations are thus expected to be about 0.004 Å for C-C distances, 0.03 Å for C-H distances, about 15' for C-C-C angles, 1° for C-C-H angles and about 2° for H-C-H angles.

An attempt to interpret the anisotropic temperature parameters of the carbon atoms in terms of rigid-body motion (Schomaker & Trueblood, 1968) proved to be unsuccessful. The root-mean-square deviations between the observed values of  $U_{ij}$  and those calculated

Table 4. *Bond distances and angles involving hydrogen atoms*

H(12)-C(1)	0.99 Å	H(12)-C(1)-C(2)	105	H(18)-C(10)	0.99 Å	H(18)-C(10)-C(8)	106
H(13)-C(3)	1.00	H(12)-C(1)-C(9)	108	H(19)-C(9)	1.03	H(18)-C(10)-C(11)	111
H(14)-C(4)	1.00	H(13)-C(3)-C(2)	119	H(20)-C(9)	1.05	H(19)-C(9)-C(1)	108
H(15)-C(5)	0.98	H(13)-C(3)-C(4)	120	H(21)-C(11)	0.96	H(19)-C(9)-H(20)	107
		H(14)-C(4)-C(3)	121			H(20)-C(9)-C(1)	110
		H(14)-C(4)-C(5)	119			H(20)-C(9)-H(20')	114
		H(15)-C(5)-C(4)	122			H(21)-C(11)-C(10)	111
		H(15)-C(5)-C(6)	119			H(21)-C(11)-H(22)	112
						H(21)-C(11)-H(23)	111
H(16)-C(6)	0.99	H(16)-C(6)-C(5)	120	H(22)-C(11)	0.99	H(22)-C(11)-C(10)	111
		H(16)-C(6)-C(7)	119			H(22)-C(11)-H(23)	107
H(17)-C(8)	0.99	H(17)-C(8)-C(7)	108	H(23)-C(11)	1.06	H(23)-C(11)-C(10)	104
		H(17)-C(8)-C(10)	106				

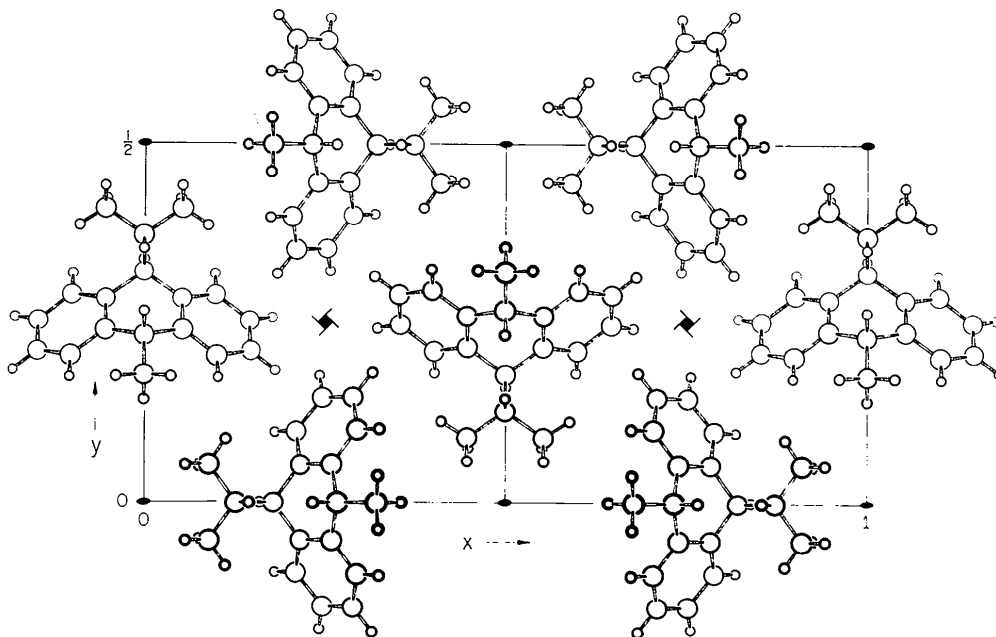


Fig. 3. A view down the *c* axis showing the packing of the molecules in the crystal.

on the assumption of rigid-body motion for two groups of atoms are as follows:

Atoms included in the analysis	r.m.s. $\Delta U_{ij}(\text{\AA}^2)$
C(1)-C(10), C(2')-C(7')	0.0026
C(1)-C(8), C(2')-C(7')	0.0023.

Since the average estimated standard deviation of the parameters  $U_{ij}$  for the atoms is about  $0.0014 \text{\AA}^2$ , it is reasonably evident that neither of the above groups can be adequately represented as a rigid body.

The equation of the least-squares plane through the benzene ring and the deviations of the individual atoms

from the plane are given in Table 5. The ring shows a slight, but significant, deviation from planarity.

A view down the  $c$  axis showing the packing of the molecules in the unit cell is given in Fig. 3. There are no short contacts between the molecules. The shortest carbon-to-hydrogen intermolecular distance is  $2.93 \text{\AA}$  between H(14) of the base molecule and C(5) of the molecule in equivalent position  $\frac{1}{2}-y, x, z-\frac{1}{4}$ . The shortest hydrogen-to-hydrogen intermolecular distance is  $2.60 \text{\AA}$  between H(16) of the base molecule and H(13) of the molecule in the equivalent position  $y, \frac{1}{2}-x, z-\frac{3}{4}$ .

A comparison of this structure with that found for

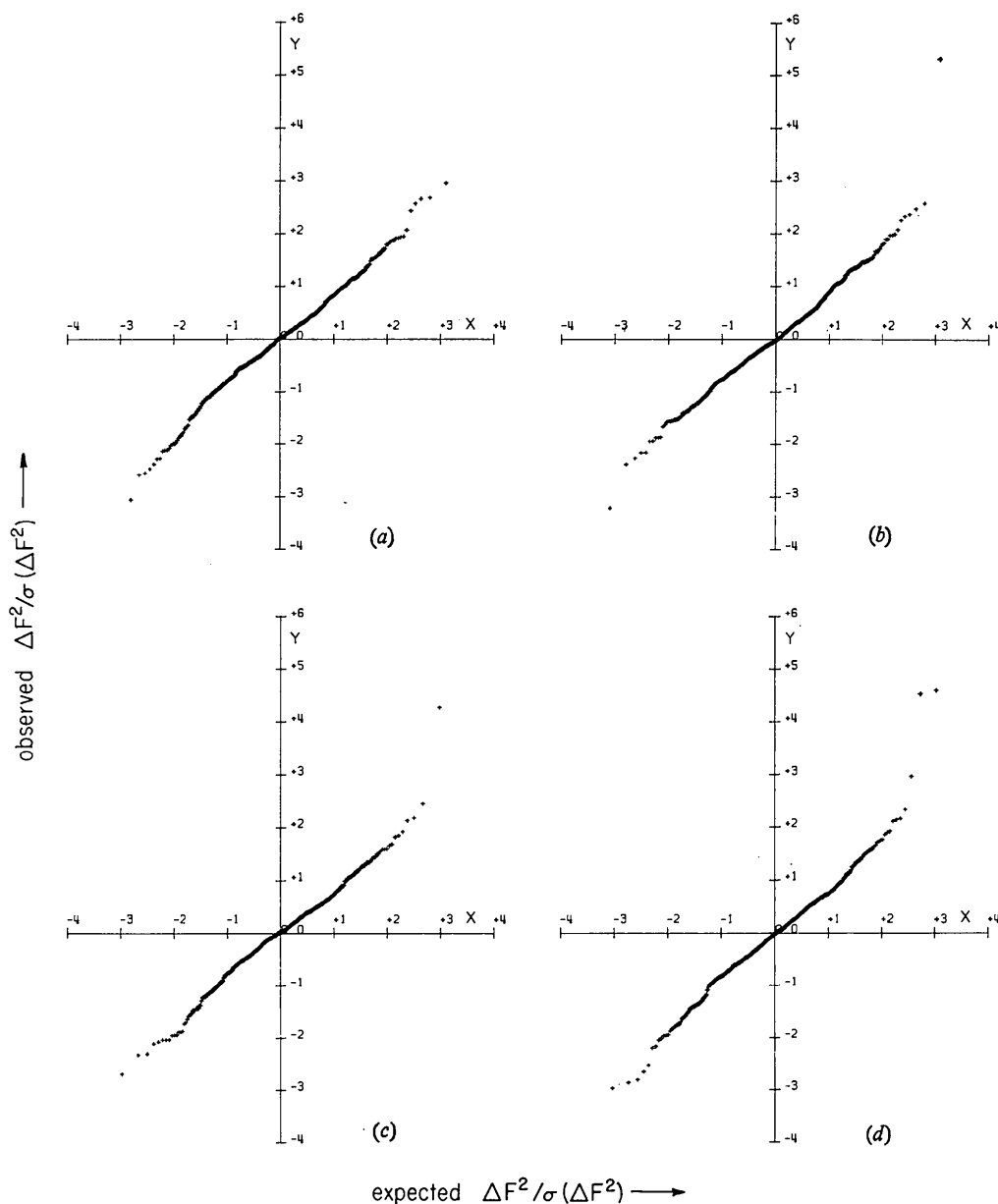


Fig. 4. Normal probability plots for the differences between single and mean observed structure factors for the four equivalent sets of data: (a)  $hkl$ ,  $h \geq k$ ; (b)  $hkl$ ,  $k > h$ ; (c)  $hkl$ ,  $h \geq k$ ; (d)  $hkl$ ,  $k > h$ .

Table 5. Least-squares plane of the benzene ring and atomic deviations from the plane

Coefficients are direction cosines relative to the crystallographic axes. Atoms C(1) and C(8) were not included in the calculations of the least-squares plane.

Plane through C(2), C(3), C(4), C(5), C(6) and C(7)  
 $0.4335X + 0.6349Y + 0.6396Z = 4.143$

	Deviation
C(1)	-0.093 Å
C(2)	-0.010
C(3)	0.004
C(4)	0.006
C(5)	-0.009
C(6)	0.002
C(7)	0.007
C(8)	-0.037

*cis*-9-methyl-10-ethyl-9,10-dihydroanthracene (Bordner *et al.*, 1973) reveals some relative effects of *cis* and *trans* substituents. Within the anthracene skeleton the corresponding interatomic distances for the two structures display excellent agreement. The bond angles, however, show marked differences in the central ring. This distortion can easily be seen in the cross-ring distance, C(1)···C(8), which is 2.85 Å in the *trans* form and 2.95 Å in the *cis*-substituted molecule, and in the intraring bond angles at C(1) and C(8), which average 108° and 112° in the *trans* and *cis* forms

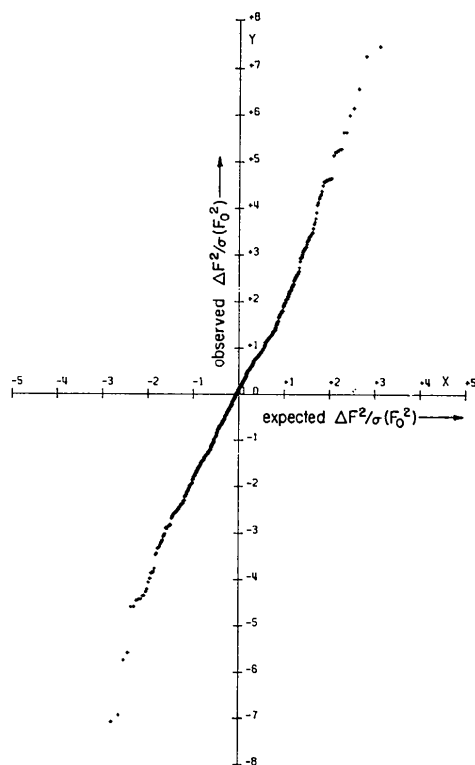


Fig. 5. Normal probability plot for the difference between the observed and calculated structure factors.

respectively. The flattening of the central ring of the *cis* form is also evident in a dihedral angle of 152° between the planes of the benzene rings, whereas this angle for the *trans* form measures only 129°.

#### Statistical analysis of the intensity data

The four sets of equivalent data which had been collected were separated into the following classes: (a)  $hkl$ ,  $h \geq k$ ; (b)  $hkl$ ,  $k > h$ ; (c)  $\bar{h}kl$ ,  $h \geq k$ ; and (d)  $\bar{h}kl$ ,  $k > h$ . Normal probability plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) are shown in Fig. 4 for each of these groups. The quantities plotted are the ordered ratios  $\Delta_i/\sigma_i$ , where  $\Delta_i$  is the difference be-

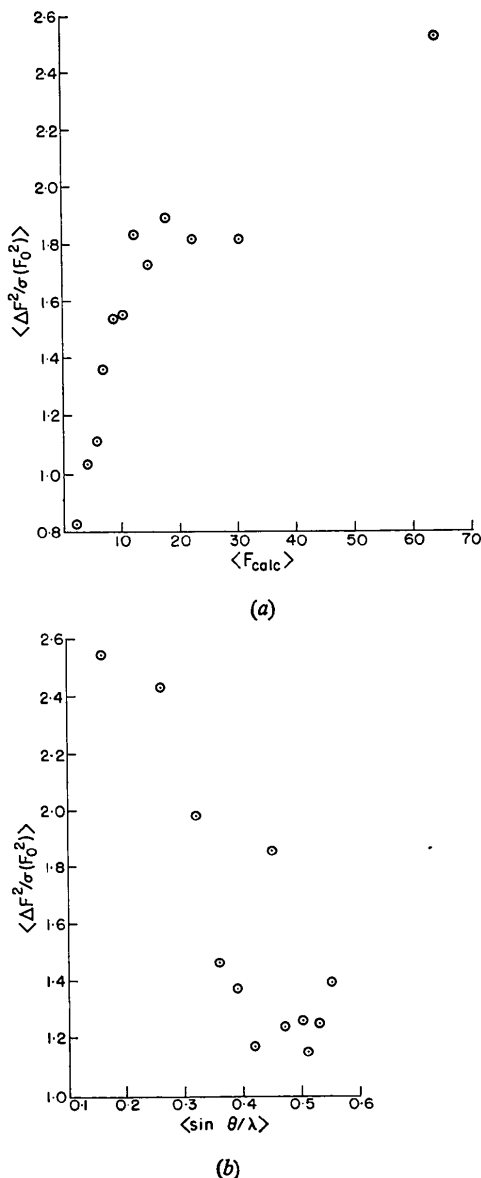


Fig. 6. The distribution of the average of  $(F_0^2 - F_c^2)/\sigma(F_0^2)$  versus (a) average  $F_c$  and (b) average  $\sin \theta/\lambda$ .

tween the value of an observation of a given set and the mean value from all four sets and  $\sigma_i$  is the estimated standard deviation of this difference. These plots are very nearly linear with unit slope and zero intercept indicating that the differences are normally distributed and that the standard deviations have been correctly estimated.

In Fig. 5 a normal probability plot is given for the differences  $F_o^2 - F_c^2$ . This plot is approximately linear, but its slope is about 2. This is in agreement with the final 'goodness-of-fit' of 2.3.

In Fig. 6 the average values of  $\Delta(F^2)/\sigma(F_o^2)$  have been plotted *versus* (a) average  $F_c^2$  and (b) average  $\sin \theta/\lambda$ . The averages were computed over intervals which contained 50 reflections. The shapes of these plots can be explained by observing that in averaging the equivalent reflections their weights are added together. This effectively reduces the dominant term in the variance of the intensity of strong reflections (which also primarily occur at low angles) to  $(0.01 S)^2$ . Since this factor is intended to account for errors which vary in proportion to the intensity (Busing & Levy, 1957), this reduction by a factor of 4 is probably unjustified.

The author is grateful to Miss Lillian Casler who prepared many of the drawings and to Dr G. G. Christoph who provided the computer program for

performing the statistical analysis of the data and for plotting the results. Figs. 2 and 3 were drawn using *ORTEP* (Johnson, 1965).

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## Détermination de la Configuration Moléculaire de la Dibromo-Vobtusine

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(Reçu le 12 juin 1973, accepté le 27 juin 1973)

Crystals of dibromovobtusine,  $\text{Br}_2\text{C}_{43}\text{H}_{48}\text{O}_6\text{N}_4$ , are monoclinic, space group  $P2_1$ , with cell dimensions:  $a = 13.80$ ,  $b = 12.86$ ,  $c = 11.86$  Å,  $\beta = 107.8^\circ$ , and two molecules per cell. 1900 observed reflexions were collected by the multiple-film equi-inclination Weissenberg technique, and the crystal structure was solved by the heavy-atom method. The molecular structure consists of an asymmetric indolic dimer with a hydroxyl group bonded to C(2). There is an internal hydrogen bond between the indole N atom and the carbonyl O atom, and short intermolecular bonds between bromine atoms and methyl groups, and between a methylene group and a carbonyl group.

### Introduction

La vobtusine est un alcaloïde dérivé de l'indole, dimère asymétrique, du type bis-aspidospermine. Isolée pour la première fois par Janot & Goutarel (1955) dans des espèces du genre *Voacanga* et reconnue comme l'un des alcaloïdes majeurs du *Callichilia subsessilis* Stapf. (Goutarel, Rassat, Plat & Poisson, 1959), sa formule est restée longtemps incertaine. Elle résiste à tous les réactifs de coupure et l'analyse chimique donne peu d'informations.

En utilisant des méthodes physiques et plus particulièrement la spectrométrie de masse à haute résolu-

tion, Poisson, Plat, Budzikiewicz, Durham & Djerassi (1966) parvenaient à établir la formule brute exacte:  $\text{C}_{43}\text{H}_{48}\text{O}_6\text{N}_4$  et à préciser la constitution des deux parties A et B de la molécule. Peu après, Gorman, Agwada, Hesse, Renner & Schmidt (1966) montraient que la vobtusine devait comporter l'enchaînement de la béninine, alcaloïde indolique monomère, trouvé à côté de la vobtusine dans l'*Hedranthera (Callichilia) barteri*, espèce voisine du *C. subsessilis*. Ils étaient conduits à proposer pour la vobtusine deux formules dont l'une était compatible avec les conclusions de Poisson *et al.* (1966). On pouvait alors retenir la formule suivante comme hypothèse de travail: