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The Crystal Structure of Iodinin

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A crystal-structure analysis of iodinin, $C_{12}H_8N_2O_4$, has been carried out at $-160°C$ and at room temperature. The crystals are monoclinic, space group $P2_1/a$, with (at $-160°C$) $a=15\cdot634$, $b=5\cdot028$, $c=6\cdot037$ Å, $\beta=91\cdot00°$, $Z=2$. The structure was determined entirely by symbolic-addition methods and refined by block-diagonal least-squares to a final R index of 0·060. The structure consists of endless ribbons of nearly coplanar molecules, extended in the directions $\langle 011 \rangle$. Adjacent molecules in a ribbon are linked by the intermolecular branches of bifurcated hydrogen bonds. The binding force is sufficient to cause a non-bonded oxygen–oxygen contact of 2·591 Å.

Introduction

The X-ray crystal structure analysis of myxin (I) has revealed an unexpectedly short intermolecular distance, a phenomenon tentatively attributed to the formation of bifurcated hydrogen bonds (Hanson, 1968). The intermolecular branches of these bonds join adjacent molecules together as weak dimers (II) in which the innermost oxygen atoms, although not bonded to each other, are constrained to lie only 2·577 Å apart. (The dimerization must be described as 'weak' in recognition of the fact that it occurs for only one of the two independent pairs of molecules in the structure; for the other pair the reduction in energy offered by dimerization is presumably less than that realized by more efficient packing.)

It was considered that the crystal structure of iodinin (III) might present a further example of intermolecular attraction by bifurcated hydrogen bonds. However, iodinin has the opportunity to form such bonds on both sides, and thus polymerization, rather than dimerization, is to be expected. The expectation is strengthened by the high density and sparing solubility of the material. The crystal structure analysis was undertaken in order to investigate this point and to provide data for the further study of the bifurcated hydrogen bond.
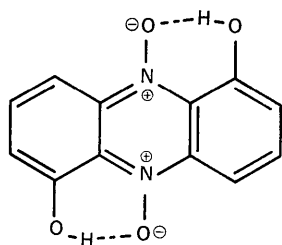
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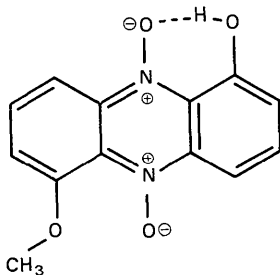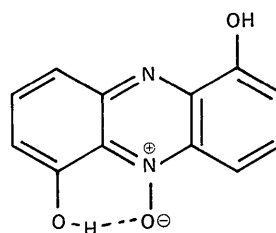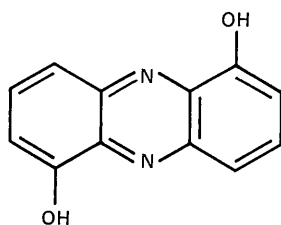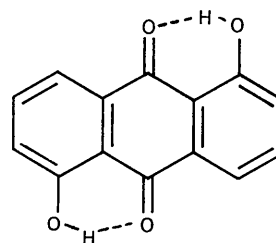
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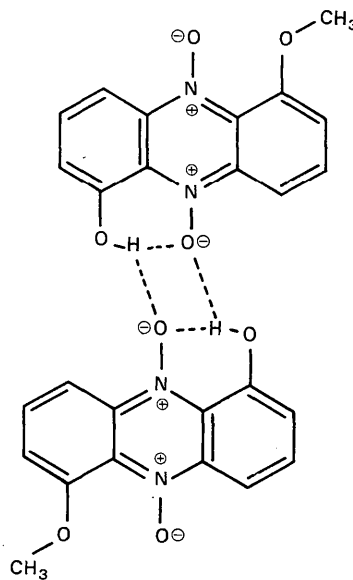
II

III

IV

V

VI

The first available sample of iodinin proved ultimately to be unsuitable. A single crystal was selected from it, and the structure analysis was carried out in routine fashion both at − 160 °C and at room temperature. At the conclusion, however, it became clear that the material was not pure, molecules of iodinin having been replaced in significant proportions by the related molecule IV, or V, or perhaps both. As the sample was of biosynthetic origin, it was not surprising that such impurities were present. Gerber & Lechevalier (1965) have shown that bacterial action can transform III to V, and V to III, with IV as an intermediate in each case. The ability of these impurities to form solid solutions with iodinin, and the sparing solubility of iodinin itself, presumably make their detection and removal rather difficult. The results of the investigation of this material are obviously of questionable value, and when the presence of the impurity was discovered attention was directed to procuring a sample of pure material. Such a sample was obtained from Hoffmann–Laroche Inc., through the courtesy of Dr W. Leimgruber. This material proved difficult to crystallize suitably, as only very thin plates of irregular outline could be grown. A marginally acceptable specimen was nevertheless selected, and the analysis was repeated both at − 160 °C and at room temperature.

Experimental

The crystal is monoclinic, and the space group is $P2_1/a$. (The systematic absences are found, from Weissenberg and precession photographs, to be $h0l$ for h odd; $0k0$ for k odd.) The formula is $C_{12}H_8N_2O_4$ and the formula weight is 244·2. The density of the material indicates that $Z=2$; the molecule therefore makes use of a centre of symmetry. Further crystal data and summaries of the several crystal-structure analyses are given in Table 1.

The cell constants and the relative intensities were measured with a four-circle diffractometer equipped with a scintillation counter. Copper $K\alpha$ radiation was used, with a $K\beta$ filter and a pulse-height analyser. Intensities were measured with the θ–2θ scan method. Absorption corrections were considered to be unnecessary and were not made. For the low-temperature studies the specimen was maintained at − 160 °C by immersion in a stream of cold gaseous nitrogen which was itself surrounded by an envelope of dry nitrogen at room temperature.

The original sample consisted of deep red fragments of no obvious habit. The specimen used was of approximate dimensions 0·2 × 0·2 × 0·1 mm. The second sample, of pure material, crystallized in extremely thin plates with principal faces {100} and no other obvious faces. The material was deep red by transmitted light, but the predominant faces displayed a pronounced metallic sheen when viewed by reflected light. The specimen used was approximately 0·1 × 0·1 × 0·02 mm in size.

Structure determination

The structure was initially determined from the low-temperature data set derived from the first (impure)

Table 1. *Summary of crystal data and refinement*

Quantity (units)	Ordered structure $-160\,^\circ$C	Ordered structure Room temperature	Disordered structure $-160\,^\circ$C	Disordered structure Room temperature
a (Å)	$15\cdot634\pm0\cdot010$	$15\cdot870\pm0\cdot010$	$15\cdot782\pm0\cdot010$	$16\cdot035\pm0\cdot010$
b	$5\cdot028\pm0\cdot003$	$5\cdot079\pm0\cdot003$	$5\cdot038\pm0\cdot003$	$5\cdot089\pm0\cdot003$
c	$6\cdot037\pm0\cdot004$	$6\cdot023\pm0\cdot004$	$5\cdot962\pm0\cdot004$	$5\cdot952\pm0\cdot004$
β (°)	$91\cdot00\pm0\cdot05$	$90\cdot50\pm0\cdot05$	$90\cdot86\pm0\cdot05$	$90\cdot31\pm0\cdot05$
V (Å^3)	$474\cdot5$	$485\cdot5$	$474\cdot0$	$485\cdot7$
D_m (g.cm^{-3})	—	$1\cdot64\pm0\cdot03$	—	$1\cdot63\pm0\cdot01$
D_x (g.cm^{-3})	$1\cdot71$	$1\cdot67$	$1\cdot71$	$1\cdot67$
Accessible reflexions	1051	1081	1053	1087
Observed reflexions	682	516	930	894
Reflexions given zero weight	34	27	8	13
Reflexions corrected for extinction	0 (strongest reflexion given zero weight)	0 (strongest reflexion given zero weight)	10 (Max. correction 20% of F_o)	11 (Max. correction, 22% of F_o)
Weighting scheme	$w = w_1 w_2$ where $w_1 = F_o/13\cdot14$ for $F_o\leq13\cdot14$ $= 13\cdot14/F_o$ for $F_o > 13\cdot14$ $w_2 = 1\cdot41 \sin\theta$ for $\sin\theta\leq0\cdot707$ $= 0\cdot707/\sin\theta$ for $\sin\theta > 0\cdot707$	$w = w_1 w_2$ where $w_1 = F_o/12$ for $F_o\leq12$ $= 12/F_o$ for $F_o > 12$	$w = w_1 w_2$ where $w_1 = F_o/4\cdot0$ for $F_o\leq4\cdot0$ $= 4\cdot0/F_o$ for $F_o > 4\cdot0$ $w_2 = 3\cdot96 \sin^3\theta$ for $\sin\theta\leq0\cdot632$ $= 1$ for $\sin\theta > 0\cdot632$	$w = w_1 w_2$ where $w_1 = F_o/4\cdot0$ for $F_o\leq4\cdot0$ $= 4\cdot0/F_o$ for $F_o > 4\cdot0$ $w_2 = 3\cdot96 \sin^3\theta$ for $\sin\theta\leq0\cdot632$ $= 1$ for $\sin\theta > 0\cdot632$
Mean e.s.d. of coordinates				
Non-hydrogen atoms	$0\cdot0025$	$0\cdot0050$	$0\cdot0013$	$0\cdot0022$
Hydrogen atoms	$0\cdot035$	$0\cdot045$	$0\cdot023$	$0\cdot030$
Final R index ($R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, observed reflexions only)	$0\cdot060$	$0\cdot075$	$0\cdot051$	$0\cdot052$

sample. The solution was obtained entirely by symbolic addition procedures, using the Σ_2 relationship (Karle & Karle, 1966). The K curve, the E values and the listing of Σ_2 triplets were obtained with the aid of the programs of Hall (Ahmed, Hall, Pippy & Huber, 1966). The signs were generated manually. Eventually the signs of 112 reflexions were defined in terms of two symbols, so that four sets of signs had to be considered. As the structure cannot have significant electron density at a centre of symmetry, each set was first evaluated in terms of the density at the origin of the corresponding E map. One set was seen to have an unacceptably high origin peak (and was discarded for this reason), two had moderate peaks, and one had practically none. The complete E map was calculated first for the last set which, however, turned out to be wrong. (The map indicated clearly a plausible but completely fictitious organic molecule, quite unlike iodinin. Disinterested curiosity prompted an attempt to refine this obviously wrong structure. Reassuringly, no significant refinement was achieved.) The E map for one of the two remaining sets indicated a meaningless collection of peaks, but that of the other showed clearly all the non-hydrogen atoms in the structure.

Refinement was begun with Fourier syntheses and completed with block-diagonal least-squares analysis. The least-squares program used was that of Ahmed (Ahmed *et al.*, 1966). The quantity minimized was $\Sigma\, w(F_o - F_c)^2$. The thermal motion of the hydrogen atoms (located initially in a difference map) was assumed to be isotropic and that of the other atoms anisotropic. The scattering-factor curves used were those of Hanson, Herman, Lea & Skillman (1964). Further details of this and subsequent refinement procedures are given in Table 1. Extinction corrections were applied to the most intense reflexions of the data sets from the impure material, as indicated. No such correction was applied to the data sets from the pure material, but the most intense reflexion in each set was assigned zero weight. Other reflexions given zero weight were of low intensity and, because of poor agreement with calculated values, were assumed to be in error. The various weighting schemes indicated were selected to remove strong dependence of $w(F_o - F_c)^2$ on F_o and $\sin\theta$ (Cruickshank, 1965). It has been the authors' experience that such dependence occurs with unit weights or with weights inversely proportional to the variances of F_o. The reason, presumably, is that the residuals represent not only random errors in F_o, but also systematic errors in F_c, resulting from the use of an imperfect and oversimplified model. Such errors can be expected to be dependent on amplitude and Bragg angle.

When the refinement appeared to be complete a difference map was computed. A section of this map in the mean plane of the molecule is shown in Fig. 1. The peaks which occur at the mid points of all the bonds in the phenazine nucleus resemble those frequently observed in low-temperature studies of organic molecules, and presumably represent bonding

electrons. However, the large trough in the neighbourhood of the oxygen atom O(9) is a remarkable and unexpected feature. It represents a deficiency of perhaps one electron for this atom. The only reasonable explanation for the deficiency seems to be that the structure is disordered as suggested in the introduction. Some molecules of iodinin are replaced by the molecules IV or V, but the only obvious change in the average structure is the incomplete occupancy of the site of the oxygen atom involved. The refinement was continued with the occupation factor of this atom treated as a refinable parameter. From an initial value of 0·90 the factor rapidly converged to 0·864 ($\sigma = 0.007$). As might be expected, there were accompanying substantial changes in the thermal parameters of O(9), but changes in the other structural parameters were slight. Finally, a further cycle of refinement was initiated with the occupation factor for O(9) arbitrarily reduced to 0·80. The value resulting from this cycle was 0·863. It is concluded that the occupation factor indicated by the least-squares refinement may be treated with some confidence.

The structure corresponding to the set of data obtained at room temperature was refined in like manner, but with the occupation factor of O(9) fixed at 0·864.

While the progress of these refinements was satisfying from a methodological point of view, it was obvious that the results obtained for this disordered, average structure (specifically, the intermolecular distances involving oxygen atoms) were of little general interest. Attention was therefore directed to the determination of the structure of the pure material. The sets of data obtained from the very small specimen of this material were by no means as accurate or as complete as one might wish. Many reflexions were too weak to
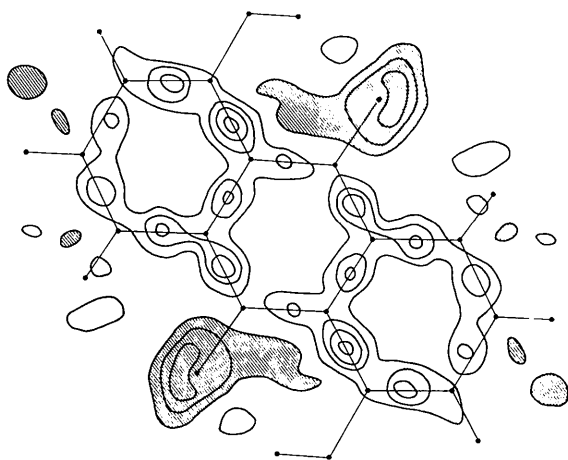
Fig. 1. A section, in the molecular plane, of the three-dimensional difference synthesis. [Disordered structure at $-160\,^{\circ}C$, before adjustment of occupation factor of O(9)]. Contours are at intervals of 0·1 e.Å^{-3}, with the zero contour omitted. The shaded areas are negative regions bounded by the contour at -0.1 e.Å^{-3}.

Table 2(a). *Final parameters and e.s.d.'s of non-hydrogen atoms* $\pm(x,y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,z)$

$$TF = \exp\{-2\pi^2(U_{11}a^{*2}h^2 + 2U_{12}a^{*}b^{*}hk + 2U_{13}a^{*}c^{*}hl + U_{22}b^{*2}k^2 + 2U_{23}b^{*}c^{*}kl + U_{33}C^{*2}l^2)\}$$

B_i are the equivalent isotropic B values in the directions of the principal axes of the vibration ellipsoids.

	x (×10⁵)	y (×10⁵)	z (×10⁵)	U_{11} (Å²×10⁴)	U_{12} (Å²×10⁴)	U_{13} (Å²×10⁴)	U_{22} (Å²×10⁴)	U_{23} (Å²×10⁴)	U_{33} (Å²×10⁴)	B_1 (Ų)	B_2 (Ų)	B_3 (Ų)
C(1)	−19307 (18)	35924 (64)	15765 (48)	122 (12)	26 (12)	−24 (11)	125 (14)	−21 (11)	220 (14)	0·77	1·08	1·85
C(2)	−18589 (17)	17536 (66)	33250 (45)	105 (12)	−31 (13)	16 (10)	219 (15)	13 (11)	151 (13)	0·75	1·12	1·87
C(3)	−12016 (17)	34406 (58)	34406 (44)	102 (12)	−60 (13)	10 (10)	93 (14)	16 (12)	130 (13)	0·46	0·96	1·55
C(4)	−5855 (16)	−708 (66)	16940 (47)	113 (12)	4 (13)	−3 (10)	114 (12)	−11 (11)	176 (13)	0·72	0·89	1·41
N(5)	736 (14)	18469 (49)	16986 (37)	118 (11)	−25 (11)	−22 (8)	97 (12)	33 (10)	133 (13)	0·69	0·79	1·41
C(6)	6703 (17)	18240 (60)	442 (37)	125 (11)	11 (11)	8 (8)	130 (14)	10 (11)	146 (10)	0·51	1·18	1·23
C(7)	13483 (17)	36690 (61)	1010 (46)	128 (12)	32 (13)	13 (11)	176 (13)	−17 (12)	159 (13)	0·72	1·00	1·59
O(8)	−11497 (12)	17457 (43)	51609 (32)	130 (9)	−25 (11)	−10 (8)	179 (11)	−11 (10)	172 (12)	0·88	1·05	1·86
O(9)	1468 (13)	36188 (46)	32532 (33)	178 (10)	10 (9)	8 (7)	204 (10)	10 (9)	196 (9)	0·79	1·40	2·37

be observed, and of those observed many were close to the threshold intensity. Nevertheless, the refinements proceeded fairly smoothly. A tendency of the parameters to oscillate was checked at one point by the use of convergence acceleration factors of 0·5, but this practice was discontinued for the final cycles. In these refinements, as in the others summarized in Table 1, none of the shifts indicated in the final cycle exceeded ⅓ of the corresponding estimated standard deviations. The final parameters for the low-temperature ordered structure are given in Table 2.

Table 2(b). *Final parameters and e.s.d.'s of hydrogen atoms*

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B (Å^2)
H(1)	−2439	4838	1444	0·4
	25	88	65	0·8
H(2)	−2294	1811	4552	−1·4
	19	67	51	0·5
H(7)	1403	−4692	1284	−1·5
	19	65	51	0·5
H(8)	−740	−2688	4992	0·2
	25	85	63	0·8

Table 3. *Observed and calculated structure factors* ($\times 10$)

An asterisk following $10F_o$ indicates that the reflexion was too weak to be observed; the estimated threshold value is given instead. A minus sign preceding $10F_o$ indicates that the reflexion was omitted from the least squares analysis.

Thermal motion and correction of bond lengths

An analysis in terms of rigid-body modes, in the manner described by Cruickshank (1956), was attempted for the low-temperature ordered structure. For the 14-atom phenazine nucleus only small librations, of maximum root mean square amplitude $1\cdot7°$, were indicated. Presumably because of experimental errors, or possibly the presence of non-rigid modes, a very small *negative* r.m.s. amplitude (about $1\cdot3°$) was indicated for one axis. It was concluded that rigid-body libration of the phenazine nucleus was too small to warrant any correction of bond lengths. An analysis including the oxygen atoms indicated librations of as much as $2\cdot8°$, demonstrating the occurrence of non-rigid motion (probably wagging) of the C–O and N–O bonds. These bond distances have therefore been corrected for riding motion (Busing & Levy, 1964). Where appropriate, intermolecular distances have been corrected, assuming that the thermal motions of the atoms concerned are uncorrelated. In some cases an upper limit (assuming correlated antiparallel displacements) is given also (Busing & Levy, 1964). [It must be emphasized that such procedures are only as meaningful as the unverifiable assumptions on which they are based. The intention here is to provide some idea of the uncertainties involved in the estimates of these distances, and to facilitate comparison with the structure of myxin, for which thermal motions of similar types and magnitudes were deduced, and corresponding 'corrections' applied (Hanson, 1968).]

Assessment of results

The agreement between observed and calculated structure amplitudes is reasonable for all analyses, and there can be no doubt as to the essential correctness of the proposed structures. Values of F_o and F_c for the low-temperature ordered structure (henceforth considered to be the definitive structure) are given in Table 3. The corresponding data for the other three structures have been placed in the Depository for Unpublished Data, National Science Library, National Research Council of Canada, Ottawa. Canada, and copies are available to interested persons.

The final difference syntheses for the several analyses reveal no detail inconsistent with the proposed structures. For the disordered structures the residual features are physically reasonable (bonding electrons and the like). This claim cannot be made for the ordered structures (for which, however, the data sets are less complete and accurate). For the low-temperature ordered structure the residual electron density lies between the limits $\pm 0\cdot25$ e.Å^{-3}.

The mean e.s.d.'s of atomic position have been listed in Table 1. These values are presumably inappropriate for the disordered structures (because a unique structure is not represented) and optimistic for the ordered structures (because the data sets are somewhat incomplete). It is therefore rather surprising to find that within the limits of accuracy implied by these values, the bond lengths found in the four structures agree very well. A comparison of bond lengths (generally uncorrected for thermal motion) is given in Table 4. Differences between values found for ordered and disordered structures at a given temperature are significant only for the N–O bond. Differences between values found for the same material at different temperatures (and thus presumably indicative of experimental error) are not significant. It is true that the difference *becomes* significant for the C–O bond in the ordered structure when reasonable corrections are made for thermal motion. However, the room-temperature ordered structure has been determined with only 45% of the accessible data, and the discrepancy, although apparently significant at the $0\cdot1\%$ level, should probably be discounted.

Discussion

Some details of the low-temperature ordered structure are illustrated in Figs.2,3, and 4. The bond lengths agree well with those found in other compounds (in-

Table 4. *Comparison of bond lengths for the several structures*

Bond lengths given in parentheses have been corrected for riding motion.

Bond length (e.s.d.) (Å)

Bond		Ordered structure $-160°C$	Ordered structure Room temperature	Disordered structure $-160°C$	Disordered structure Room temperature
C(1)	C(2)	1·406 (4)	1·394 (7)	1·406 (2)	1·402 (3)
C(2)	C(3)	1·368 (4)	1·367 (7)	1·374 (2)	1·367 (3)
C(3)	C(4)	1·441 (4)	1·431 (6)	1·440 (2)	1·437 (3)
C(4)	N(5)	1·364 (4)	1·366 (6)	1·365 (2)	1·364 (3)
N(5)	C(6)	1·379 (4)	1·375 (6)	1·376 (2)	1·373 (3)
C(6)	C(7)	1·409 (4)	1·399 (7)	1·411 (2)	1·403 (3)
C(7)	C(1) (1)	1·374 (4)	1·360 (6)	1·377 (2)	1·372 (3)
C(4)	C(6) (1)	1·422 (4)	1·419 (7)	1·421 (2)	1·417 (3)
C(3)	O(8)	1·348 (3) (1·352)	1·360 (6) (1·374)	1·342 (2)	1·343 (3)
N(5)	O(9)	1·298 (3) (1·306)	1·293 (5) (1·315)	1·285 (2)	1·279 (3)

cluding myxin) and with the exception of the N–O distance (to be discussed later) merit no further comment. The phenazine nucleus is nearly planar but the oxygen atoms are displaced slightly from the phenazine plane, in opposite directions as though to avoid too close

contact. It is to be noted that the centre of symmetry at $0, -\frac{1}{2}, \frac{1}{2}$ lies only 0·04 Å from the phenazine plane. Adjacent molecules related by the centre are therefore practically coplanar, and the structure is thus seen to consist of endless ribbons extended in the directions
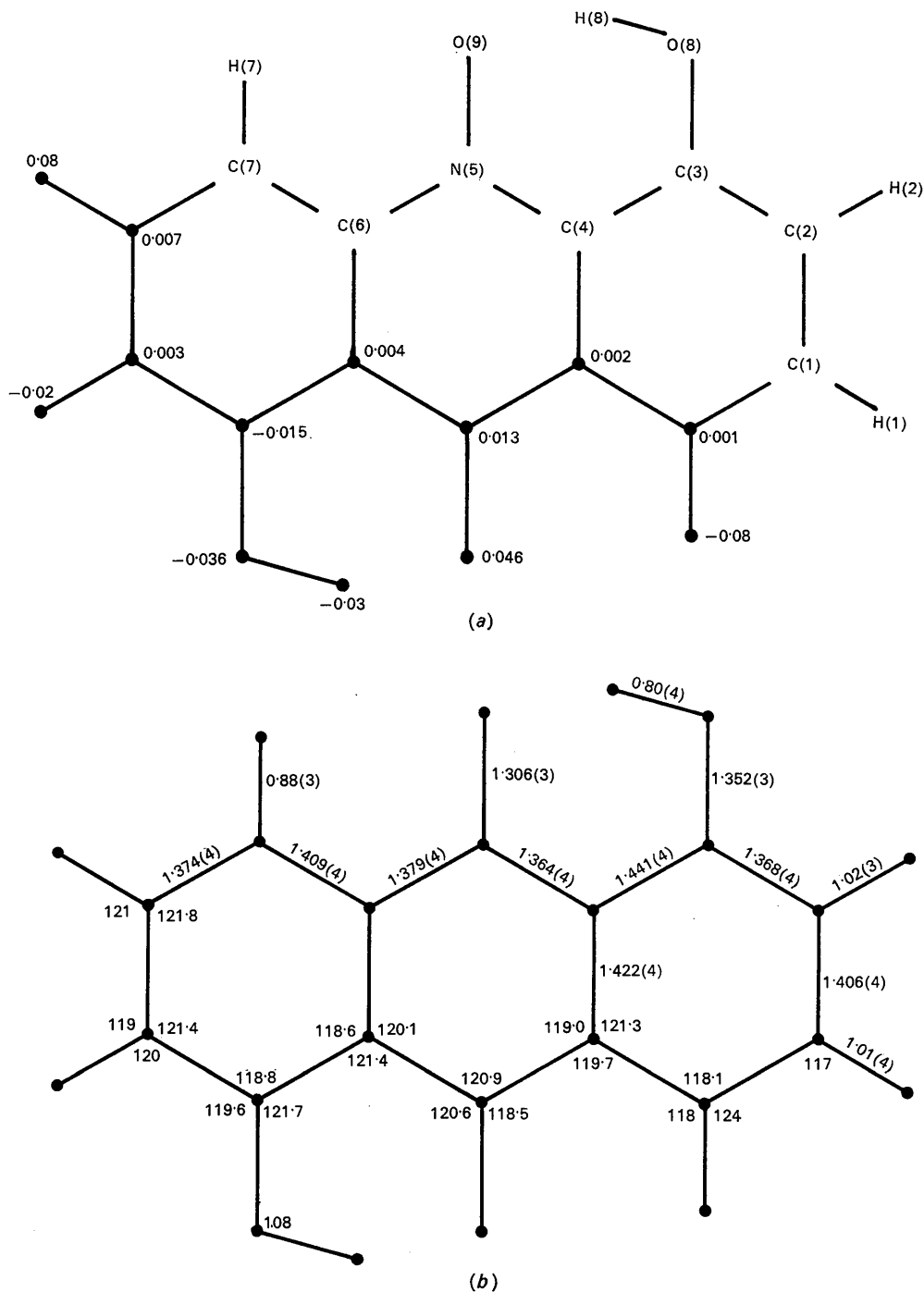
Fig. 2. Molecular geometry. (a) Numbering scheme and the distances of the atoms (in Å) from the mean plane of the phenazine nucleus. (Equation $0·5526x + 0·6490y + 0·5230z = 0$, in the orthogonal coordinate system with $x\|\mathbf{a}$, $y\|\mathbf{b}$, $z\|\mathbf{c}^*$.) (b) Bond lengths (e.s.d.'s) and angles.

⟨011⟩, as illustrated in Fig.3. The predominance of the (100) plane in the crystal habit is now explained; it is the only plane which does not terminate a ribbon.

Although the mean separation between adjacent parallel ribbons is only 3·26 Å, inter-ribbon contacts are consistent with van der Waals interaction. Minimum inter-ribbon distances are: O–O, 3·26; N–O, 3·10; C–O, 3·16; C–N: 3·34; C–C, 3·53 Å. However, the distance between adjacent molecules in the same ribbon is unusually small and, as in the case of myxin, indicates the presence of some intermolecular binding force. Details of the intermolecular association are given in Fig. 4. It is suggested that the hydrogen atom H(8) joins O(8) not only to O(9) but also to O(9)(1). Thus H(8) participates in a bifurcated bond, with one intramolecular and one intermolecular branch. The combined pull of the two symmetry-related intermolecular branches forces the non-bonded atoms O(9) and O(9)(1) into unusual proximity. The situation is very similar to that found in myxin, but a comparison of corresponding distances suggests that in iodinin the intermolecular branch of the bifurcated bond has been strengthened at the expense of the intramolecular branch. Thus O(8)–O(9)(1) and H(8)–O(9)(1) are *decreased*, O(8)–O(9) and H(8)–O(9) are *increased*, and H(8)has moved to a position closer to the bisector of O(9)–O(8)–O(9)(1). In addition, the length of the N–O bond has decreased (to 1·306 Å). In the analysis of myxin it was found that the length of the N–O bond was 1.323 or 1·288 Å depending on whether the oxygen atom did or did not participate in hydrogen bonding. The increased length of the former bond was attributed

to the delocalizing effect of the nearby hydrogen atom on the lone-pair electrons of the oxygen atom, with a consequent reduction in the ionic character of the bond. The N–O distance in iodinin is thus consistent with a weakened intramolecular hydrogen bond. It may be argued that the concomitant strengthening of the intermolecular hydrogen bond would have a compensating effect on the N–O distance. However, at 2·973 Å the intermolecular bond is still rather weak, and perhaps has little influence on the charge distribution of O(9).

Comparison of the room-temperature with the low-temperature structure reveals no important differences, although the intermolecular separation shows moderate temperature dependence. At room temperature the non-bonded O–O distance (corrected for thermal motion) is 2·648 Å (range 2·601 to 2·694 Å). The corresponding value at the lower temperature is, as we have seen, 2·591 Å (range 2·573 to 2·609 Å). (The lower limit of the range is taken to be the uncorrected distance, while the upper limit is the distance corrected for correlated antiparallel displacement. It is clear that the measure of the temperature dependence is itself critically dependent on the assumptions used in the corrections for thermal motion. It is probably true that absolute measurements of intermolecular distances, and discussion based on such measurements, are of limited value for work done at temperatures much above absolute zero.)

It is not surprising that the average intermolecular separation in the disordered structure is somewhat smaller. At the lower temperature the non-bonded O–O distance (uncorrected) is 2·535 Å, compared with 2·573 Å in the ordered structure. At room temperature
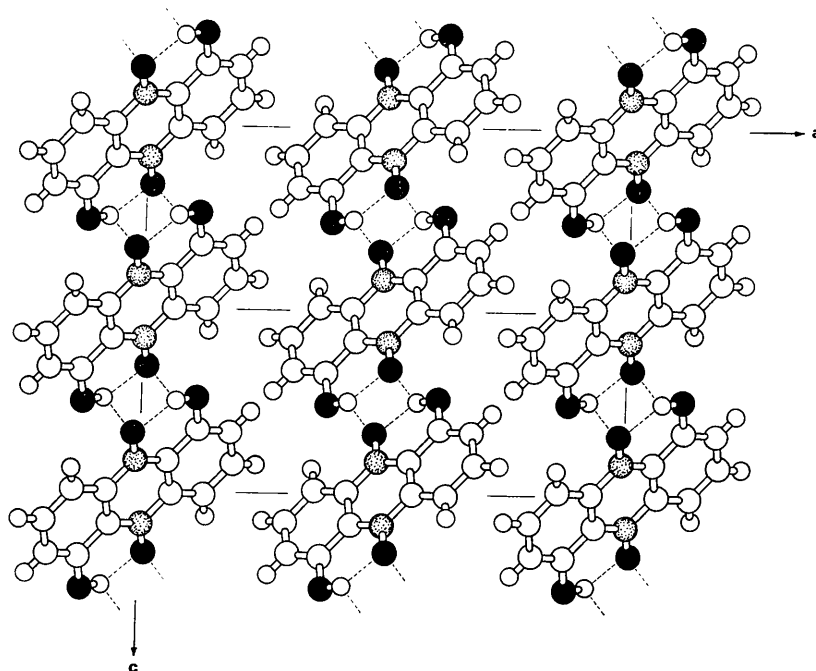

Fig.3. The structure viewed along b.

the corresponding values are 2·576 and 2·601 Å. What is surprising is that the substitution of different molecules makes so little difference to the average structure. It is estimated that in the disordered structure about a quarter of all the intra-ribbon contacts have been grossly modified by the removal of one or more of the juxtaposed oxygen atoms, and yet the effect on the average structure is barely detectable.

The crystal structure of iodinin resembles very closely that found for anthrarufin (VI) (Hall & Nobbs, 1966; Guilhem, 1967a,b). The space group is the same, the cell constants nearly so, and each structure consists of ribbons extended along $\langle 011 \rangle$. In anthrarufin the intermolecular, intraribbon hydrogen-bonded O–O distance is 3.00 Å, and the non-bonded O–O distance 2·79 Å. In iodinin the corresponding distances (at room temperature, uncorrected for thermal motion) are 2·98 and 2·60 Å. The fit of adjacent coplanar molecules presumably results from equilibrium of attractive (hydrogen-bonding) and repulsive (steric) forces. As the lengths of the hydrogen bonds involved are nearly equal, it seems reasonable to assume that the attractive forces are equal also. If this is so, then the repulsive forces are equal despite the considerable difference in the non-bonded O–O distances. The implied difference in the effective packing radius must result from a difference in the electron distribution around the atom, and this in turn must be related to the electronegativity of the adjacent covalently-bonded atom, carbon for anthrarufin and nitrogen for iodinin.

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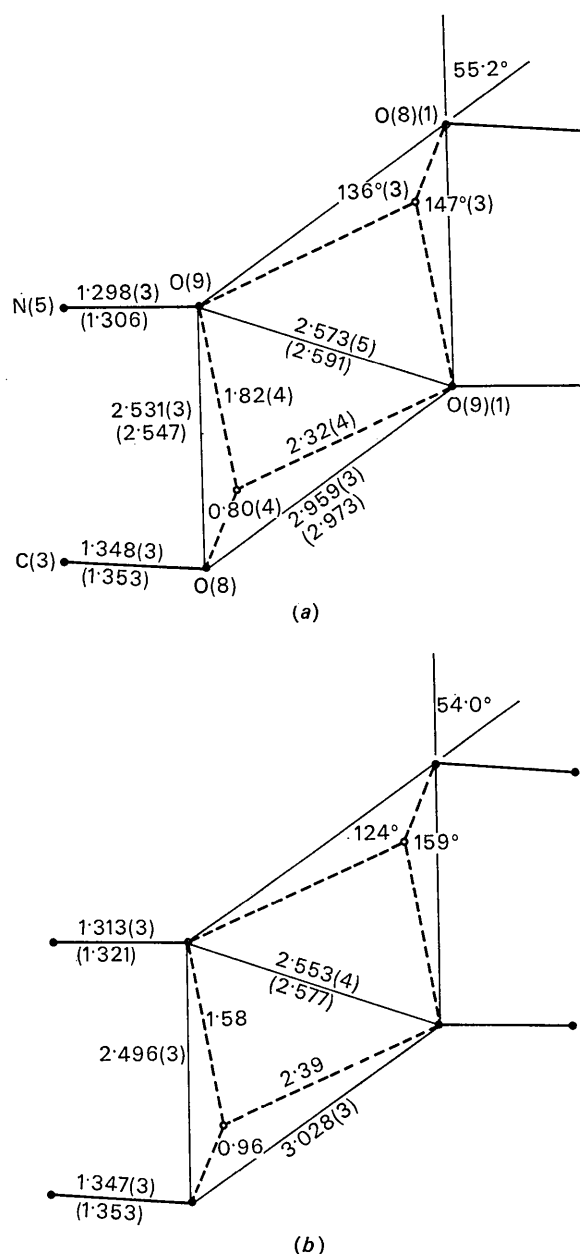
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Fig. 4. Details of the intermolecular contacts. Distances given in parentheses have been corrected for thermal motion assuming riding motion for bond distances, and uncorrelated motion for intermolecular distances. (a) Iodinin, (b) myxin.

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