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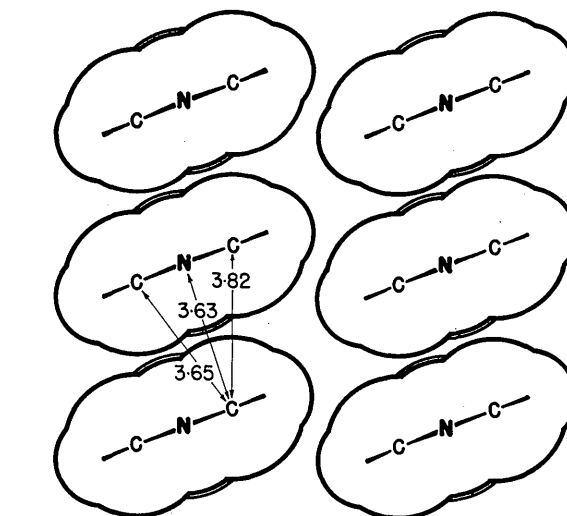LAING, M. & SALE, A. (1969). *Acta Cryst.* B**25,** 1674.

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Fig. 5. Mode of packing of the molecules related by simple translations along a and b, viewed in projection down c.

A Further Investigation of the Crystal Structures of Naphthazarin

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The crystal structures of two modifications of naphthazarin (formally 5,8-dihydroxy-1,4-naphthaquinone) have been further refined, using three-dimensional X-ray counter data in one case, and previously reported photographic data in the other. The carbon skeleton of the molecule is shown to possess D_{2h} symmetry within the standard deviation in carbon—carbon bond length, which was 0·006 Å in the more accurate study. The phenolic hydrogen atom, which is involved in an intramolecular hydrogen bond between the phenolic and quinonoid oxygen atoms, appears to be non-symmetrically placed between them. This structure can be interpreted in terms of resonance between the zwitterion contributors:
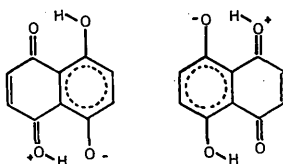
Introduction

Although the compound known as naphthazarin is commonly described as 5,8-dihydroxy-1,4-naphthaquin-

one, there has been some doubt as to its true structure. There is little difference in nuclear arrangement between the equivalent structures (I) and (III), and it seemed possible that these may have been canonicals of a sym-

metrical structure such as (V).

(II)

(I)

(III)

(IV)

(V)

(VI)

(VII)

(VIII)
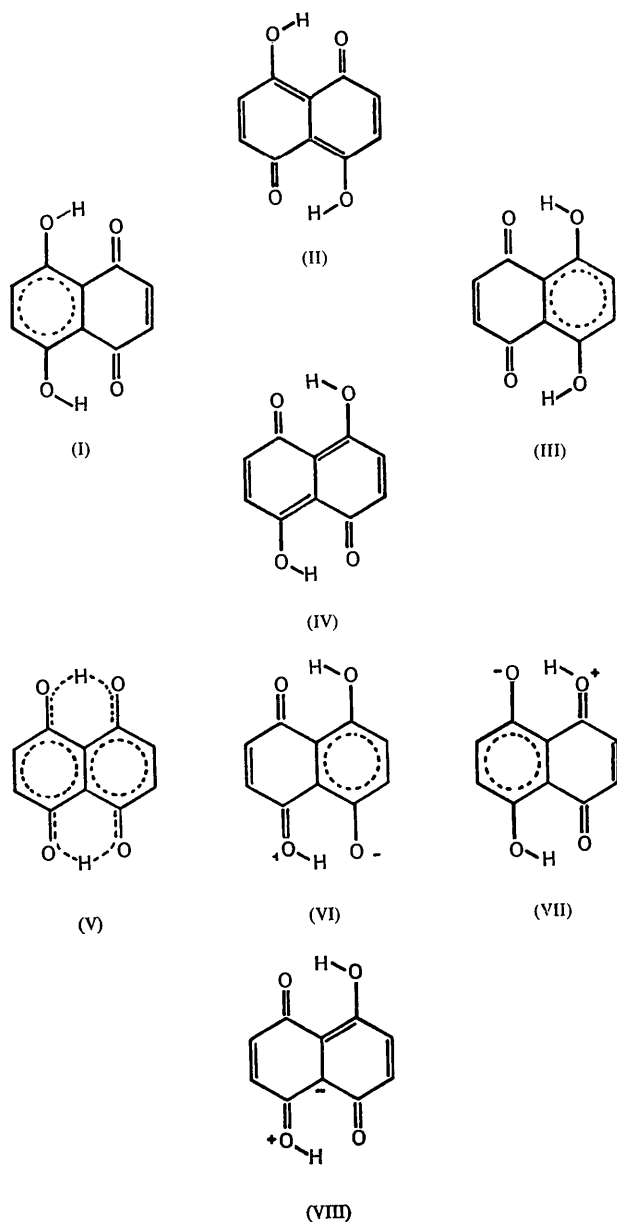
An infrared study (Josien, Fuson, Lebas & Gregory, 1953) failed to detect any O–H streching band, whence it was deduced that each hydrogen atom must indeed be equidistant from the two oxygen atoms, and that structure (V) was correct. Subsequently (Hadzi & Sheppard, 1953) a broad band with $\nu_{max}2920$ cm^{-1} was identified with the O–H stretching vibration; it was

considered that a symmetrical O–H–O system should show a frequency of ca. 1800 cm^{-1}, and thus conversely (V) was incorrect. It is not obvious that the well known relationship involving bond length and frequency in hydrogen-bonding systems (Nakamato, Margoshes & Rundle, 1955) can in fact be so applied to a rigid intra-molecular system, but the conclusion that in this compound the hydrogen atom is asymmetrically placed has been supported by other studies. For instance, in the structure determination of 1,5-dihydroxyanthraquinone (Hall & Nobbs, 1966) for which ν (O–H) is similar (2950 cm^{-1}), the molecule clearly has the expected asymmetric structure.

Naphthazarin exists in three crystalline modifications, which have been the subject of numerous studies (Palacios & Silva, 1938; Billy, 1955, 1958; Borgen, 1956; Watase, Osaki & Nitta, 1957; Srivastava, 1958, 1959, 1961; Golder & Zhdanov, 1958; Pascard-Billy, 1961, 1962a, b, c, d). The structures of all three are in space group $P2_1/c$ (or equivalent), and are such that the molecules are required to be centrosymmetric. At first sight this appears to eliminate the 1,4-quinone structure, (I), but the centrosymmetry could be only apparent; such a near-symmetrical molecule, for which all available hydrogen bonds would presumably be intramolecular, might well be disordered in the crystalline state. The most significant of the above investigations were those of Pascard-Billy, in which the results for all modifications were interpreted in terms of the 1,5-quinone structure (II). This interpretation appears to be based more on the fact that the pattern of bond lengths deviates from D_{2h} symmetry than that it actually fits structure (II); indeed it is questionable whether any of the analyses were sufficiently precise to permit such a deduction. A further argument in support of (II) was that the phenolic hydrogen atoms, which were located from projection studies only, do appear to be asymmetrically placed between the oxygen atoms, but again the accuracy of these observations is uncertain.

It may further be noted that Watase et al. (1957) reported that a few weak reflexions which contravene the space-group extinctions were observed on very long exposure photographs of crystals of modification A (using Pascard-Billy's nomenclature), but their significance was not further investigated.

Recently the nuclear magnetic resonance spectra, in chloroform solution, have been reported (Moore & Scheuer, 1966) for naphthazarin and various related compounds. Unsymmetrical derivatives show the number and pattern of signals expected from the supposed formula, but naphthazarin itself shows one signal only for the carbon-bound hydrogen atoms, and thus on

Table 1. Cell parameters for modification A

a	b	c	β	Reference
3·81 Å	7·63 Å	14·55 Å	97·2°	Borgen (1956)
3·74	7·63	14·55	97·4	Watase et al. (1957)
3·75	7·66	14·50	97·0	Pascard-Billy (1962b)
3·743 ± 0·004	7·622 ± 0·008	14·549 ± 0·015	97·7 ± 0·1	This work

this time scale the molecule is apparently symmetrical. These observations were interpreted in terms of a rapid tautomerism involving structures (I)–(IV).

It was apparent that a further crystallographic investigation of this compound was warranted, and in view of the observation by Watase et al., new data were collected for modification A. It was noted that the previous refinement of modification C (Pascard-Billy, 1962d), which was based on three-dimensional photographic data, had not proceeded beyond the assumption of isotropic thermal motion, and in the belief that the full potential of these data had not been realized, this refinement was further continued.

Experimental

Naphthazarin was prepared according to Zahn & Ochwat (1928), and crystallized from glacial acetic acid as dark green needles of modification A. Cell parameters were obtained from precession photographs (Patterson & Love, 1960), and are listed in Table 1, together with values previously reported. The space group was confirmed as apparently $P2_1/n$, with two molecules per unit cell. A crystal of dimensions $0.57 \times 0.095 \times 0.07$ mm. was mounted about a, and intensity data for the layers $0kl$–$2kl$ were collected using a PAILRED automated linear diffractometer. Crystal monochromatized Cu $K\alpha$ radiation was used; the linear absorption coefficient was 10.3 cm^{-1}, and no corrections for absorption were made. The ω-scan procedure was used, and background counted before and after each reflexion scan. A reflexion was regarded as unobserved if $\sigma(I)/I > 0.5$, where $I = T - tB$, $\sigma I = (T + t^2 B)^{1/2}$, for $T =$ scan count, $B =$ total background count and $t =$ ratio of scan time to total background count time. All data were collected at the normal scan speed of $1°\min^{-1}$. The $h0l$ terms for which $h+l$ is odd were then rescanned at $0.1°\min^{-1}$. Of the 48 reflexions studied, only 3 gave a positive intensity such that $\sigma(I)/I$ was less than 0.5, and none gave $\sigma(I)/I$ less than 0.3. None of the forbidden reflexions reported to have been observed by Watase et al. gave $\sigma I/I$ less than 0.8. It was considered that this investigation gave no evidence for supposing that the space group was other than $P2_1/n$. A data set of 355 observed reflexions was obtained.

Refinement of modification A

The carbon and oxygen atom coordinates listed by Pascard-Billy (1962b) were assumed, and were refined using the program ORFLS (Busing, Martin & Levy, 1962). Scattering factors were assumed as in International Tables for X-ray Crystallography (1962), and weights were calculated as $w = a^2/[a^2 + (F-b)^2]$, with $a = 3.1$, $b = 3.6$ Å, these values being chosen so that $\langle w\Delta F^2 \rangle$ was invariant with F. On the assumption of anisotropic thermal motion and with the removal of 8 terms apparently suffering from secondary extinction, R converged at 0.071.

Table 2. Atom coordinates and thermal parameters, for modification A

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	−0·1549 (13)	0·1564 (6)	0·1450 (4)	0·053 (4)	0·088 (3)	0·067 (3)	−0·007 (3)	0·013 (2)	−0·035 (3) Å²
C(2)	−0·0153 (11)	0·0134 (6)	0·1286 (2)	0·045 (3)	0·084 (3)	0·044 (2)	−0·006 (2)	0·007 (2)	0·003 (2)
C(3)	0·0421 (9)	−0·0609 (5)	0·0365 (2)	0·039 (3)	0·037 (2)	0·050 (2)	−0·002 (2)	0·009 (1)	0·002 (1)
C(4)	0·1820 (11)	−0·2294 (5)	0·0176 (3)	0·046 (3)	0·044 (2)	0·087 (3)	−0·002 (2)	0·011 (2)	0·009 (2)
C(5)	0·2348 (13)	−0·2725 (7)	−0·0758 (3)	0·056 (4)	0·053 (2)	0·097 (3)	−0·004 (2)	0·020 (3)	−0·029 (3)
O(1)	0·0609 (10)	−0·1216 (5)	0·1975 (2)	0·094 (3)	0·141 (4)	0·055 (2)	0·002 (2)	0·014 (2)	0·032 (2)
O(2)	0·2667 (10)	−0·3441 (5)	0·0823 (3)	0·095 (3)	0·060 (2)	0·122 (3)	0·020 (2)	0·016 (2)	0·032 (2)
H(1)	0·168 (13)	0·806 (8)	0·789 (3)			Isotropic $B = 10\cdot2$ Å⁻²			
H(3)	−0·228 (18)	0·271 (6)	0·857 (3)			7·4			
H(5)	0·325 (13)	0·612 (7)	0·913 (3)			9·0			

A difference synthesis was then calculated through the mean plane of the molecule, using the program *FORDAP* (provided by Dr A. Zalkin), and the hydro-

Table 3. *Observed and calculated structure factors* (× 10), *modification A*

Reflexions affected by extinction are not listed.

gen atoms were readily located, as may be seen in Fig. 1. These atoms were given isotropic temperature factors equal to the mean equivalent value of the atom to which they are attached, and refinement of all parameters was then continued. The scattering curve for hydrogen was that given by Mason & Robertson (1966). Refinement converged with conventional R at 0·0514, and with R_w (as defined by Hamilton, 1965). at 0·0481. Finally the hydrogen thermal parameters were permitted to be anisotropic, when the statistics were $R=0·048$, $R_w=0·046$. According to Hamilton's (1965) criterion this decrease in R_w is not significant at the 0·05 probability level, and the final parameters were taken as those at $R=0·0514$. These are listed in Table 2, and the observed and calculated structure factors in Table 3. The bond lengths and angles corresponding to the coordinates of Table 2 are shown in the upper half of Fig. 2. The thermal motions were analysed in terms of rigid-body movements by Cruickshank's (1956) procedure, as outlined in Table 4. The bond lengths corrected for libration effects (Busing & Levy, 1964) are shown in the lower half of Fig. 2.

Refinement of modification C

Cell parameters as listed by Pascard-Billy (1962*d*) are $a=7·906$, $b=7·324$, $c=14·05$ Å, $\beta=96°35'$, space group $P2_1/n$, 4 molecules per unit cell. There are two independent molecules in the cell, centred on 0,0,0 and $\frac{1}{2}$,0,0. The data and positional parameters of Pascard-Billy (1962*d*) were assumed, and the structure refined as above.* On the assumption of anisotropic thermal parameters R decreased from the previous 0·19 to 0·134. Ten reflexions which appeared to be affected by extinction were removed from the data set, and the hydrogen

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* In order to convert the F(obs) values given in Table 3 of Pascard-Billy to an absolute scale, we found it necessary to multiply them by 0·465.
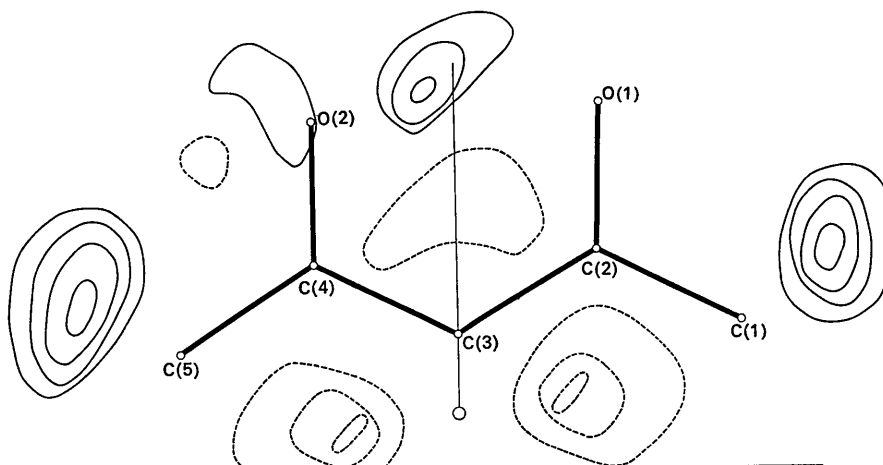

Fig. 1. Difference synthesis in the plane of molecule, modification A, showing the hydrogen atoms. Contours are at intervals of 0·07 e.Å^{-3}, which equals the standard deviation in electron density.

atoms were located from a difference synthesis. Further refinement, which assumed isotropic thermal motion for the hydrogen atoms, converged at $R=0.095$. Atom coordinates and thermal parameters are listed in Table 5, and bond lengths and angles shown in Fig. 3. The thermal motions of the carbon atoms were interpreted in terms of rigid-body motions by Cruickshank's (1956) procedure, leading to a discrepancy index between observed and calculated U of 6·9% for molecule 1 and 5·4% for molecule 2. The relatively high value for molecule 1 suggests that the anisotropic parameters are correcting for more than just thermal motion, and no attempt was made to correct the bond lengths for librational effects.

Results

The most obvious feature of Fig. 2 is that, apart from the hydrogen atom, the molecular symmetry is indeed very close to D_{2h}, and the suggestion that the molecule is a 1,5-quinone is clearly incorrect. Surprisingly, however, the hydrogen atom is not symmetrically placed between the oxygen atoms, as might be expected from structure (V), nor does it appear as two half-atoms, corresponding to a disordered situation. It was considered desirable to test these possibilities specifically.

First, the hydrogen atom was moved 0·3 Å from its refined position, within the plane of the molecule, such that the two O–H separations were equal at 1·33 Å. The agreement indices R and R_w increased to 0·0555 and 0·0535 respectively, a significant increase at the 0·005 probability level, assuming the hypothesis to be

of dimension 4 with 256 degrees of freedom. On refinement, allowing all parameters to vary but maintaining the hydrogen in a symmetrical position, R_w decreased to 0·0504, which is still significantly higher than 0·0481 at the 0·005 level. When the hydrogen parameters were permitted to vary, the atom immediately returned to the non-symmetric position and all parameters converged on their previous values.

Second, the hydrogen atom was replaced by two half-weight hydrogen atoms, one in the same position as H(3) and the other, H(3′), symmetrically placed and making a bond of 1·07 Å with O(1). R and R_w then increased to 0·0549 and 0·0541 respectively. On refinement, R and R_w decreased to 0·0501 and 0·0472 respectively, lower figures than for the single non-symmetric hydrogen atom model, although assuming a hypothesis of dimension 5 the difference narrowly fails to be significant at the 0·05 probability level. However, after the first refinement cycle the temperature factors for H(3) and H(3′), initially 7·5 Å², were 2·1 (σ 1·5) and 13·9 (σ 2·3) Å² respectively, and after three cycles were 2·0 and 16·0 Å². The refinement was repeated,* maintaining the temperature factors of the half-weight hydrogen atoms at 7·5 Å² but permitting their site-occupancy factors to vary. After the first cycle the occupancy factors for H(3) and H(3′) changed from 0·5 to 0·86 (σ 0·13) and 0·19 (σ 0·18) respectively, and after three further cycles were 0·97 and 0·13, with R and R_w at 0·0502 and 0·0483 respectively. The fact that H(3′) assumed either a very high temperature factor or a very low occupancy factor could only be interpreted as indi-

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* On suggestion by the referee.

Table 4. *Rigid-body thermal analysis of the naphthalene nucleus, modification A*

$T=0.041\ (2)$ 0·004 (2)   0·001 (2)   in Å²
                0·047 (2)   0·007 (2)
                              0·035 (4)

R.m.s. vibrations along molecular axes are 0·20, 0·22, 0·19 Å respectively.

$\omega=0.0028\ (7)$ -0.0002 (5) -0.0012 (5)   in rad.²
               0·0018 (23) -0.0010 (9)
                           0·0110 (5)

R.m.s. vibrations about molecular axes are 3·1, 2·4, 6·0° respectively.

Observed and calculated U_{ij} with respect to molecular axes.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	obs	0·111	0·050	0·053	-0.014	0·012	0·006
	calc	0·108	0·052	0·053	-0.014	0·013	0·003
C(2)	obs	0·060	0·069	0·044	-0.018	0·009	-0.005
	calc	0·058	0·069	0·044	-0.016	0·008	-0.002
C(3)	obs	0·042	0·047	0·036	0·007	-0.001	0·002
	calc	0·041	0·052	0·036	0·004	0·001	0·005
C(4)	obs	0·057	0·077	0·042	0·022	-0.001	0·003
	calc	0·058	0·069	0·042	0·023	-0.003	0·002
C(5)	obs	0·103	0·051	0·053	0·022	0·003	0·010
	calc	0·108	0·052	0·052	0·022	0·003	0·007

Molecular axes are with x and y in the plane of the molecule, parallel and perpendicular respectively to bond C(3)–C(3′), and with z perpendicular to the molecule.

cating that the half-atom model is not supported by the experiment, and that the slightly lower agreement indices should be interpreted as a consequence of the increased number of parameters.
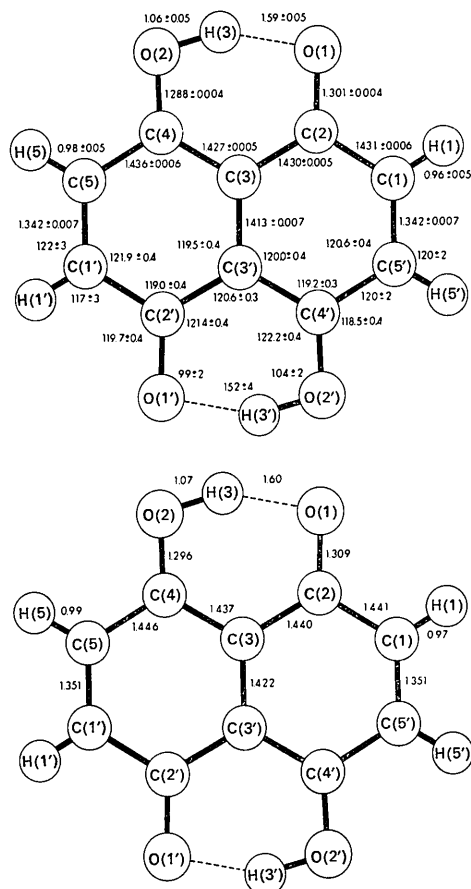

Fig. 2. Bond lengths and angles, before and after correction for thermal motion, modification *A*.

For both molecules of modification *C* the pattern of carbon–carbon and carbon–oxygen bond lengths is, within error, identical to that observed for modification *A*, and the heavy-atom skeleton again shows, at least very nearly, D_{2h} symmetry. The hydrogen atoms H(13) and H(23) again appear to be non-symmetrically positioned between the two oxygen atoms, but the accuracy of their location is too low for this observation to be considered meaningful. Nonetheless the molecular structure in modification *C* is, within error, identical with that observed in the more precise study of modification *A*.

Discussion

This result, that the heavier-atom structure is symmetrical but the phenolic hydrogen is not symmetrically disposed, was unexpected, and the possibility that systematic errors may have influenced the apparent position of the hydrogen atom cannot be ignored. The difference synthesis, Fig. 1, supports the least-squares result, but not so clearly with respect to background noise as to eliminate suspicion completely. Nevertheless, a molecular structure as in Fig. 2 could be described in terms of a resonance system to which the principal contributors are (VI) and (VII). These are in effect zwitterions corresponding to the expected 1,4-quinone (I) and its equivalent (III). It can be argued that as the hydrogen bond is not sufficiently strong for the proton to be more or less equally disposed between the two oxygen atoms, structures (I) and (III) are not equivalent and resonance between them is then not possible. For the zwitterions this is not so; structures (VI) and (VII) are equivalent and the resonance stabilization that results presumably more than compensates the energy required for ionization. Obviously structure (IV) could also be a canonical, but there is little evidence in the bond-length pattern of a significant contribution. Canonicals such as (VIII) would seem to be more important. It is notable that this structure is consistent with

Table 5. *Atom coordinates and thermal parameters* ($Å^2$), *modification C*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(11)	−0·0537 (7)	0·1664 (7)	−0·1601 (4)	0·045 (3)	0·041 (3)	0·040 (3)	0·003 (2)	0·008 (2)	0·013 (2)
C(12)	0·0430 (6)	0·2119 (6)	−0·0705 (3)	0·035 (3)	0·032 (2)	0·037 (2)	−0·001 (2)	0·003 (2)	0·004 (2)
C(13)	0·0452 (6)	0·0862 (6)	0·0072 (3)	0·033 (2)	0·031 (2)	0·028 (2)	0·001 (2)	0·002 (2)	0·001 (2)
C(14)	0·1379 (6)	0·1250 (7)	0·0985 (3)	0·036 (3)	0·036 (3)	0·034 (2)	−0·004 (2)	0·006 (2)	−0·005 (2)
C(15)	0·1381 (7)	−0·0084 (7)	0·1737 (3)	0·046 (3)	0·048 (3)	0·031 (2)	−0·002 (2)	0·000 (2)	0·003 (2)
O(11)	0·1246 (5)	0·3668 (5)	−0·0627 (3)	0·058 (3)	0·039 (2)	0·058 (2)	−0·010 (2)	0·002 (2)	0·013 (2)
O(12)	0·2231 (5)	0·2762 (5)	0·1154 (3)	0·052 (2)	0·041 (2)	0·051 (2)	−0·015 (2)	−0·007 (2)	−0·006 (2)
C(21)	0·6845 (7)	0·2358 (7)	0·0989 (4)	0·037 (3)	0·043 (3)	0·048 (3)	−0·013 (2)	0·005 (2)	−0·004 (2)
C(22)	0·6068 (6)	0·2311 (7)	0·0013 (4)	0·036 (3)	0·031 (2)	0·043 (2)	−0·002 (2)	0·006 (2)	−0·004 (2)
C(23)	0·5093 (6)	0·0746 (6)	−0·0324 (3)	0·029 (2)	0·026 (2)	0·031 (2)	0·001 (2)	0·001 (2)	−0·001 (2)
C(24)	0·4310 (6)	0·0641 (7)	−0·1280 (3)	0·033 (2)	0·042 (3)	0·027 (2)	0·004 (2)	0·001 (2)	0·001 (2)
C(25)	0·3326 (6)	−0·0943 (8)	−0·1593 (3)	0·034 (3)	0·055 (3)	0·035 (2)	−0·002 (2)	−0·004 (2)	−0·010 (2)
O(21)	0·6288 (6)	0·3681 (5)	−0·0553 (3)	0·070 (3)	0·030 (2)	0·064 (2)	−0·013 (2)	0·011 (2)	0·010 (2)
O(22)	0·4450 (5)	0·1962 (6)	−0·1898 (3)	0·055 (2)	0·061 (3)	0·040 (2)	0·002 (2)	−0·005 (2)	0·021 (2)
H(11)	−0·056 (9)	0·248 (10)	−0·215 (5)	Isotropic $B =$			7 (2)		
H(15)	0·210 (8)	0·021 (8)	0·237 (4)				5 (1)		
H(13)	0·211 (12)	0·370 (14)	0·039 (7)				10 (2)		
H(25)	0·271 (9)	−0·127 (9)	−0·223 (5)				6 (1)		
H(21)	0·761 (8)	0·327 (9)	0·117 (4)				5 (1)		
H(23)	0·541 (9)	0·297 (9)	−0·137 (5)				6 (1)		

the infrared spectrum, in that the hydrogen atom is non-symmetrically positioned, and also with the single observed C–H n.m.r. signal, as the environment of all carbon-bound hydrogens is identical, other than for the phenolic hydrogen.

The mean plane through the carbon atoms of modification A, and the displacements of individual atoms from this plane, are given in Table 6. The phenolic oxygen O(2) is significantly displaced, and to a lesser extent so is the phenolic hydrogen H(3), but otherwise the molecule is accurately planar. A similar distortion of the phenol group was observed in 1,5-dihydroxy-anthraquinone (Hall & Nobbs, 1966) and also in the rather similar intramolecular hydrogen-bonding system in chloranilic acid (Anderson, 1967a) and chloranilic acid dihydrate (Anderson, 1967b), and thus it appears to be a common result of such intramolecular strain.

Table 6. *Displacement from mean molecular plane, modification A*

Mean plane: $-0.9162x+0.3620y-0.1719z=0$ with respect to axes abc^*.

	Displacement		Displacement
C(1)	0.002 (5)	O(1)	−0.009 (4)
C(2)	0.000 (4)	O(2)	−0.018 (3)
C(3)	0.001 (3)	H(1)	−0.06 (5)
C(4)	0.001 (4)	H(5)	−0.03 (5)
C(5)	0.001 (4)	H(3)	−0.12 (5)

As described previously (Pascard-Billy, 1962b,d), the molecules pack in a herring-bone pattern in both modifications, similar to that characteristic of aromatic hydrocarbon atoms. In A, successive molecules along a are parallel, with perpendicular separation of 3.42 Å, and the molecular normal is inclined to a at 23.6°. In C, the two distinct molecules are very nearly parallel (making an angle of 1°), and thus there are also successive parallel molecules along c, with perpendicular separation of 3.4 Å, and with molecular normals inclined at a mean of 31°. The shorter intermolecular contacts for A are listed in Table 7.

Table 7. *Intermolecular contacts, modification A*

Atom 1	Atom 2	Vector to be applied to atom 2	Distance
H(1)	O(1)	$\frac{1}{2}-x-1, \frac{1}{2}+y, \frac{1}{2}+z$	2.58 Å
H(5)	O(2)	$x-1, y+1, z$	2.54
O(1)	H(1)	$\frac{1}{2}-x-1, \frac{1}{2}+y-1, \frac{1}{2}+z$	2.58
H(1)	H(3)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	2.55
H(5)	O(2)	$x, y+1, z$	3.01
H(3)	H(1)	$\frac{1}{2}-x, \frac{1}{2}+y-1, \frac{1}{2}+z$	2.55

The thermal motions of atoms for modification A were analysed on the alternative assumptions that the atoms of the carbon skeleton would behave as a rigid body (Table 4), and that the oxygen atoms would do so as well. The agreement between observed and calculated U values in the latter case was distinctly worse, as measured by a χ^2-test, resulting from the fact that the

oxygen atoms do in fact show a much larger out-of-plane vibration than do the carbon atoms.

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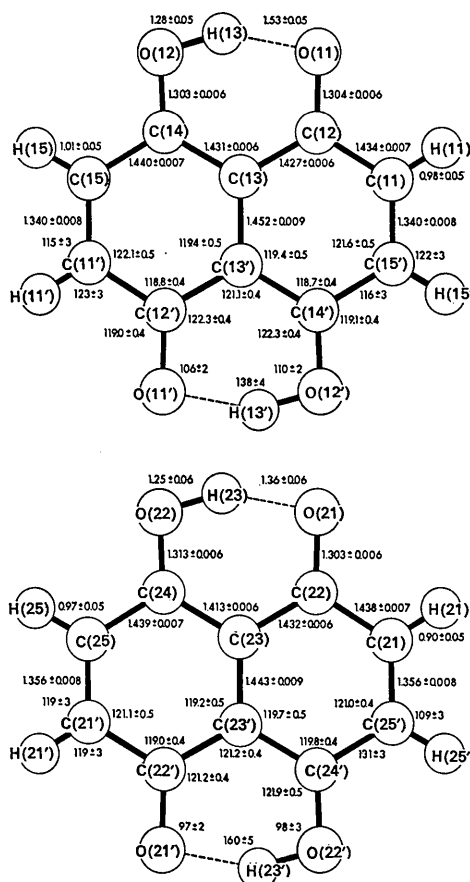
Fig. 3. Bond lengths and angles in the two independent molecules, modification C.

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Die Kristallstruktur von Hexachlorborazol

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Hexachloroborazine crystallizes with rhombohedral symmetry with one formula unit per rhombohedral unit cell; the lattice parameters are $a = 6\cdot151$ Å and $\alpha = 91\cdot8°$ (rhombohedral cell) or $a = 8\cdot835$, $c = 10\cdot313$ Å (trigonal cell), space group $R3$. The crystal structure was deduced from stereochemical considerations and refined by the method of least-squares to a reliability index of $R = 4\cdot5\%$ for the 153 crystallographically independent observed reflexions. The structure is built up from planar layers of $(BN)_3Cl_6$ molecules lying perpendicular to the trigonal c axis and can be derived from a cubic closest packing of Cl atoms by substituting the cube corner atoms by $(BN)_3$ rings. Owing to positional disorders in the layer sequence all crystals are polysynthetic twins with microdomains oriented in such a way that the formal description with the terms obverse and reverse for rhombohedral cells is possible. The shape and dimensions of the hexachloroborazine molecule are almost identical with those of hexachlorobenzene, which crystallizes in a related structure.

Einleitung

Im Rahmen von Strukturuntersuchungen an Aziden ergab sich bei Versuchen, für kristallographische Untersuchungen geeignete Einkristalle vom trimeren Bordichloridazid zu gewinnen, dass sich dieses in Lösung unter bestimmten Umständen zu Hexachlorborazol, $(BN)_3Cl_6$, zersetzt (Müller, 1971). Durch die entsprechende thermische Zersetzung des Bordichloridazids war das Hexachlorborazol erstmals von Paetzold (1963) erhalten worden. Weitere Darstellungsmöglichkeiten sind von Haasnot & Groeneveld (1967) und von Wiberg, Raschig & Schmid (1967) beschrieben worden. Da orientierende Röntgenbeugungsdiagramme erkennen liessen, dass die Kristallstruktur von Hexachlorborazol einige Besonderheiten aufweist, erschien dessen Strukturaufklärung lohnend.

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Experimentelles und Kristalldaten

Für die röntgenographische Untersuchung geeignete Einkristalle von Hexachlorborazol wurden aus einer Lösung in CCl_4 gewonnen, indem das Lösungsmittel unter vermindertem Druck partiell verdunstet wurde. Die dabei ausgeschiedenen Kristallnadeln haben die Gestalt von hexagonalen Prismen, auf deren Seiten sich häufig kleine Stufen zu Treppen aneinanderreihen; als Begrenzungsflächen scheinen nur die Flächen mit den trigonalen Indices $\{10\bar{1}0\}$ und $\{0001\}$ vorzukommen. Von den Kristallen wurden einige isoliert und unter Feuchtigkeitsausschluss in je eine dünnwandige Kapillare aus Quarzglas abgefüllt.

Ein Drehkristalldiagramm und mehrere Weissenberg-Aufnahmen, die mit Cu $K\alpha$-Strahlung bei Drehung um die Nadelachse (trigonale c-Achse) zunächst angefertigt wurden, ergaben eine trigonale Elementarzelle (Laue-Symmetrie $\bar{3}$). Im weiteren Verlauf der Strukturbestimmung zeigte sich, dass das Hexachlorborazol rhomboedrisch kristallisiert. Eine Guinier-