767. *The Crystal Structure of 2 : 3-Dihydro-2 : 3-methylene-1 : 4-naphthaquinone.*

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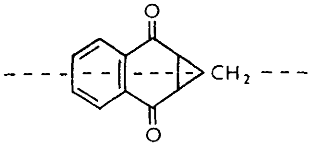
The compound (I) crystallises in a form that is convenient for structure analysis by *X*-ray diffraction. The crystals belong to the monoclinic system, with $a = 6{\cdot}98$, $b = 10{\cdot}55$, $c = 5{\cdot}46$ Å, and $\beta = 94\frac{1}{2}°$, and there are two molecules in the unit cell, with the space group $P2_1/m$. The molecule is bisected by a crystallographic plane of symmetry. The benzenoid ring, which lies perpendicular to this plane, is itself coplanar; but the quasi-quinonoid residue is non-coplanar, and the two carbonyl bonds are not collinear. Bond lengths and bond angles have been determined with moderate accuracy, including those in the three-membered ring; and the stereochemistry has been studied in some detail at the heavily strained carbon atoms by which this ring is fused to the naphthaquinone system.

2 : 3-DIHYDRO-2 : 3-METHYLENE-1 : 4-NAPHTHAQUINONE (I), prepared and described by Buchanan and Sutherland,[1] is of uncommon interest for metrical study because it includes a three-membered ring—very few examples of which have been studied—and because the carbon atoms by which this ring is fused to the naphthaquinone residue must be under severe strain. Fortunately its crystal structure is favourable for study by *X*-ray methods. In three independent projections the atoms are usefully resolved, so that two-dimensional methods of analysis are likely to be unusually effective. A progress report on this work has been published.[2]



(I)

EXPERIMENTAL

Crystallographic Data.—The material used was kindly supplied by Dr. G. L. Buchanan; it had been recrystallised from toluene and melted at 128—130°. The crystals showed straight extinction in polarised light, and formed laths with pointed or wedge-shaped ends, elongated in the direction of *b*. The (100) pinakoids were most prominent, and the domes (011) and/or (110) were usually present; (001) pinakoids were sometimes recognisable. The following unit-cell parameters were derived from single-crystal rotation, oscillation, and moving-film photographs, copper-K_α radiation being used throughout: $C_{11}H_8O_2$, Mol. wt. = 172·2. *Monoclinic prismatic,* $a = 6{\cdot}98$, $b = 10{\cdot}55$, $c = 5{\cdot}46$ Å (each $\pm 0{\cdot}02$ Å), $\beta = 94\frac{1}{2}°$, volume of unit cell = 400·9 Å^3, density measured by flotation = 1·40 g./c.c., density calculated for *two molecules* per cell = 1·426, absorption coefficient for *X*-rays = 9·2 cm.$^{-1}$, $F(000) = 180$. *Absent reflexions* are $0k0$ when k is odd, implying that the space group is either $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). The Wilson ratio, $N(z)$, and variance tests were applied to the intensity data in the $hk0$-zone, and they all unambiguously indicated centro-symmetry. Furthermore, when placed on the same scale, average intensities in the $h0l$ zone were greater than those in $hk0$ by a factor of about two; this is evidence for a plane of symmetry perpendicular to *b*, which again implies centro-symmetry. The *space group* $P2_1/m$ was therefore adopted, and the subsequent progress of the analysis corroborated the choice.

This space group requires the presence of mirror-planes at $y = \frac{1}{4}b$ and $\frac{3}{4}b$; and two molecules of formula (I) can be accommodated only if they are each bisected by one of these planes in the manner suggested by the broken line. It follows that the crystal structure is a simple one, for which preliminary *y*-co-ordinates could at once be written down from a knowledge of standard bond-lengths.

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[1] Buchanan and Sutherland, *J.*, 1954, 1060; 1956, 2620.
[2] Grant, Vos, and Speakman, *Acta Cryst.*, 1957, **10**, 806.

Structure Analysis.—The multiple-film technique was used to measure the intensities of some 189 independent reflexions in the three principal zones, out of about 234 accessible to copper radiation. The crystals used had dimensions of the order 0·2 mm., so that absorption of X-rays would be small and was neglected. Trial structures were found for each axial projection and refined in the usual way by double Fourier series. The final electron-density calculations were made on the digital computer designed by Robertson,[3] and completed in a total time of about 8 hr. The results are displayed in the maps reproduced in Fig. 1. All the

FIG. 1. *Electron-density projections along the c-, a-, and b-axes. (The contour-lines are at intervals of* 1 *electron per sq. Å, with the zero-line broken.)*

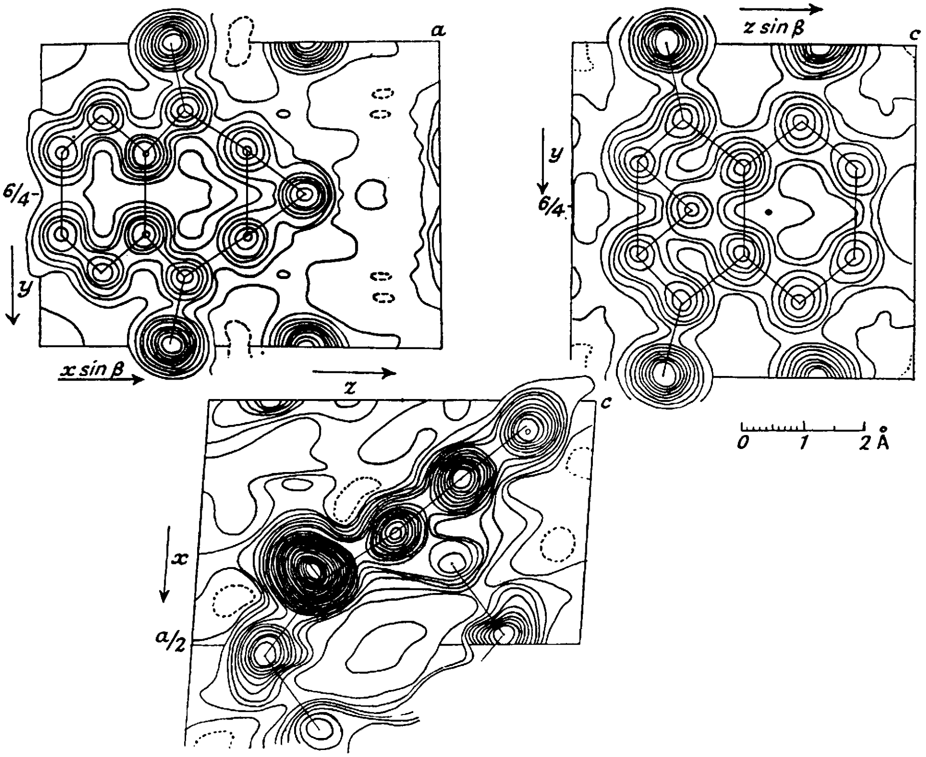

TABLE 1. *Atomic co-ordinates (x, y, and z, as fractions of unit-cell edges), values of the "reliability index" (R), and Debye temperature factors (B, in Å²) for the three independent zones.*

Zone	*hk*0		*h*0*l*		0*kl*	
	x	y	x	z	y	z
O	0·327	0·003	0·330	0·270	0·000	0·270
C(1)	0·050	0·182	0·047	0·830	0·182	0·833
C(2)	0·150	0·120	0·150	0·667	0·117$_5$	0·670
C(3)	0·263	0·182	0·267	0·503	0·183	0·507
C(4)	0·363	0·115	0·363	0·327	0·115	0·327
C(5)	0·523	0·177	0·523	0·190	0·175	0·190
C(6)	0·667	0·250	0·667	0·347	0·250	0·347
R	0·130		0·113		0·122	
$B_{\rm O}$	Ranging from 3·5 parallel to x to 2·5 parallel to y		3·5		Ranging from 3·5 parallel to z to 2·5 parallel to y	
$B_{\rm C}$	2·8		3·3		2·8	

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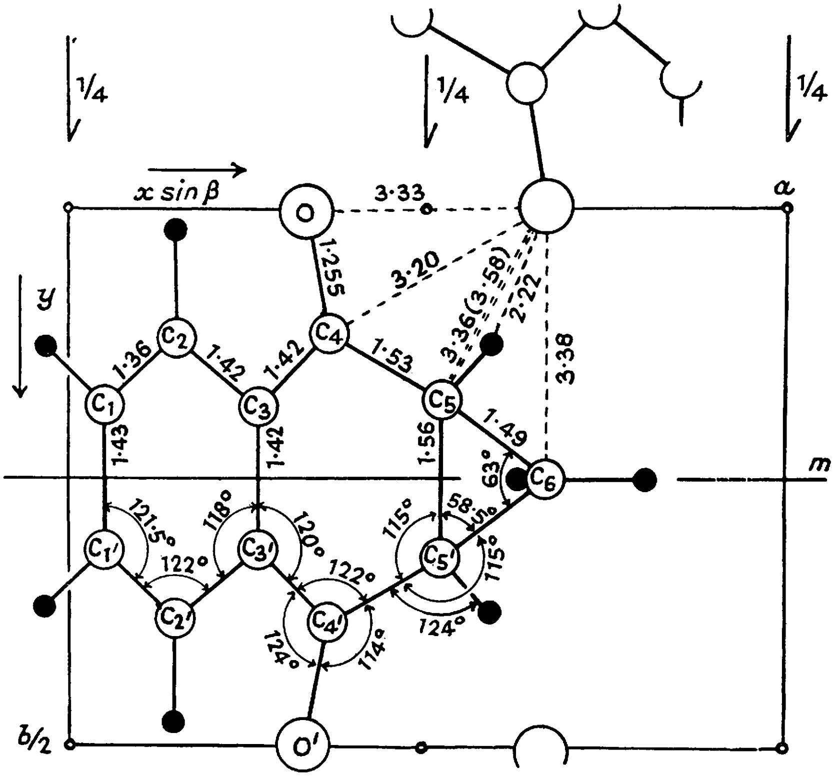
[3] Robertson, *Acta Cryst.*, 1954, **7**, 817; 1955, **8**, 286.

atoms, other than hydrogens, are resolved in the projections along *a* and *c*; whilst along *b* all pairs of atoms related by the mirror-plane are precisely superposed and are represented by discrete peaks of double height, apart from the partial overlap of the four atoms of the carbonyl groups. To have effected substantial resolution of the atoms in all three projections is remarkable with a non-coplanar molecule of this type, and it opened the possibility of attaining moderate accuracy of analysis without recourse to three-dimensional methods.

Further refinement was by repeated " difference " syntheses. Standard atomic-scattering functions [4] were used; they were modified by Debye temperature factors, with the *B*-values shown in Table 1—isotropic for carbon, and usually anisotropic for oxygen. The direction of the anisotropy is consistent with some libration of the molecule about its centre of mass.

FIG. 2. *The molecule and some of its environment in the c-axis projection, showing the numbering of the atoms, interatomic distances* (Å), *and bond-angles.*



Each principal projection of the structure was refined independently. For this reason observed, F_o, and calculated, F_c, values of the structure amplitudes for reflexions common to two zones are not quite identical in each, though only with $F(100)$ is the difference other than trivial.

At an early stage of the refinement hydrogen atoms were introduced in plausible positions and their introduction sensibly improved the agreement between F_o and F_c. In difference syntheses, where only the contributions due to carbon and oxygen atoms had been subtracted, peaks with heights of 0·6—1·0 electron per sq. Å appeared at the expected positions; but they were not definitive enough to warrant their use in any systematic emendation of the hydrogen co-ordinates.

Results.—Final atomic co-ordinates for each projection are listed in Table 1, which also shows values of *R*, the " agreement index." The numbering of atoms is explained in Fig. 2; the hydrogen atoms are numbered according to the adjacent carbon atom. Mean values of these (fractional) co-ordinates are given in Table 2, in which also appear co-ordinates (X', Y, and Z', in Å) with respect to orthogonal axes. Final values of observed structure amplitudes

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[4] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

and calculated structure factors are collected in Table 4. Unobserved reflexions are omitted; only in 10 cases out of 45 did the magnitude of F_c imply that the reflexion should have been just detectable. The bond-lengths and angles derived from the co-ordinates in Table 2 are shown in Fig. 2. All intermolecular contacts, except those shown specifically, exceed 3·4 Å. The general conformation of the molecule is demonstrated by the perspective sketch in Fig. 3*a*; the viewer is supposed to be looking down at an angle of about 45° on to the equatorial plane of molecular symmetry.

Accuracy.—Two methods for assessing accuracy are applicable here. First, since every atomic co-ordinate has been determined in two independent zones, corresponding values can be compared. The standard deviations (σ) of the co-ordinates from their means are given in Table 3, row (*a*). The estimates thus derived for the six carbon atoms, taken together, were

FIG. 3*a*.

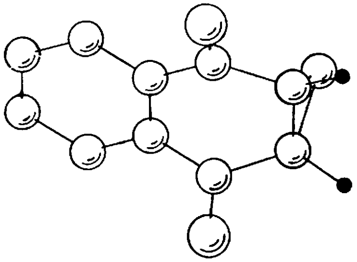

FIG. 3*b*.

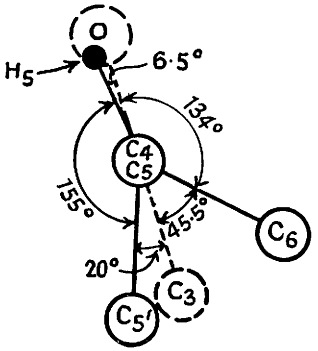

FIG. 3. (*a*) *A perspective view of the molecule.* (*b*) *Distribution of bonds about* C(4) *and* C(5), *as viewed along the direction of the bond between these two atoms; the dihedral angles are shown.*

TABLE 2. *Atomic co-ordinates, with respect to an origin located at a centre of symmetry, x, y, and z being expressed as fractions of the unit-cell edges. X′, Y, and Z′, which are in Å, are measured along orthogonal axes, X′ being parallel to x, and Y to y. The numbering of the atoms is shown in Fig. 2; the hydrogen atoms are numbered according to their respective carbon atoms.*

Atom	x	y	z	X'	Y	Z'
O	$0{\cdot}328_5$	$0{\cdot}001_5$	0·270	2·177	0·016	1·470
C(1)	$0{\cdot}048_5$	0·182	$0{\cdot}831_5$	−0·018	1·920	4·526
C(2)	0·150	$0{\cdot}118_8$	$0{\cdot}668_5$	0·761	1·253	3·639
C(3)	0·265	$0{\cdot}182_5$	0·505	1·633	1·925	2·749
C(4)	0·363	0·115	0·327	2·394	1·213	1·780
C(5)	0·523	0·176	0·190	3·569	1·857	1·034
C(6)	0·667	0·250	0·347	4·507	2·638	1·889
H(1)	−0·03	0·13	0·97	−0·64	1·40	5·26
H(2)	0·15	0·02	0·67	0·76	0·18	3·64
H(5)	0·59	$0{\cdot}12_5$	0·03	4·13	1·32	0·18
H(6)	0·63	0·25	0·53	4·26	2·64	2·89
H(6′)	0·81	0·25	0·33	5·40	2·64	1·80

TABLE 3. *Estimates of the standard deviations* (σ) *in the final atomic co-ordinates* (Å); σ(*r*) *is the R.M.S. positional deviation.*

			σ(*x*)	σ(*y*)	σ(*z*)	σ(*r*)
(*a*)	C and O atoms		0·0080	0·0101	0·0063	—
(*b*)	C atoms	*hk*0	0·020	0·022	—	—
		*h*0*l*	0·008	—	0·008	—
		0*kl*	—	0·009	0·012	—
	O atom	*hk*0	0·009	0·010	—	—
		0*kl*	—	0·004	0·005	—
(*c*)	R.M.S. values	C	0·0133	0·0149	0·0090	0·0126
		O	0·0085	0·0085	0·0057	0·0082

hardly affected if the deviation for the oxygen atom was also included; and, since the data for this atom were not sufficiently numerous to warrant separate consideration, the standard deviation based on all seven atoms has been adopted for both carbon and oxygen. Secondly, as the resolution is so good, Cruickshank's method [5] can be applied with confidence, and it leads to the σ-values shown in the Table, row (*b*). The σ-values thus derived are decidedly least favourable for the zone giving the best projection of the molecule, though the *R*-value is hardly inferior. This typical result can be related to the larger number of reflexions in the *hk*0-zone. Root-mean-square deviations, based on the three independent estimates, appear in the last row (*c*) of Table 3.

These last standard deviations of co-ordinates have been used to assess σ-values for bond-lengths and angles: σ(C–O) = ±0·015 Å; σ(C–C) = ±0·018 Å in general, but for the bonds, such as C(1)–C(1′), lying across the plane of symmetry, C–C depends only on the *y*-co-ordinate, and σ(C–C) is then ±0·030 Å. For a bond-angle (θ) near to 120°, σ(θ) = ±1·1°. The positions of the hydrogen atoms are known only roughly, for the reasons already given. It is possible that they have been located within 0·2 Å of their correct positions.

TABLE 4. *Observed structure amplitudes and calculated structure factors.* (*In each set of three columns, the first lists the value of the varying index, the second* $|F_o|$, *and the third* F_c.)

*hk*0-zone

	0*k*0		8	4·2	−3·8	9	1·6	−0·3	12	2·9	+2·9	2	1·9	+0·9	8	6·6	+6·8
2	12·5	−14·1	9	3·3	+2·3	10	3·3	−2·4		4*k*0		3	14·2	+13·5	9	1·4	+2·3
4	3·8	−2·1	10	2·8	−1·0	11	2·1	+1·5	0	3·1	−4·4	4	7·0	−6·9			
6	25·0	+24·6	11	6·8	−6·0				1	8·2	−7·9	5	3·4	−3·2		7*k*0	
8	8·1	+6·9	12	3·5	−2·8		3*k*0		2	14·3	−12·9	6	8·2	−7·0	0	3·5	−3·0
10	11·5	+10·4	13	1·1	+0·2	0	23·2	+22·6	3	2·8	+2·0	7	8·2	−7·8	1	3·5	+3·6
12	4·0	+3·4				1	1·3	+0·6	4	2·9	−1·6	8	2·7	+1·7	2	1·2	+2·2
				2*k*0		2	10·5	+10·5	5	4·8	+5·6	9	3·0	+2·8	3	2·2	−1·7
	1*k*0		0	12·2	−11·9	3	5·8	−6·2	6	9·7	+8·7	11	2·3	+3·5	7	0·7	−1·3
0	17·1	−17·1	1	21·7	−19·8	4	18·7	+17·4	7	9·9	−10·5						
1	28·4	−29·6	2	18·1	−16·5	5	1·0	+1·6	8	14·3	−13·4		6*k*0			8*k*0	
2	6·4	−5·9	3	9·2	+6·7	6	2·7	+2·7	9	4·6	+4·6	0	8·0	+9·5	0	0·9	+1·8
3	23·9	−23·0	4	12·3	−12·0	7	7·2	+7·0	12	1·9	+4·7	1	4·5	−3·8	1	4·6	−6·6
4	8·2	−8·2	5	0·9	+0·8	8	7·6	+7·5				2	4·6	+4·7	2	0·7	−0·9
5	15·0	+15·0	6	1·5	−1·0	9	2·2	−0·8		5*k*0		4	0·9	+1·6	3	1·0	+1·4
6	4·6	−3·3	7	2·3	−1·4	10	3·7	+2·2	0	8·5	−11·3	5	1·9	+2·5	4	2·5	−4·0
7	2·7	−4·1	8	9·1	−10·8	11	1·4	+2·0	1	3·0	−1·9	6	1·1	−0·2	5	0·9	+2·8

*h*0*l*-zone

	00*l*		0	24·2	−22·5	1	66·0	+76·3	2	8·2	+6·4	3	18·1	−12·8	0	10·7	+11·0
1	32·3	−32·1	1	3·4	+4·9	2	20·3	−25·7	3	3·5	+3·2				1	3·1	−4·2
2	35·2	−36·6	2	11·8	+11·6	3	19·9	−19·9	4	2·5	−1·0		50*l*		2	6·2	−6·2
3	4·6	+4·3	3	8·0	+7·7	5	6·7	+8·1	5	6·2	−6·8	$\bar{3}$	9·2	+8·9	3	12·4	+11·1
4	5·5	+4·4	4	10·9	−10·5	6	2·3	−2·3				$\bar{2}$	3·8	−3·7	4	7·8	−4·8
5	6·3	−6·4	5	5·3	−5·2					40*l*		$\bar{1}$	10·5	−9·6			
6	10·4	+10·4	6	2·9	+3·2		30*l*		$\bar{5}$	5·5	+5·7	0	9·9	−10·7		70*l*	
						$\bar{5}$	3·3	−2·5	$\bar{4}$	10·2	+9·3	1	15·5	+14·5	$\bar{2}$	3·3	+2·7
	10*l*			20*l*		$\bar{4}$	9·2	+8·3	$\bar{3}$	21·2	−25·3	2	11·4	+10·4	$\bar{1}$	3·2	−5·0
$\bar{6}$	1·9	−1·7	$\bar{6}$	2·7	+2·9	$\bar{3}$	6·2	+6·0	$\bar{2}$	2·9	+4·0	4	5·5	−5·7	0	3·2	−3·1
$\bar{5}$	6·3	+6·2	$\bar{5}$	11·6	+11·2	$\bar{2}$	16·5	−14·8	$\bar{1}$	16·1	+15·1						
$\bar{4}$	3·1	−1·4	$\bar{4}$	18·8	−14·6	$\bar{1}$	14·7	−14·8	0	2·8	−4·4		60*l*			80*l*	
$\bar{3}$	15·6	−14·6	$\bar{2}$	8·1	+6·5	0	26·1	+24·7	1	6·6	−6·5	$\bar{3}$	6·0	+5·9	$\bar{2}$	2·2	+3·4
$\bar{2}$	11·8	+11·1	$\bar{1}$	6·9	−8·4	1	2·1	−1·1	2	19·1	+19·0	$\bar{2}$	12·8	−14·6	$\bar{1}$	2·5	−4·6
$\bar{1}$	10·2	+14·5	0	14·5	−13·2												

0*kl*-zone

	0*k*0		3	5·5	+5·4	3	8·0	−8·4	2	16·9	+17·7	5	1·3	−2·0		0*k*6	
2	15·8	−17·3	4	1·0	−1·4	4	6·3	−7·3	3	1·7	+0·6	6	9·3	+6·9	0	9·0	+8·7
4	3·5	−5·0	5	3·3	−2·9	5	4·5	+5·8	4	4·1	−2·2	7	2·6	+1·3	2	3·2	−4·1
6	25·8	+25·4	6	1·8	+3·0	6	8·6	−8·3	5	1·9	−3·1	8	1·5	−0·9	3	1·1	+1·1
8	9·5	+8·2	7	1·6	+1·6	7	2·6	−2·0	6	14·1	−14·1	10	1·2	+1·1	4	3·1	−4·1
10	11·6	+9·3	8	4·7	−5·0	8	12·5	−10·5	7	1·9	+2·8						
12	3·3	+3·1	10	2·3	−2·9	10	4·4	−3·8	8	18·1	+17·0		0*k*5				
						12	1·2	−1·1				0	5·2	−5·3			
	0*k*1			0*k*2						0*k*4		2	3·2	−3·2			
0	32·6	−30·5	0	33·7	−36·1		0*k*3		0	4·0	+3·8	5	1·4	+1·3			
1	8·9	−7·8	1	7·4	+7·7	0	3·6	+3·6	2	3·4	+5·8	7	1·2	−1·5			
2	1·9	+2·7	2	17·6	−17·5	1	3·8	+4·2	4	3·5	+6·1	8	2·6	−2·6			

DISCUSSION

The structure found for this molecule will be discussed in three aspects: the naphthaquinone residue; the *cyclo*propane ring; and the valency distribution about the heavily strained atom, C(5).

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[5] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

Benzoquinone is one of the fundamental aromatic structures analysed by Robertson.[6] His *X*-ray measurements have recently been recalculated by Trotter,[7] using current methods of refinement. The molecule is centrosymmetric, so that the two C–O bonds are necessarily parallel; and in fact they are collinear within close limits, the molecule being virtually planar. The bond lengths, now amended, are C=O = 1·19, C–C = 1·49, and C=C = 1·31 Å, each with an estimated standard deviation of ±0·03 Å. An electron-diffraction study of the molecule in the gaseous state [8] yielded results in good agreement, *viz.*, C=O = 1·23, C–C = 1·49, C=C = 1·32 Å. Anthraquinone has a similar structure according to Sen's determination,[9] which corrected an earlier study: the molecule is centrosymmetric and virtually coplanar, with C–C = 1·39 in the benzenoid rings, C=O = 1·15, and C–C adjacent to the carbonyl groups = 1·50 Å. Bailey's careful analysis of the large molecule indanthrone [10] led to similar results in the anthraquinone residues, with C–O = 1·20—1·23 Å; the same author finds C–O = 1·25 Å in her recent work on 1 : 5-dichloroanthraquinone.[11]

The most obvious difference between these structures and that now found for molecule (I) is the non-collinearity of the C–O bonds. The deviation is evident in both *a*- and *c*-axis projections (Fig. 1), and at the oxygen atom it amounts to nearly 0·4 Å, which is highly significant. [The dihedral angle between C(2)–C(3) and C(4)–O about C(3)–C(4) is 14°.] There is distortion of the carbonyl bonds in 1 : 5-dichloroanthraquinone too; this is due to steric repulsion between oxygen and chlorine atoms. The distortion of the quasi-quinonoid part of molecule (I) is qualitatively similar to that observed in each anthraquinonoid moiety of dianthronylidene (dianthrone).[12] But, as dianthrone is a typically over-crowded molecule and (I) is not, the causes of the distortion must differ. Two intramolecular factors may operate to maintain molecule (I) in its configuration: (*a*) the difference (~0·2 Å) between the lengths of bonds C(3)–C(3′) and C(5)–C(5′) will tilt the carbonyl groups towards the benzenoid ring; (*b*) the *cis*-fusion of the three-membered ring forces carbon atoms 5 and 5′ to adopt an eclipsed conformation, and the angle C(4)–C(5)–C(5′) is much less than 120°, for which reasons the atoms 4, 5, 5′ and 4′ take up positions resembling those of carbon atoms in (half of) a *cyclo*hexane molecule in its less stable, " boat " form; and hence the C–O bonds are tilted towards positions that would be those occupied by the " bowsprit " of the boat. The conformation may also be sustained by an intermolecular factor. The hydrogen atom attached to C(5) is directed very nearly towards the oxygen atom of a neighbouring molecule, as is shown in Fig. 2; the total separation C(5) • • • O″ is 3·36 Å, whilst H • • • O″ is about 2·2 Å. This might represent hydrogen bonding, which—though very weak—would be sufficient to exert an influence on the C–O-bond, and to fix its orientation about the C(4)–C(5)-bond. That compound (I) melts at a temperature 50° higher than its homologue, in which these two hydrogen atoms are replaced by methyl groups,[1] may possibly be related to this intermolecular bonding. (O″ belongs to the neighbouring molecule at the top of Fig. 2.)

The bond C(3)–C(4) is significantly shorter than is the corresponding bond in benzoquinone, and the carbonyl bond is possibly significantly longer. These differences would imply that there is more conjugation here between the aromatic ring and the carbonyl group than is normal in a quinone. This is also in accord with the angles round C(4). At first sight a lengthening in the ketonic group might be expected to be accompanied by a diminution of the C–O stretching frequency. But the band at 1675 cm.$^{-1}$ assigned to this vibration is at a slightly higher frequency than the cognate band in the spectrum of benzoquinone (1667 cm.$^{-1}$). However the carbonyl stretching frequency is insensitive to small

[6] Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106.
[7] Trotter, Thesis, Glasgow, 1957.
[8] Swingle, *J. Amer. Chem. Soc.*, 1954, **76**, 1409.
[9] Sen, *Indian J. Phys.*, 1948, **22**, 347.
[10] Bailey, *Acta Cryst.*, 1955, **8**, 182.
[11] *Idem, ibid.*, 1958, **11**, 103.
[12] Harnik and Schmidt, *J.*, 1954, 3295.

changes in length.[13] (In a personal communication Dr. Bailey informs us that this frequency lies at 1680 cm.$^{-1}$ in solid 1 : 5-dichloroanthraquinone, a value which hardly differs from that in anthraquinone, 1678, though the bond in the chloro-compound is longer). It is possible that the environment has a special influence on the C–O bond in (I); there is a roughly parallel C–H bond on C(5), as is seen in Fig. 3(*b*), and carbonyl groups of neighbouring molecules oppose one another across the centre of symmetry at $\frac{1}{2}$, 0, $\frac{1}{2}$, in anti-parallel arrangement, as shown in Fig. 2; the possibility of hydrogen bonding has already been indicated. (This bonding is to a different molecule, related to the one shown by the centre of symmetry at $\frac{1}{2}$, 0, 0.)

The benzenoid ring is planar within experimental error, but C(4) lies out of this plane, in the direction of the oxygen atom, by about 0·1 Å, which appears to be significant. The bonds, C(1)–C(1′), C(1)–C(2), C(2)–C(3), C(3)–C(3′), and C(3)–C(4), are very similar in length, with values within the aromatic range. Only C(1)–C(2) is appreciably different, and the shortening of it has not more than possible significance. But it is noteworthy that the lengths found for all five bonds are extraordinarily similar to those occurring in analogous situations in the molecules of naphthalene, anthracene,[14] acridine,[15] and related compounds. Should this evidence be admitted, it provides further evidence in favour of unusual conjugation to the carbonyl group.

Very few measurements have yet been made of the dimensions of three-membered rings. Bastiansen and Hassel [16] found C–C = 1·54 Å from an electron-diffraction analysis of *cyclo*propane itself. In *spiro*pentane,[17] *cyclo*propyl chloride,[18] and *cyclo*propylidene dichloride [18] somewhat shorter values (1·48—1·52 Å) have been obtained by the same method. More exact results can be derived from micro-wave spectra, provided that sufficient isotopically substituted species are available; a study [19] of *cyclo*propyl chloride, though incomplete, led to C–C = 1·47 Å and indicated unequivocally that the C–C bond was shorter than a normal single bond. A similar length was found from the spectrum of ethylene oxide.[20] A *cyclo*propane ring system occurs in the molecule of Feist's acid; [21] and, according to Petersen's preliminary report [22] of a three-dimensional *X*-ray diffraction analysis, two of the bonds in the ring have C–C = 1·49, 1·50 Å, whilst the third, between the two carboxyl groups, has 1·55 Å. The experimental evidence is thus decidedly in favour of the view that this formally single bond is contracted. Coulson and Moffitt [23] have considered the structure of strained hydrocarbon rings in its theoretical aspect. For *cyclo*propane in particular they use the concept of " bent " bonds, and hence suggest an explanation of the paradox, that there is a diminution in the internuclear distance between carbon atoms, though—on the evidence of the force constant—the bond appears to be weakened.

In the present analysis, bond C(5)–C(6) is probably shorter than 1·54 Å. The length found for the other, non-equivalent, bond, C(5)–C(5′), exceeds 1·54 Å, but the difference is certainly not significant. On the other hand, that this bond may be significantly longer than C(5)–C(6) is just possible; and, if this be so, the difference is in the same sense as that in Feist's acid, and it can be readily attributed to the unusual conditions obtaining around this bond. The co-ordinates in Table 2 lead to an angle of 110° between the C–H bonds of the methylene group and to 124° for C(4)–C(5)–H, but these deviations from the tetrahedral angle are not significant.

[13] Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.
[14] Cruickshank, *Acta Cryst.*, 1956, **9**, 915; 1957, **10**, 504.
[15] Phillips, *ibid.*, 1956, **9**, 248.
[16] Bastiansen and Hassel, cited in *Acta Chem. Scand.*, 1947, **1**, 156.
[17] Donohue, Humphrey, and Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 332.
[18] O'Gorman and Schomaker, *ibid.*, 1946, **68**, 1138.
[19] Friend, Schneider, and Dailey, *J. Chem. Phys.*, 1955, **23**, 1557.
[20] Cunningham, Boyd, Myers, Gwinn, and Le Val, *ibid.*, 1951, **19**, 676.
[21] Lloyd, Downie, and Speakman, *Chem. and Ind.*, 1954, 222, 492
[22] Petersen, *ibid.*, 1956, 904.
[23] Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1.

The other bond-angles at the heavily stressed atom, C(5), are shown in Fig. 2. In connexion with the stereochemistry of this atom, certain dihedral angles are also relevant. These are represented in Fig. 3(*b*), which shows the relative directions and projected lengths of the adjacent bonds, as they appear when viewed along the C(5)–C(4) bond. The bonds (or, better, the interatomic vectors) from C(5) to C(5′), C(6) and H(5) are shown by the continuous lines; those from C(4) to O and C(3) by broken lines. The standard deviation in these dihedral angles is perhaps ±2°, except where the hydrogen atom is involved, when it will be considerably larger.

A feature of this molecule that was not wholly expected is that the methylene and phenylene groups are in a *cis*-configuration to one another, with respect to the intervening part of the molecule. [Small internal rotations about the two C(4)–C(5) bonds would lead to the *trans*-configuration.] A tentative explanation may be based on Fig. 3(*b*): the *cis*-configuration allows the bond C(4)–C(3) to take up an azimuthal position between the bonds C(5)–C(5′) and C(5)–C(6), and the polar bond C(4)–O to lie nearly in a plane with C(5)–H. The intermolecular contact described above may also help to settle the molecule in its conformation.

In discussing the situation at C(5), it is important to have reliable information about the position of H(5); and at present this is known only very roughly. Greater certainty on this point, as well as more precise knowledge of other details of this remarkable crystal structure, must wait on the three-dimensional study which it may be possible to undertake in due course.

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