Smith, J. V. (1954). *Acta Cryst.* **7**, 479.

Smith, J. V., Karle, I. L., Hauptman, H. & Karle, J. (1960). *Acta Cryst.* **13**, 454.

Steinfink, H. (1958). *Acta Cryst.* **11**, 195.

Steinfink, H. (1961). *Acta Cryst.* **14**, 198.

Steinfink, H. & Brunton, G. (1956). *Acta Cryst.* **9**, 487.

Steinfink, H., Post, B. & Fankuchen, I. (1955). *Acta Cryst.* **8**, 420.

Takéuchi, Y. & Donnay, G. (1959). *Acta Cryst.* **12**, 465.

Takéuchi, Y. & Sadanaga, R. (1959). *Acta Cryst.* **12**, 945. Also personal communication containing refined bond distances.

Waring, J. R. S. (1961). Ph.D. thesis, University of Cambridge.

Wallmark, S. & Westgren, A. (1937). *Ark. Kemi Min. Geol.* **12**, No. 35.

Young, R. A. & Post, B. (1962). *Acta Cryst.* **15**, 337.

Zoltai, T. (1961). Private Communication.

Zoltai, T. & Buerger, M. J. (1959). *Z. Kristallogr.* **111**, 129.

Acta Cryst. (1963). **16**, 811

The Crystal Structure of Acenaphthenequinone

By T. C. W. Mak and J. Trotter

Department of Chemistry, The University of British Columbia, Vancouver, Canada

(*Received* 26 *July* 1962 *and in revised form* 26 *November* 1962)

The crystal structure of acenaphthenequinone has been determined by two-dimensional Fourier methods. There are four molecules in the orthorhombic unit cell, which has dimensions

$$a = 7{\cdot}81,\ b = 27{\cdot}0,\ c = 3{\cdot}851\ \text{Å}\ .$$

The space group is $P2_12_12_1$. The molecule is planar, and the molecular dimensions and intermolecular distances are normal for this type of structure.

Introduction

Study of the crystal structure of acenaphthenequinone was undertaken as part of an investigation of a series of acenaphthene derivatives.

Experimental

A crystalline sample of acenaphthenequinone was kindly made available to us by Mr I. G. Csizmadia and Dr L. D. Hayward. It consisted of orange-yellow needles elongated along the c-axis, with the (010) face well developed. The cell dimensions were determined from Weissenberg and precession photographs of a crystal mounted about the c-axis. The density was measured by flotation in aqueous potassium iodide.

Crystal data

Acenaphthenequinone (1,2-acenaphthenedione), $C_{10}H_6(CO)_2$; $M = 182{\cdot}2$; m.p. 273–274 °C.

Orthorhombic, $a = 7{\cdot}81 \pm 0{\cdot}01$, $b = 27{\cdot}0 \pm 0{\cdot}05$, $c = 3{\cdot}851 \pm 0{\cdot}005$ Å.

Volume of the unit cell $= 812$ Å^3.

Density, calculated (with $Z = 4$) $= 1{\cdot}49$, measured $= 1{\cdot}48$ g.cm^{-3}.

Absorption coefficients for X-rays, $\lambda = 1{\cdot}5418$ Å, $\mu = 9{\cdot}83$ cm^{-1}; $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}24$ cm^{-1}.

Total number of electrons per unit cell $= F(000) = 376$.

Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

Space group is $P2_12_12_1$–D_2^4, as confirmed later in the analysis.

For intensity purposes the $hk0$ reflexions were recorded on multiple-film Weissenberg photographs, using unfiltered Cu $K\alpha$ radiation. The $0kl$ data were collected on precession films with related time exposures, Mo $K\alpha$ radiation being used. The intensities were estimated visually. The relative values of the structure amplitudes were derived by applying the usual Lorentz and polarization factors, the absolute scale being established later by correlation with the calculated structure factors.

Absorption correction was considered unnecessary since the crystal used had a mean diameter of 0·06 mm. 152 independent $hk0$ reflexions were observed (excluding the 020 reflexion, which was cut off by the beam trap), representing 54% of the total number theoretically observable with Cu $K\alpha$ radiation. Only 33 $0kl$ reflexions were recorded, representing about 20% of the total number observable.

Structure analysis

Space group $P2_12_12_1$ is non-centrosymmetric, but it has centrosymmetric projections (plane group pgg) in all three principal directions. The relations between space group and our projection coordinates are those formulated in Table 1.

Table 1. *Transformations between space group and projection coordinates*

Space group coordinates	Projection coordinates (001)	(100)	(010)
x	$x' = x - \frac{1}{4}$	$x'' = x$	$x''' = x$
y	$y' = y$	$y'' = y - \frac{1}{4}$	$y''' = y$
z	$z' = z$	$z'' = z$	$z''' = z - \frac{1}{4}$

[001] *projection*

The shortness of the c-axis promised good resolution of all the atoms in this projection. Packing and symmetry considerations suggested that the four molecules in the unit cell must be lined up approximately in the direction of the b-axis. Our search for a trial structure was guided by the observation that the 0*k*0 reflexions exhibit a distinctive feature, being relatively weak for $k=4n+2$ and strong for $k=4n$. The very strong 0,24,0 reflexion corresponds to a planar spacing of 1·13 Å, which is slightly less than half the width of a benzene ring. This indicated that in the [001] projection the aromatic carbon atoms must lie very close to the (0,24,0) planes. The angle between the molecular plane and the (001) plane was estimated to be about 24° by comparing the lengths of the molecule and the a-axis. (The final results show it to be 29°.) The orientation of the aromatic nucleus was also in complete agreement with that deduced from the 'benzene' reflexions. The x- and y-parameters, referred to the molecular origin (defined as centre of the C(5*a*)–C(8*b*) bond) were obtained from the projection of a CENCO Petersen molecular model held in the deduced orientation.

Examination of the Patterson projection along [001] confirmed the above deductions. From the multiple vector peak between naphthalene rings related by symmetry, the coordinates of the molecular origin were estimated as $Y' \simeq 0{\cdot}125$, $X' \simeq 0{\cdot}190$ or 0·310. The former value for X' was taken since it gave better agreement between the observed and calculated structure amplitudes for some low-order reflexions. (The final coordinates of the molecular origin are $X'=0{\cdot}1762$, $Y'=0{\cdot}1249$). *hk*0 structure factors were now calculated by means of the carbon and oxygen scattering factors from *Tabellen zur Röntgenstrukturanalyse* (Sagel, 1958), with an overall isotropic temperature factor $B=4{\cdot}5$ Å^2. The reliability factor R for the observed reflexions was 40·8%, but there appeared to be no serious discrepancy between the observed and calculated structure amplitudes. 123 terms (including $F(000)$) were used in a Fourier synthesis, which gave good resolution of all the atoms. Recalculation of the structure factors with atomic coordinates determined from the electron-density map reduced R to 28·8%. Refinement of positional and

Table 2. *Observed and calculated structure factors**

h k l	F_o	F_c
0 2 0	not obs.	−4·6
0 4 0	75·9	−85·5
0 6 0	<0·6	1·8
0 8 0	60·8	−55·6
0 10 0	10·6	12·2
0 12 0	14·6	16·6
0 14 0	6·0	−8·4
0 16 0	16·2	−16·1
0 18 0	2·7	−1·4
0 20 0	9·5	−12·2
0 22 0	<1·3	1·7
0 24 0	29·5	29·4
0 26 0	<1·3	1·8
0 28 0	<1·2	−2·9
0 30 0	<1·2	−0·9
0 32 0	<0·9	−2·3
0 34 0	<0·7	−0·3
1 1 0	14·7	−15·9
1 2 0	62·3	−55·7
1 3 0	9·7	11·4
1 4 0	<0·5	−1·3
1 5 0	19·4	21·0
1 6 0	20·2	−20·5
1 7 0	6·5	−8·4
1 8 0	13·7	−13·2
1 9 0	15·5	17·0
1 10 0	52·1	−48·4
1 11 0	30·6	−29·8
1 12 0	2·0	4·0
1 13 0	6·3	−6·9
1 14 0	19·6	20·6
1 15 0	21·9	20·6
1 16 0	4·0	5·4
1 17 0	<1·1	−1·1
1 18 0	12·7	12·0
1 19 0	<1·2	0·0
1 20 0	2·1	−1·9
1 21 0	10·6	−10·3
1 22 0	11·3	12·8
1 23 0	<1·3	1·8
1 24 0	<1·3	−1·0
1 25 0	4·5	7·8
1 26 0	10·3	−12·0
1 27 0	<1·3	−4·1
1 28 0	<1·2	1·3
1 29 0	<1·2	1·5
1 30 0	<1·1	−0·5
2 0 0	17·5	21·4
2 1 0	38·8	−38·9
2 2 0	16·3	−15·2
2 3 0	8·9	−12·7
2 4 0	30·8	−28·1
2 5 0	2·6	−2·3
2 6 0	11·1	13·4
2 7 0	<0·7	1·8
2 8 0	3·7	−4·8
2 9 0	21·4	20·4
2 10 0	4·1	6·9
2 11 0	17·7	−16·8
2 12 0	30·7	29·4
2 13 0	7·0	6·6
2 14 0	<1·0	−2·2
2 15 0	3·1	4·5
2 16 0	6·8	−8·1
2 17 0	12·7	−11·8
2 18 0	3·5	3·4
2 19 0	<1·2	−1·1
2 20 0	5·7	5·5
2 21 0	2·2	4·3
2 22 0	4·5	−5·8
2 23 0	<1·3	3·2
2 24 0	9·1	−6·5
2 25 0	<1·3	2·0
2 26 0	1·6	1·7
2 27 0	2·2	1·1
2 28 0	<1·2	−0·8
2 29 0	3·5	−3·2
2 30 0	<1·1	0·9
3 1 0	37·5	31·8
3 2 0	8·4	11·1
3 3 0	15·7	−14·9
3 4 0	38·8	−32·9
3 5 0	3·7	−3·5
3 6 0	<0·9	1·8
3 7 0	27·3	−26·7
3 8 0	11·1	11·6
3 9 0	25·2	−22·5
3 10 0	<0·9	−2·3
3 11 0	26·0	26·0
3 12 0	5·5	6·4
3 13 0	15·5	16·0
3 14 0	4·2	−2·9
3 15 0	<1·2	−2·5
3 16 0	13·7	−14·0
3 17 0	<1·2	0·7
3 18 0	<1·2	2·9
3 19 0	12·1	−12·7
3 20 0	<1·3	4·7
3 21 0	3·9	−6·5
3 22 0	<1·3	1·1
3 23 0	10·4	11·3
3 24 0	2·2	4·0
3 25 0	4·9	6·5
3 26 0	3·0	−4·3
3 27 0	2·1	−3·5
3 28 0	3·4	−3·1
3 29 0	<1·1	−0·3
4 0 0	<0·9	−1·5
4 1 0	26·2	−24·0
4 2 0	22·8	−21·6
4 3 0	2·8	−5·5
4 4 0	5·9	−6·7
4 5 0	15·7	14·5
4 6 0	5·9	6·1
4 7 0	2·7	−6·1
4 8 0	16·2	14·4
4 9 0	<1·1	−0·4
4 10 0	<1·1	−1·0
4 11 0	6·0	−6·4
4 12 0	5·5	−5·3
4 13 0	<1·2	−3·0
4 14 0	8·2	10·6
4 15 0	12·8	10·6
4 16 0	4·3	−5·0
4 17 0	3·5	3·1
4 18 0	4·2	6·9
4 19 0	3·6	−2·1
4 20 0	6·5	4·6
4 21 0	<1·4	1·1
4 22 0	10·4	−11·0
4 23 0	<1·3	1·6
4 24 0	<1·3	−0·3
4 25 0	<1·2	−2·9
4 26 0	<1·2	−2·2
5 1 0	7·9	−8·5

Table 2 (*cont.*)

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
5 2 0	5·0	−5·2	6 14 0	3·2	−4·9	8 3 0	6·1	−6·2	0 9 1	<4·4	4·5
5 3 0	<1·1	−3·1	6 15 0	14·7	−12·3	8 4 0	4·3	−4·5	0 10 1	18·5	−21·1
5 4 0	6·0	7·3	6 16 0	14·5	−12·3	8 5 0	5·2	−5·3	0 11 1	14·3	−13·3
5 5 0	17·6	13·5	6 17 0	<1·3	−0·7	8 6 0	4·2	2·2	0 12 1	<4·7	−4·4
5 6 0	<1·2	1·5	6 18 0	<1·3	2·9	8 7 0	5·2	5·1	0 13 1	9·6	−9·0
5 7 0	7·6	−10·1	6 19 0	6·5	5·0	8 8 0	6·5	3·2	0 14 1	18·8	16·1
5 8 0	17·7	20·5	6 20 0	2·9	4·0	8 9 0	<1·4	2·2	0 15 1	7·0	−4·5
5 9 0	2·5	−2·7	6 21 0	<1·2	−3·2	8 10 0	<1·2	−0·5	0 16 1	11·5	−11·5
5 10 0	<1·2	−2·1	6 22 0	<1·1	0·8	8 11 0	<1·2	0·9	0 17 1	<5·4	−2·6
5 11 0	12·8	13·0	6 23 0	<1·0	1·3	8 12 0	<1·1	1·2	0 18 1	6·7	−5·5
5 12 0	6·5	5·0	6 24 0	<0·9	1·2	8 13 0	<1·1	−0·9	0 19 1	<5·7	0·3
5 13 0	<1·3	3·0	6 25 0	<0·9	−0·5	8 14 0	<1·0	0·5	0 20 1	13·9	−14·7
5 14 0	7·0	7·2	6 26 0	4·2	3·3	8 15 0	3·5	−2·9	0 21 1	<5·9	−2·9
5 15 0	<1·3	−1·2				8 16 0	<1·2	0·2	0 22 1	<5·9	2·6
5 16 0	19·3	−18·6	7 1 0	4·0	−3·2	8 17 0	<1·0	0·0	0 23 1	12·9	11·0
5 17 0	<1·4	−1·1	7 2 0	5·0	4·8	8 18 0	<0·9	0·2	0 24 1	<6·2	00·1
5 18 0	9·1	−8·0	7 3 0	3·2	4·9	8 19 0	4·0	3·1	0 25 1	10·7	9·9
5 19 0	4·0	−1·9	7 4 0	7·2	4·0	8 20 0	<0·7	−1·3	0 26 1	<6·4	−1·5
5 20 0	2·8	−2·3	7 5 0	<1·4	1·5				0 27 1	<6·5	−5·9
5 21 0	<1·3	0·2	7 6 0	13·8	−12·7	0 2 0	not obs.	5·3			
5 22 0	5·2	4·9	7 7 0	4·5	6·0	0 4 0	86·7	−95·9	0 1 2	<5·2	−2·6
5 23 0	<1·2	1·4	7 8 0	10·4	−8·8	0 6 0	<2·8	−1·4	0 2 2	<5·2	13·0
5 24 0	<1·2	2·3	7 9 0	<1·3	−4·4	0 8 0	65·7	−60·6	0 3 2	<5·2	−2·5
5 25 0	3·3	−3·7	7 10 0	10·4	6·7	0 10 0	14·1	−13·2	0 4 2	<5·2	−8·3
5 26 0	<1·0	−2·1	7 11 0	<1·3	−1·8	0 12 0	15·5	10·9	0 5 2	<5·3	−6·1
			7 12 0	<1·3	−0·2	0 14 0	6·9	9·6	0 6 2	12·3	−15·3
6 0 0	8·5	7·4	7 13 0	3·8	−3·4	0 16 0	18·2	−17·1	0 7 2	14·7	15·6
6 1 0	3·7	−4·3	7 14 0	<1·3	−0·4	0 18 0	<4·5	2·0	0 8 2	10·5	13·5
6 2 0	8·6	10·1	7 15 0	3·7	−4·0	0 20 0	12·3	−12·1	0 9 2	10·6	15·0
6 3 0	5·7	−3·5	7 16 0	4·1	3·9	0 22 0	<5·1	−1·8	0 10 2	<5·4	−3·5
6 4 0	<1·2	0·9	7 17 0	4·9	5·3	0 24 0	34·9	29·3	0 11 2	7·5	−7·8
6 5 0	8·1	−7·4	7 18 0	<1·1	2·0				0 12 2	<5·5	−1·8
6 6 0	2·2	2·0	7 19 0	<1·0	−1·0	0 1 1	43·8	43·3	0 13 2	<5·8	2·3
6 7 0	11·1	11·1	7 20 0	<1·0	1·6	0 2 1	33·9	40·1	0 14 2	7·8	9·3
6 8 0	11·9	−11·6	7 21 0	3·3	1·2	0 3 1	47·0	−49·0	0 15 2	<5·9	−4·1
6 9 0	15·2	14·6	7 22 0	<0·9	−0·3	0 4 1	67·6	58·6	0 16 2	16·2	15·6
6 10 0	14·2	−13·3				0 5 1	<3·9	−2·1	0 17 2	<5·9	−6·8
6 11 0	2·2	−2·9	8 0 0	<1·3	3·0	0 6 1	<4·0	−4·8	0 18 2	<6·0	−1·2
6 12 0	16·3	13·8	8 1 0	<1·5	2·7	0 7 1	27·5	29·0	0 19 2	<6·1	−2·0
6 13 0	<1·4	0·8	8 2 0	2·2	−1·9	0 8 1	32·8	30·7	0 20 2	8·5	−6·2

* The phases of the *hk*0 and 0*kl* structure factors are referred to the respective origins of the (001) and (100) projections. The calculated 0*k*0 structure amplitudes are not the same since hydrogen-atom contributions are not included in computing 0*kl* structure factors.

temperature parameters proceeded by computing successive $(F_o - F_c)$ syntheses, and after five cycles R dropped to 15·0%.

At this point, the contributions of the hydrogen atoms were considered. The positional parameters were obtained by measurement on a molecular model. An isotropic temperature factor of 5·0 Å^2 was assigned to each of the six hydrogen atoms. The inclusion of these hydrogen atom contributions led to a significant improvement in the agreement of the low-order data, especially the 0*k*0 reflexions, and the R factor was lowered to 13·9%.

Measured and calculated structure factors are compared in Table 2, and the final *hk*0 F_o synthesis is shown in Fig. 1.

[100] *projection*

Since the number of observed 0*kl* reflexions was smaller than the number of parameters to be determined, good resolution was not expected in this projection. Approximate z-coordinates for the carbon and oxygen atoms were obtained by measurement on a molecular model. The initial 0*kl* discrepancy was 13·0%, for the observed reflexions, and this was reduced by an $(F_o - F_c)$ synthesis to 11·6%. Hydrogen-atom contributions were not considered. Measured and calculated 0*kl* structure factors are included in Table 2. The final electron density projection along [100] is shown in Fig. 2.

Coordinates and molecular dimensions

The final positional and individual temperature parameters are listed in Table 3 where the atomic coordinates are referred to the space-group origin and expressed as fractions of the unit-cell edges. The deviations of the atoms from the best plane are listed in the last column of Table 3.

The bond lengths and valency angles, calculated from the x, y, z-coordinates of Table 3, are shown in Fig. 3.

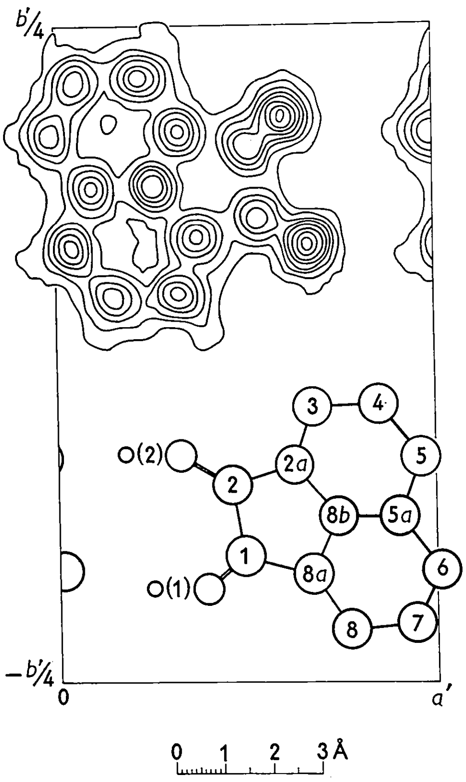

Fig. 1. Electron-density projection along [001]. Contour lines are drawn at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

Table 3. *Final parameters**

Atom	x	y	z	B (Å^2)	Δ (Å)
C(1)	0·7542	0·1556	0·296	5·2	0·032
C(2)	0·7852	0·1025	0·170	5·2	0·028
C(2*a*)	0·6267	0·0864	−0·005	4·3	0·057
C(3)	0·5745	0·0427	−0·143	4·1	−0·030
C(4)	0·4006	0·0407	−0·276	4·9	−0·047
C(5)	0·2910	0·0802	−0·262	4·5	0·003
C(5*a*)	0·3437	0·1242	−0·109	4·1	0·044
C(6)	0·2390	0·1659	−0·062	4·5	0·016
C(7)	0·3048	0·2052	0·118	4·9	−0·045
C(8)	0·4779	0·2097	0·253	4·1	−0·013
C(8*a*)	0·5757	0·1683	0·201	4·3	0·016
C(8*b*)	0·5086	0·1256	0·037	3·6	−0·012
O(1)	0·8533	0·1793	0·457	5·7	−0·029
O(2)	0·9168	0·0805	0·223	5·7	−0·024
H(3)	0·658	0·013		5·0	
H(4)	0·364	0·006		5·0	
H(5)	0·161	0·073		5·0	
H(6)	0·111	0·163		5·0	
H(7)	0·237	0·236		5·0	
H(8)	0·517	0·240		5·0	

* The numbering of the carbon atoms (see Fig. 3) follows the rules recommended by the I.U.P.A.C. (1958). Numbers given to hydrogen atoms are those of the carbon atoms to which they are attached.

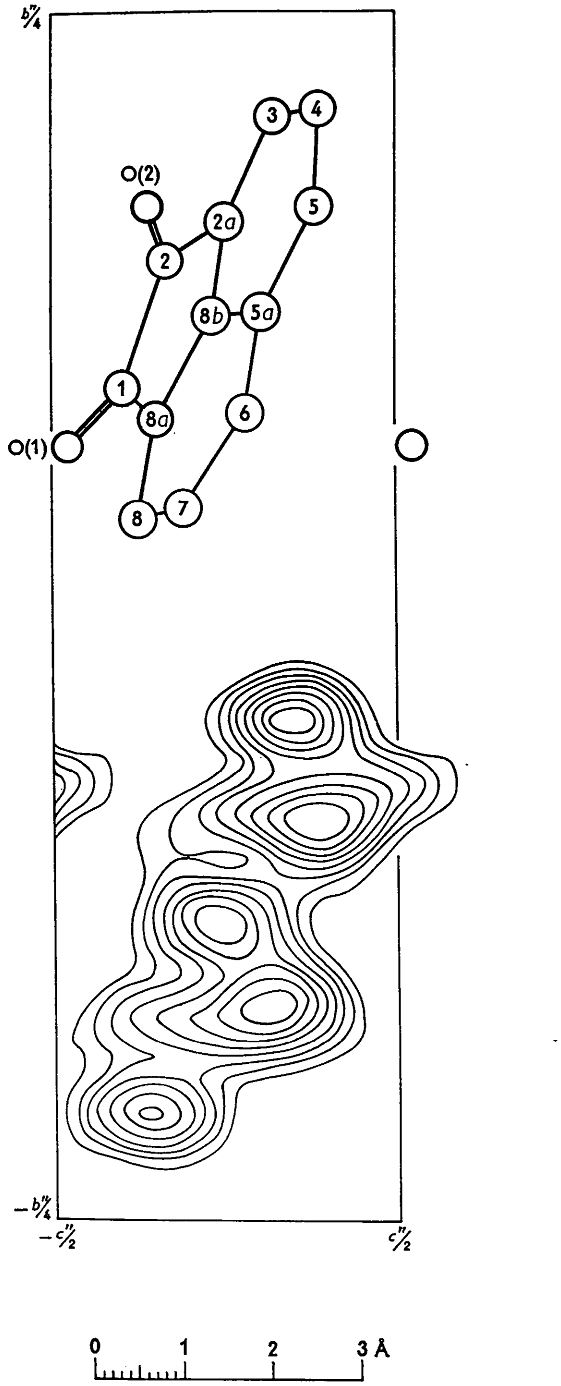

Fig. 2. Electron-density projection along [100]. Contour lines are drawn at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

The orientation of the molecule in the crystal is given in Table 4 in terms of the angles χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; and χ_N, ψ_N, ω_N which the molecular axes L, M (Fig. 3) and the plane normal N make with the crystallographic axes. The axis L was taken through the midpoints of the C(3)–C(4) and C(7)–C(8) bonds, and axis M through atom C(5*a*) and the centre of the C(1)–C(2) bond. L, M and N are thus not exactly orthogonal, the angles being $\angle LM = 88{\cdot}5°$, $\angle MN = 90{\cdot}9°$, and $\angle LN = 89{\cdot}9°$. The angle between the plane of the molecule and the (001) plane is 28·9°.

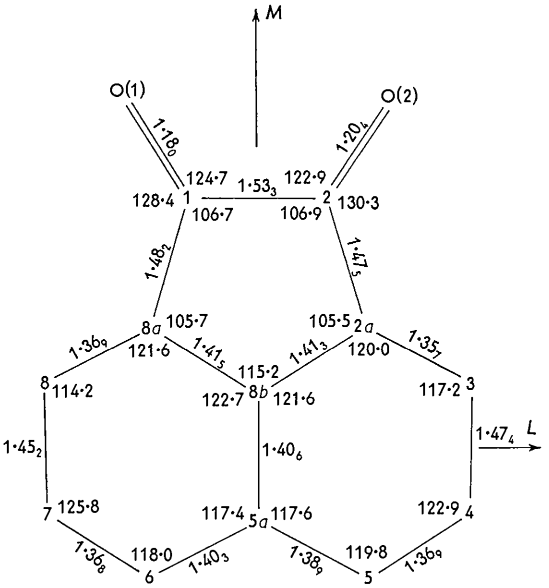

Fig. 3. Numbering and dimensions of the acenaphthenequinone molecule.

Table 4. *Molecular orientation in the unit cell*

$\chi_L = 81\cdot0°$	$\chi_M = 21\cdot7°$	$\chi_N = 109\cdot2°$
$\psi_L = 159\cdot3°$	$\psi_M = 89\cdot8°$	$\psi_N = 110\cdot8°$
$\omega_L = 108\cdot5°$	$\omega_M = 68\cdot4°$	$\omega_N = 28\cdot9°$

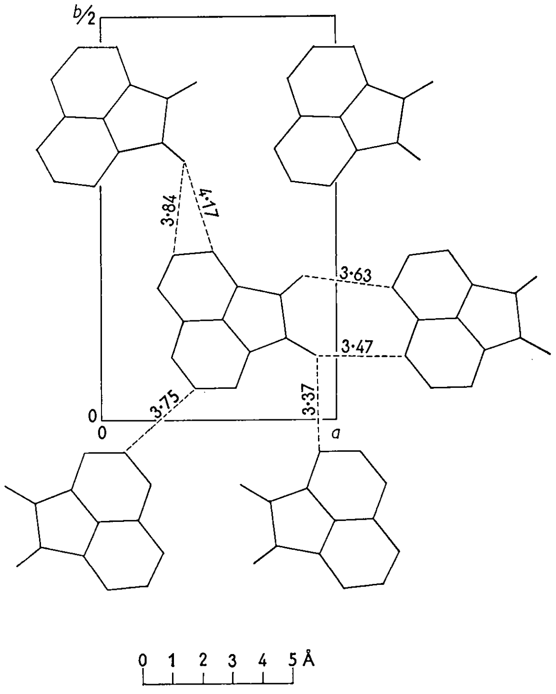

Fig. 4. Projection of the structure along [001], showing the shorter intermolecular distances.

The standard deviations for the x and y coordinates, calculated from the $hk0$ data using Cruickshank's (1949) formulae, are $\sigma(x)=\sigma(y)=0\cdot015$ Å for carbon, $0\cdot011$ Å for oxygen. $\sigma(z)$ was not calculated from the $0kl$ structure factors, which are few in number, but is certainly somewhat greater. The standard deviations of the bond lengths are about $0\cdot02_1$ Å for C–C bonds and $0\cdot01_9$ Å for C–O bonds. These values may be compared with the root-mean-square deviation of the individual bond lengths from the mean distances of chemically equivalent bonds, which is only 0·007 Å. All valency angles have a standard deviation of approximately 1·9°.

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between molecules related by translation c is 3·37 Å. Packing of the molecules and some shorter lateral intermolecular contacts are illustrated in Fig. 4.

Discussion

The acenapthenequinone molecule is probably planar within the limits of experimental error. The maximum deviation from the mean plane is 0·057 Å for carbon atom C(2a), but this, and other apparently large, deviations from planarity are due to the fact that the z coordinates have been determined somewhat imprecisely.

The good agreement between chemically equivalent bond lengths and valency angles (Fig. 3) suggests that the molecular dimensions have been determined with better accuracy than is indicated by the estimated standard deviations; since the parameters have been derived from two-dimensional data only, however, we will not attempt any comparison of these dimensions with those of similar molecules. Since our chief interest was in the nitrate esters of this series, no three-dimensional work on acenaphthenequinone was carried out.

We are grateful to Mr I. G. Csizmadia and Dr L. D. Hayward for their continued interest in the problem, and for much helpful discussion and advice. We are also indebted to Dr F. R. Ahmed for kindly making available his IBM 1620 Fourier and Structure Factor programs, and to the staff of the University of British Columbia Computing Centre for assistance with the operation of the computer. Finally, we wish to thank the National Research Council of Canada for financial support and for the award of a studentship to one of us (T. C. W. M.).

References

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
I.U.P.A.C. 1957 Rules (1958). *Nomenclature of Organic Chemistry* 1957. London: Butterworth.
Sagel, K. (1958). *Tabellen zur Röntgenstrukturanalyse.* Berlin: Springer.