Acta Cryst. (1971). B**27**, 1846

The Crystal and Molecular Structure of 2-Methyl-4,5-dimethoxy-*p*-quinone (Fumigatin Methyl Ether), $C_9H_{10}O_4$

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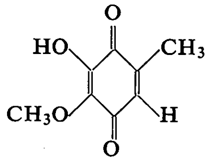
(*Received* 18 *December* 1970)

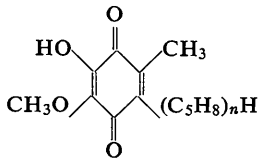
Crystals of fumigatin methyl ether are monoclinic, space group $C2/c$, with unit-cell dimensions $a=28{\cdot}008$, $b=3{\cdot}948$, $c=16{\cdot}445$ Å, $\beta=102{\cdot}53°$. The structure was derived from a three-dimensional Patterson synthesis and refined to an R value of 9·0% for 1105 reflexions [866 counter data ($\theta\le 58°$) and 239 film data ($\theta>58°$)]. The molecules are stacked in columns along [010] with $>C=O$ of one molecule over the centre of the ring of the next. Perpendicular distance between the rings of consecutive molecules is 3·48 Å.

Introduction

The crystal structure of fumigatin methyl ether (FME) is of interest because of its relation to the ubiquinones or coenzymes Q, which contain the FME moiety extended by an isoprenoid side chain at position 3.



Fumigatin



Ubiquinones, $n=6\ldots10$

A proposed structure of the isoprenoid side chain has been given by MacGillavry (1959).

Experimental

When crystallized from ethyl alcohol, FME forms orange-red needles along [010], exhibiting the forms {110} and {201} and sometimes {001}. The needles show perfect cleavage along (001). The following cell constants were derived by a least-squares technique from zero-layer Weissenberg diagrams about [010] and [110], calibrated with Al powder lines:

$$a=28{\cdot}008\pm0{\cdot}003 \text{ Å}$$
$$b=\ 3{\cdot}948\pm0{\cdot}002 \qquad \beta=102{\cdot}53\pm0{\cdot}01°\,.$$
$$c=16{\cdot}445\pm0{\cdot}002$$

Indicated limits of accuracy are the standard deviations. The density as found by flotation is 1·36 g.cm^{-3}; calculated density for $Z=8$ is 1·364 g.cm^{-3}. The extinctions hkl (when $h+k$ is odd) and $h0l$ (when l is odd) are consistent with space groups $C2/c$ or Cc.

Two independent sets of intensities were collected. The first one consisted of photometrically measured intensities obtained from integrated Weissenberg diagrams of the first four layers about [010]. The layers were correlated provisionally by means of a zero-layer Weissenberg diagram about [110]. Exposures were made with Cu $K\alpha$ radiation. In all, 1105 independent reflexions were measured. Because of the small size of the crystal, absorption corrections were assumed to be negligible ($\mu=10{\cdot}6$ cm^{-1}). The second set of intensities consisted of 866 reflexions with $\theta\le58°$, remeasured on a Nonius three-circle diffractometer by means of the θ–2θ scan technique. We employed a scintillation counter, Ni-filtered Cu $K\alpha$ radiation and a pulse-height analyser. The crystal was mounted with [010] parallel to the φ axis. Again, no absorption correction was applied, although it is not altogether negligible for this crystal (dimensions about $0{\cdot}2\times0{\cdot}6\times0{\cdot}7$ mm).

Structure determination and refinement

The structure was determined from a three-dimensional Patterson synthesis, which could be interpreted on the basis of the space group $C2/c$. From the peaks surrounding the origin, the orientation of the rings could be found except for an ambiguity with respect to the attachment of the methoxyl and methyl groups. Packing considerations enabled us to identify the peaks corresponding to vectors joining the ring centres across the centres of symmetry, thereby fixing the positions of the molecules relative to the centres of symmetry.

The above mentioned ambiguity resolved itself during the refinement which started with [010] electron density projections and proceeded *via* generalized [101] projections and three-dimensional electron density syntheses to three-dimensional least-squares calculations. Individual layer-scale factors of the earlier stages of refinement were replaced by an overall scale factor when anisotropic thermal parameters were introduced. Hydrogen atoms were located from a difference synthesis. Their parameters were included in the final least-squares cycles, but they were not refined. The hydrogen atoms were allotted isotropic temperature parameters (B) equal to the equivalent

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Table 1. *Final positional and thermal parameters*

Estimated standard deviations given in parenthese refer to the last decimal positions. U_{ij} are the components of the mean-square displacement tensor $\mathbf{u}^2=\sum\sum l_i l_j U_{ij}$

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1)	+0·12551 (17)	+0·30897 (120)	+0·56000 (28)	+0·0484 (26)	+0·0469 (29)	+0·0421 (23)	+0·0103 (40)	+0·0027 (39)	+0·0174 (38)
C(2)	+0·17861 (18)	+0·21314 (122)	+0·58211 (29)	+0·0469 (25)	+0·0455 (28)	+0·0475 (25)	+0·0017 (39)	+0·0129 (39)	+0·0097 (40)
C(3)	+0·19739 (18)	+0·05034 (130)	+0·52508 (32)	+0·0442 (25)	+0·0535 (30)	+0·0554 (28)	+0·0114 (41)	+0·0074 (44)	+0·0189 (43)
C(4)	+0·16789 (17)	−0·03814 (122)	+0·44311 (30)	+0·0463 (26)	+0·0474 (29)	+0·0512 (26)	+0·0148 (39)	+0·0040 (40)	+0·0309 (42)
C(5)	+0·11608 (16)	+0·05448 (115)	+0·42011 (26)	+0·0413 (23)	+0·0443 (27)	+0·0389 (22)	+0·0031 (36)	−0·0015 (35)	+0·0205 (36)
C(6)	+0·09548 (16)	+0·21698 (122)	+0·47750 (28)	+0·0388 (22)	+0·0495 (28)	+0·0462 (24)	+0·0203 (38)	−0·0023 (38)	+0·0227 (37)
C(7)	+0·20706 (23)	+0·30872 (151)	+0·66674 (33)	+0·0684 (36)	+0·0707 (37)	+0·0487 (28)	+0·0062 (57)	+0·0027 (50)	−0·0009 (51)
C(8)	+0·10164 (27)	+0·13416 (170)	+0·27427 (32)	+0·0962 (46)	+0·0805 (40)	+0·0365 (24)	+0·0240 (67)	+0·0038 (49)	+0·0205 (53)
C(9)	+0·01119 (20)	+0·23496 (178)	+0·40021 (38)	+0·0420 (29)	+0·0980 (43)	+0·0683 (37)	+0·0264 (55)	−0·0519 (64)	−0·0092 (52)
O(1)	+0·10810 (15)	+0·46783 (113)	+0·60982 (22)	+0·0674 (25)	+0·1016 (32)	+0·0464 (20)	+0·0499 (45)	−0·0339 (40)	+0·0212 (37)
O(2)	+0·18679 (14)	−0·19952 (106)	+0·39348 (25)	+0·0596 (23)	+0·0797 (28)	+0·0654 (24)	+0·0403 (39)	−0·0190 (39)	+0·0439 (38)
O(3)	+0·08996 (13)	−0·04668 (90)	+0·34502 (20)	+0·0534 (20)	+0·0651 (23)	+0·0427 (17)	+0·0051 (33)	−0·0110 (31)	+0·0142 (29)
O(4)	+0·04903 (12)	+0·31694 (106)	+0·47048 (23)	+0·0363 (18)	+0·0900 (28)	+0·0621 (23)	+0·0306 (34)	−0·0338 (39)	+0·0123 (32)
H(1)	+0·230	−0·025	+0·537						
H(2)	+0·245	+0·190	+0·690						
H(3)	+0·194	+0·215	+0·712						
H(4)	+0·207	+0·520	+0·676						
H(5)	+0·137	+0·250	+0·306						
H(6)	+0·092	+0·035	+0·230						
H(7)	+0·068	+0·280	+0·250						
H(8)	−0·021	+0·310	+0·417						
H(9)	+0·006	+0·075	+0·408						
H(10)	+0·020	+0·330	+0·346						

isotropic B (Hamilton, 1959) of the atoms to which they are attached. The refinement with the photographic data brought the R value down to 10·3%. The 11 strongest reflexions, which had consistently high calculated structure factors and apparently suffered from extinction, were omitted from the last calculations.

Two least-squares cycles were run with the resulting parameters, using the counter data. These converged to an R value of 6·1%. The four strongest reflexions, suffering from extinction, were omitted.

Finally, a few cycles were run using counter data supplemented by photographic data for $\theta > 58°$. These converged to $R = 9{\cdot}0\%$.

Final parameters from the last, mixed refinement are listed in Table 1.*

The least-squares program used was a block-diagonal one; the weighting scheme was that suggested by Cruickshank *et al.* (1961). The scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Results and discussion

In Fig. 1(*a*), which is obtained from the refinement of the photographic data, conspicuous differences occur between the two O–CH_3 distances, between the two C–O–CH_3 angles and between the angles C(5)–C(6)–O(4) and C(6)–C(5)–O(3). As at first sight the two OCH_3 groups appeared equivalent, the significance of these differences is open to question. Repeating the refinement with the counter data gave the results of Fig. 1(*b*). But the differences persisted, though the O–CH_3 distances were considerably shortened, suggesting that the above mentioned features, especially the angular ones, are real after all. As the counter data were far from complete ($\theta \leq 58°$), it was thought that refinement with the counter data supplemented by the photographic data for $\theta > 58°$ might give the most reliable results. Therefore, in the following discussion the results from the mixed refinement are used.

Bond distances and angles

Fig. 1(*c*) gives the bond distances and interbond angles from the mixed refinement. The two C=O distances differ by 0·026 Å which, with the calculated standard deviation of 0·007 Å for the individual bonds, would be just significant. Their average of 1·228 Å agrees well with the values of 1·222 and 1·223 Å as found for *p*-benzoquinone (Trotter, 1960) and 2,5-dimethyl-*p*-benzoquinone (DMPQ) (Hirshfeld & Rabinovich, 1967), respectively. Bond distances and angles on the side of the methyl group of C(7) are very similar to the corresponding ones in DMPQ.

The C(5)–C(6) bond is 0·033 Å longer than the C(2)–C(3) bond, which should be highly significant. This elongation can be explained partly by the con-

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* A list of structure factors can be obtained on request from the authors.

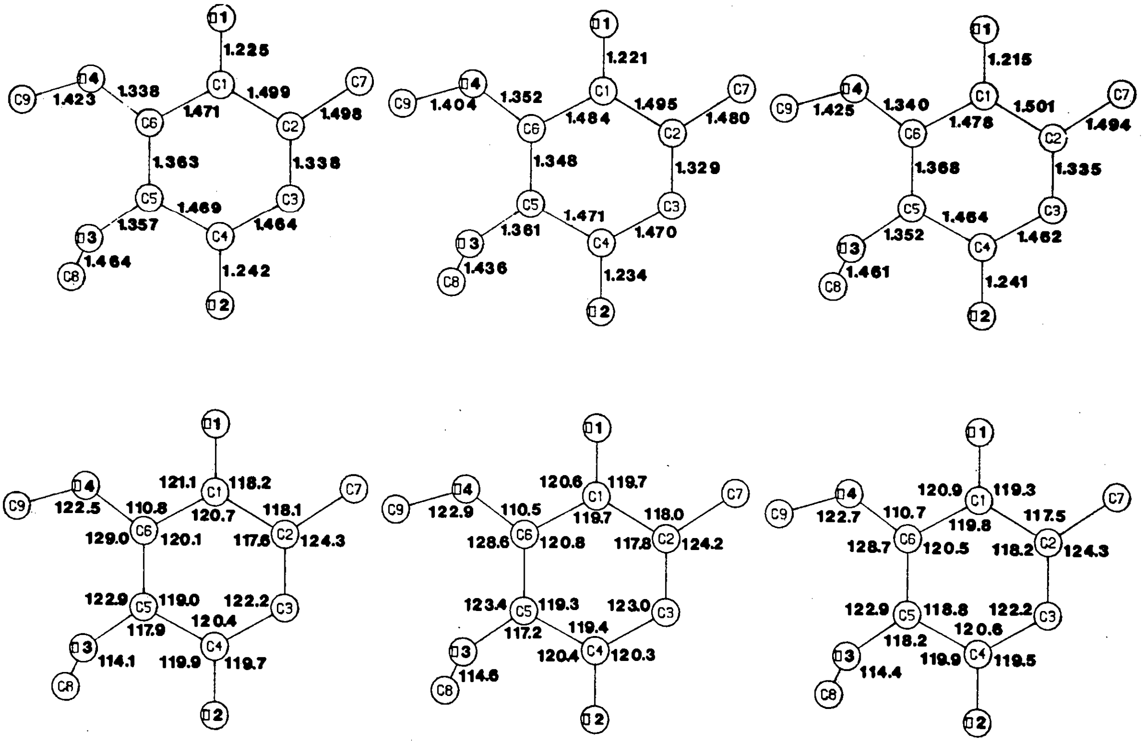
tribution of the resonance structures with a single bond between C(5) and C(6), partly as an overcrowding effect caused by the two adjacent OCH_3 groups.

The OCH_3 *groups*

The most significant features of the structure are the large differences between the two O–CH_3 distances, between the angles C(5)–O(3)–C(8) and C(6)–O(4)–C(9) and between the angles C(5)–C(6)–O(4) and C(6)–C(5)–O(3). Although little difference, chemically, is expected between the two OCH_3 groups, in fact one does exist. The distances of the atoms from the best plane through the six-membered ring are indicated in Fig. 2. Atom C(9) at 0·17 Å from this plane is practically coplanar with the ring, while C(8) is 1·17 Å out of plane. As we shall see, this renders the two OCH_3 groups inequivalent and might account for the above mentioned differences.

In molecules possessing one or more unhindered OCH_3 groups attached to a planar-conjugated system [*e.g.* 1,4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950; *p,p'*-dimethoxybenzophenone (Karle, Hauptman, Karle & Wing, 1958; 5-methoxy-2-nitrosophenol (Bartindale, Crowder & Morley, 1959], the OCH_3 groups are always approximately coplanar with the conjugated system. In this conformation, resonance is possible between the *p*-electrons of the oxygen which may be assumed to be sp_2 hybridized (Pullman & Pullman, 1963) and the π-electrons of the conjugated system; hence, the planar conformation represents in general an energy minimum. In 2-methoxy-*p*-benzoquinone, therefore, we would expect a planar conformation, but in this case two conformations must be considered [Fig. 3(*a*) and (*b*)]. If normal bond angles are maintained, the conformation of Fig. 3(*b*) would have a non-bonded O···CH_3 distance of 2·4–2·5 Å. The other conformation would have no such small distance, and one would expect 2-methoxy-*p*-benzoquinone to have the conformation of Fig. 3(*a*).

If *p*-benzoquinone carries two adjacent OCH_3 groups, three types of planar conformations have to be considered [Fig. 3(*c*), (*d*) and (*e*)]. Conformation (*c*) can be ruled out immediately as sterically quite impossible. With normal bond angles, both conformations (*d*) and (*e*) would involve two very close O···CH_3 approaches of 2·4–2·5 Å. To obtain more normal O···CH_3 distances, rather large angle deformations are necessary, and it is clear that a planar conformation of 2,3-dimethoxy-*p*-benzoquinone would involve a considerable strain energy. The observed conformation of FME suggests that this strain energy is larger than the extra resonance energy of a completely planar conformation. Apparently, a compromise exists: one OCH_3 group is essentially coplanar with the ring, the other is not. The former group interacts with the ring,



(*a*) (*b*) (*c*)

Fig. 1. Bond lengths and intrabond angles. (*a*) Refinement with photographic data, (*b*) refinement with counter data, (*c*) 'mixed' refinement.

the latter does not. Consequently, differences between the bond distances and angles might be expected.

As already mentioned, sp_2 hybridization is assumed for O(4). Because of the absence of ring conjugation for the O(3) C(8) methoxyl group, sp_3 hybridization may be postulated for O(3). Then one would expect larger C–O distances and a smaller C–O–C angle for O(3) than for O(4). Moreover, one could invoke hyperconjugation for $CH_3(9)$ to provide an additional shortening of the O(4)–C(9) bond. Hence, it is possible to account in a qualitative way for the results as found in FME. The situation is further complicated by steric repulsion between $CH_3(9)$ and O(3) (see Fig. 4), which is responsible for the large value of 129° for the angle C(5)–C(6)–O(4) and probably exerts its influence on the angle C(6)–O(4)–C(9) as well, whilst bond distances might also be affected.

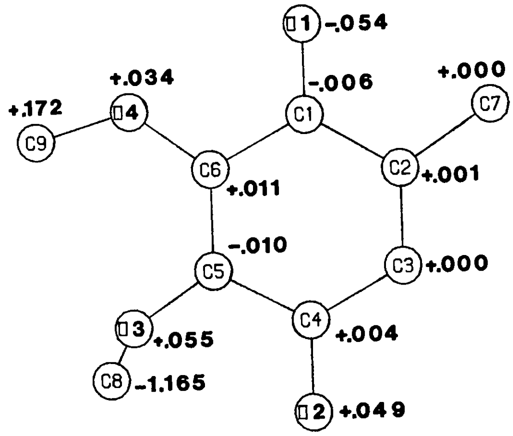
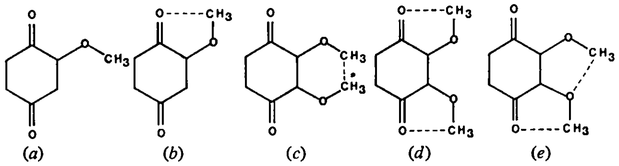


Fig. 2. Distances of the atoms from the least-squares plane of the six-membered ring.



(*a*) (*b*) (*c*) (*d*) (*e*)

Fig. 3. Planar conformations of 1-methoxy-*p*-benzoquinone and 2,3-dimethoxy-*p*-benzoquinone; short approaches are indicated by dashed lines.

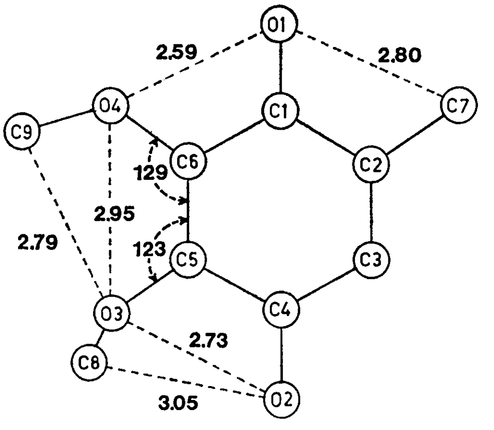


Fig. 4. Some intramolecular non-bonded distances.

The hydrogen atoms

In a difference Fourier synthesis, based on the contributions of the non-hydrogen atoms only, all hydrogen atoms are represented by maxima of 0·3 to 0·5 e.Å^{-3} at or near the expected positions. The accuracy of the positional parameters is low; C–H distances vary from 0·77 to 1·15 Å [mean 0·97 Å; σ (exp) = 0·14 Å]; H–C–H angles vary from 80 to 133° [mean 109°; σ (exp) = 18° and the C–C–H and O–C–H angles vary from 102 to 119° [mean 110°; σ (exp) = 6°].

Planarity

Table 2 lists the distances of the non-hydrogen atoms from the best planes through the following sets of atoms: C(1)···C(6); C(1)···C(6), O(1) and O(2); C(1)···C(7), O(1)···O(4). From these results, it is clear that only the six-membered ring plus C(7) is planar within the limits of accuracy, with O(1) and O(2) at 0·05 Å on opposite sides. The oxygen atoms are displaced towards the nearest ring (see next section).

Table 2. *Distances of the atoms from various planes in* 10^{-3} Å

	Plane 1	Plane 2	Plane 3
C(1)	*−6*	*+14*	*+1*
C(2)	*+1*	*+11*	*+8*
C(3)	*+0*	*−8*	*−7*
C(4)	*+4*	*−15*	*−19*
C(5)	*−10*	*−18*	*−33*
C(6)	*+11*	*+21*	*+2*
C(7)	+0	+21	*+25*
C(8)	−1165	−1192	−1214
C(9)	+172	+187	+152
O(1)	−54	*−17*	*−33*
O(2)	+49	*+13*	*+12*
O(3)	+55	+33	*+16*
O(4)	+34	+56	*+28*

Plane 1: $-0{\cdot}3211x-0{\cdot}8760y+0{\cdot}3599z-1{\cdot}6859=0$
Plane 2: $-0{\cdot}3286x-0{\cdot}8693y+0{\cdot}3689z-1{\cdot}7430=0$
Plane 3: $-0{\cdot}3225x-0{\cdot}8707y+0{\cdot}3713z-1{\cdot}7848=0$

Distances in italics correspond to the atoms which were used to define the planes.

Packing

The molecules related by the *b* translation are stacked as indicated in Fig. 5(*a*), where two adjacent molecules have been projected onto the plane of the ring. Each C=O group lies almost exactly over the centre of the ring of the next molecule in a stack. This situation has been found in several related structures [*e.g.*, both forms of quinhydrone (Sakurai, 1965 & 1968) and 1-naphthoquinone (Gaultier & Hauw, 1965)] and has been interpreted as representing a specific interaction between the polar C=O group and the π-electrons of the quinone ring (Prout & Wallwork, 1966). The shortest interatomic distances between two molecules in a stack are indicated in Fig. 5(*a*). The perpendicular distance between the rings is 3·46 Å. Thus, the molecules form columns in the [010] direction as indicated in Fig. 5(*b*).

The lateral packing of the columns is illustrated in Fig. 6. Two molecules at *xyz* and $\frac{1}{2}-x, -\frac{1}{2}-y, 1-z$ in adjacent columns form a sort of dimer across the centre of symmetry at $\frac{1}{4}, -\frac{1}{4}, \frac{1}{2}$, by means of short contacts of about 2·6 Å between O(2) and H(1). The planes of the two rings are 0·9 Å apart. A similar dimer formation, in which the planes of the molecules are 0·7 Å apart, is found in α-naphthoquinone (Gaultier, 1966). Two molecules at *xyz* and $-x, 1-y, 1-z$ also have short contacts of about 2·6 Å between O(1) and H(8) and between O(4) and H(8). In this way, the columns are connected to form sheets parallel to (001). The contacts between consecutive sheets are not particularly short. Packing is in accordance with the observed perfect cleavage parallel to (001).

Thermal motion

The principal axes of the vibration ellipsoids and their direction cosines are listed in Table 3. Though the molecule of FME is not expected to behave as a rigid body, we have applied the rigid-body analysis of Schomaker & Trueblood (1968) to get a rough idea of the possible bond length corrections involved. The librational data and $[\sum \Delta U_{ij}^2/(m-s)]^{1/2}$ are given in Table 4. This last quantity is approximately twice the σ (U_{ij}) obtained from the least-squares refinement. Corrections to the bond distances, based on the calculated librations, would be 0·005 to 0·008 Å.

Table 3. *Thermal ellipsoids*

Values of the mean-square displacements U_i (in Å^2) along the principal axes are given together with their direction cosines l_i relative to **a**, **b** and **c***, respectively.

	U_i	l_1	l_2	l_3
C(1)	+0·0530	+0·7678	+0·6389	+0·0486
	+0·0438	+0·5356	−0·5984	−0·5959
	+0·0411	+0·3516	−0·4835	+0·8016
C(2)	+0·0564	−0·5814	+0·4378	+0·6858
	+0·0472	−0·7425	−0·6302	−0·2271
	+0·0389	+0·3328	−0·6413	+0·6914
C(3)	+0·0414	+0·8537	−0·4401	+0·2782
	+0·0584	+0·1010	+0·6642	+0·7407
	+0·0540	+0·5108	+0·6043	−0·6115
C(4)	+0·0380	−0·8011	+0·5698	+0·1835
	+0·0567	+0·5378	+0·5506	+0·6385
	+0·0480	+0·2628	+0·6101	−0·7475
C(5)	+0·0374	−0·5733	+0·2297	+0·7865
	+0·0450	−0·3709	−0·9287	+0·0009
	+0·0415	−0·7306	+0·2912	−0·6176
C(6)	+0·0313	−0·8543	+0·5069	+0·1151
	+0·0559	−0·5067	−0·8615	+0·0332
	+0·0464	−0·1160	+0·0299	−0·9928
C(7)	+0·0445	+0·3522	−0·0016	+0·9359
	+0·0802	−0·8694	+0·3698	+0·3278
	+0·0693	+0·3466	+0·9291	−0·1288
C(8)	+0·0364	−0·0323	−0·0343	+0·9989
	+0·1042	+0·8918	+0·4502	+0·0443
	+0·0745	+0·4512	−0·8923	−0·0160
C(9)	+0·1229	−0·3449	−0·7925	+0·5029
	+0·0562	+0·3606	+0·6066	−0·7085
	+0·0367	+0·8666	−0·0630	+0·4950
O(1)	+0·1215	−0·4720	−0·8607	+0·1910
	+0·0570	−0·7840	+0·3108	−0·5373
	+0·0378	−0·4031	+0·4034	+0·8215
O(2)	+0·0371	−0·7754	+0·5002	+0·3855
	+0·0940	−0·4809	−0·8633	+0·1528
	+0·0697	−0·4092	+0·0669	−0·9100
O(3)	+0·0677	−0·3143	−0·9208	+0·2309
	+0·0536	+0·9440	−0·3288	−0·0264
	+0·0413	+0·1003	+0·2096	+0·9726
O(4)	+0·1045	−0·3000	−0·8666	+0·3988
	+0·0542	−0·0585	−0·4005	−0·9144
	+0·0318	+0·9521	−0·2977	+0·0695

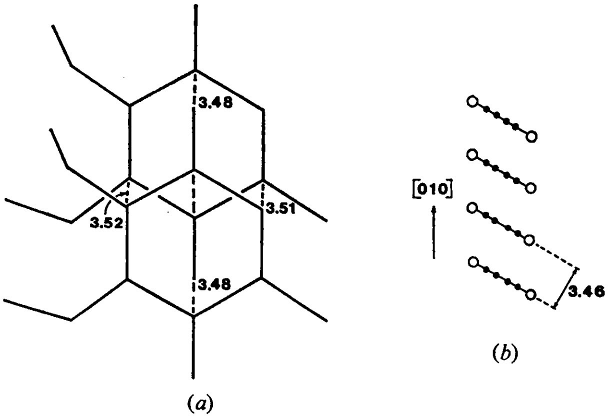


Fig. 5. Stacking of molecules related by the *b* translation. (*a*) Projection of two consecutive molecules in a column onto the plane of the quinone ring, (*b*) sequence of molecules in column.

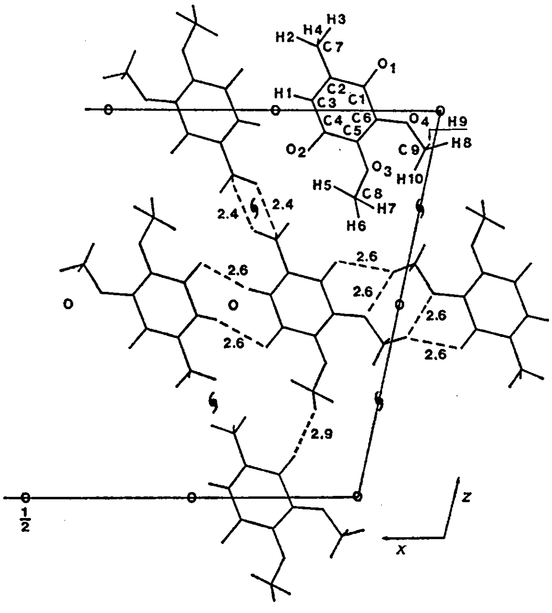


Fig. 6. Projection of the structure onto (010).

Table 4. *Principal axes of librational tensors* (*direction cosines relative to a, b and c**)

Complete molecule				*p*-Benzoquinone nucleus			
Value	Direction cosines			Value	Direction cosines		
32 $(^\circ)^2$	+0·098	+0·540	+0·836	44 $(^\circ)^2$	−0·219	+0·143	+0·965
17	+0·947	+0·208	−0·245	30	+0·795	+0·600	+0·091
6	+0·306	−0·815	+0·491	8	+0·566	−0·787	+0·244
$\left(\frac{\Sigma \Delta U_{ij}^2}{m-n}\right)^{\frac{1}{2}} = 0{\cdot}004$ Å^2				$\left(\frac{\Sigma \Delta U_{ij}^2}{m-n}\right)^{\frac{1}{2}} = 0{\cdot}003$ Å^2			

We thank Mr A. Kreuger for his expert help with the practical side of the work. We acknowledge the assistance of Mesers H. Schenk and L. W. Stam with part of the calculations. We also express our thanks to Professor C. H. MacGillavry for her advice.

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The Crystal and Molecular Structure of Azobisisobutyronitrile, $C_8H_{12}N_4$

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(*Received* 18 *January* 1971)

Azobisisobutyronitrile (AIBN, $C_8H_{12}N_4$) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell of dimensions $a = 5{\cdot}506$, $b = 8{\cdot}236$, $c = 10{\cdot}995$ Å and $\beta = 96{\cdot}07^\circ$. The structure has been determined by Patterson synthesis and refined by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms, to $R = 0{\cdot}11$. All hydrogen atoms were located by difference Fourier synthesis. The molecule has a centre of symmetry at the mid-point of the N(1) = N(1′) double bond. All atoms except those of the methyl groups are planar with a maximum deviation of 0·01 Å. This plane serves as a non-crystallographic mirror plane of the molecule. The methyl groups do not rotate and conform to the mirror plane of the molecule with a mean deviation of 0·05 Å. Thus, the symmetry of the molecule is nearly $2/m$. The most important interatomic distances are N=N 1·221, C–N= 1·490, C–CN 1·470, C–CH_3 1·530, $C\equiv N$ 1·144 Å and the mean value C–H is 0·97 Å.

Introduction

AIBN is applied as an initiator in radical polymerization. The kinetics of its decomposition in the solid state have recently been investigated in the authors' institute (Boros-Gyevi & Tüdös, 1969). The present crystal-structure determination is an extension of the previous work.

Experimental

Technical AIBN was crystallized three times from a mixture of chloroform and light petroleum at a temperature of about 3 °C. In this way colourless, slightly opaque crystals were obtained in the form of small needles. From a well shaped needle an approximately cubic sample with a cross section of about 0·5 mm was