

The Crystal and Molecular Structure of *O*-Methylobtusaquinone, C₁₇H₁₆O₃

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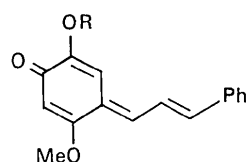
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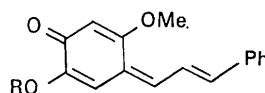
The crystal structure of *O*-methylobtusaquinone has been determined and refined on the basis of data collected by an automatic diffractometer. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a=9.596 \pm 0.005$, $b=11.030 \pm 0.005$, $c=13.966 \pm 0.006$ Å, $\beta=101.44 \pm 0.01^\circ$; there are 4 molecules per unit cell. The structure was determined by the symbolic addition procedure and was refined by least-squares calculations to an R index of 0.051. The molecule is nearly planar; the dihedral angle between the two rings is 4.86° . The second carbon atom of the aliphatic chain is *trans* to the O group of the quinone ring. There are no intermolecular hydrogen bonds in the crystal.

Introduction

Obtusaquinone, a novel *p*-quinone methide pigment isolated from the heartwood of *Dalbergia obtusa* Lecomte (Gregson, Ollis, Redman, Sutherland & Dietrichs, 1968) and *Dalbergia retusa* Hemsley (Jurd, Stevens & Manners, 1972) is highly toxic to fish (Marking, private communication) and the larvae of marine boring organisms (Bultman, private communication). The structure of obtusaquinone (and its *O*-methyl derivative) has been shown to be Ia (Ib) or IIa (IIb), but neither its spectral and chemical properties nor its synthesis allows an unambiguous assignment (Jurd *et al.*, 1972; Gottlieb, Mageswaran, Ollis, Roberts & Sutherland, 1970) of either of these geometric forms.



I(a) R=H
I(b) R=Me



II(a) R=H
II(b) R=Me

The X-ray crystallographic study reported here on *O*-methylobtusaquinone has established its structure as I(b).

Experimental

O-Methylobtusaquinone was crystallized from ethyl acetate. Attempts to obtain a suitable crystal from other solvents such as benzene, methane and heptane failed. The crystals from ethyl acetate were not always good, as evidenced by marked line broadening and the appearance of double peaks on a θ - 2θ scan at low angles.

The crystals obtained from ethyl acetate were orange colored platelets. Attempts to measure their density accurately were not successful. *O*-Methylobtusaquinone is soluble in the liquids normally used for density determination such as methylene bromide, carbon tetrachloride, bromobenzene *etc.* The crystal sinks in water, which suggests that there are 4 molecules per unit cell, since the calculated density for 4 molecules is 1.22 g cm^{-3} . The subsequent structure determination proved this to be correct.

Weissenberg and precession photographs were used to establish the space groups as $P2_1/c$. The lattice constants were obtained from high angle θ - 2θ scans of $h00$, $0k0$ and $00l$ reflections with the diffractometer set at a take-off angle of 1° . The crystal data are summarized below:

C ₁₇ H ₁₆ O ₃	F.W. 268.32
Monoclinic	Space group $P2_1/c$
$a=9.596 \pm 0.005$ Å	$Z=4$
$b=11.030 \pm 0.005$	$F(000)=568$
$c=13.966 \pm 0.006$	$D_c=1.22 \text{ g cm}^{-3}$
$\beta=101.44 \pm 0.01^\circ$	$\lambda(\text{Cu } K\alpha)=1.5418$ Å
Number of independent reflections	2300
Number of parameters refined	245

The crystal selected for intensity measurements was $0.21 \times 0.38 \times 0.29$ mm in the directions of **a**, **b** and **c**, respectively. The linear absorption coefficient μ is 6.9 cm^{-1} for Cu $K\alpha$; no correction for absorption was made. A correction for secondary extinction (Zachariasen, 1963) was applied during the final stages of refinement.

Integrated intensities were obtained with a G.E. automatic diffractometer equipped with a full-circle goniostat and controlled by means of an IBM 1800 computer operating under the MPX time-sharing monitor. The Ni-filtered Cu $K\alpha$ radiation was detected

by a scintillation counter coupled to a single-channel pulse height analyzer. Data were recorded up to $2\theta = 125^\circ$, using the θ - 2θ scanning technique. The scan rate was $1^\circ/\text{min}$ (in 2θ). Backgrounds were counted for 20 sec at 0.5° on each side of the scan limits. 2505 reflections were measured of which 2300 were independent. 114 of these were measured as zero and the intensity of 180 other reflections was less than $\sigma(I)$, where $\sigma(I)$ was calculated by the expression $\sigma(I) = [C + (T_c/2T_b)^2(B_1 + B_2) + (0.05I)^2]^{1/2}$. C is the total count in scan time T_c , B_1 and B_2 are the two background counts taken for $T_b = 20$ sec. The constant 0.05 was arbitrarily chosen to account for non-random errors. A Lorentz and polarization correction was applied to the data by means of a computer program furnished by A. Zalkin (private communication). Two standard reflections were measured after every 48 reflections; they showed no significant change in intensity during the course of the experiment.

A full-matrix least-squares program furnished by A. Zalkin (private communication) was used to refine the parameters. This program minimizes the function $\sum w(\Delta F)^2$; $\Delta F = |F_o| - |F_c|$, where F_o and F_c are the observed and calculated structure factors, and w is a weighting factor taken equal to $1/\sigma^2(F)$. The value of $\sigma(F)$ was calculated by the expression $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$ when $I > \sigma(I)$; w was set equal to zero when $I \leq \sigma(I)$.

Scattering factors for all atoms except hydrogen were taken from the tables published by Cromer & Waber (1965). The scattering factors used for hydrogen were those published by Stewart, Davidson & Simpson (1965).

Determination of the structure

Normalized structure factors $|E|$ were calculated by Wilson's method with a computer program written by

Maddox & Maddox, private communication). These values were used to calculate phases by the symbolic addition procedure (Karle & Karle, 1966). Origin determining signs were chosen for 75 $\bar{5}$, 269, and 3,10,3 as all positive. Their $|E|$ values are 4.38, 4.12 and 3.49, respectively. The eight possible combinations of signs for three additional reflections were used to calculate probable phases for the remaining 283 reflections whose $|E|$ values were equal to or greater than 1.50. One combination of signs was clearly superior to the others. The starting three reflections and their E values with correct signs are as follows:

57 $\bar{4}$	+3.87
22 $\bar{2}$	-3.76
348	+3.38.

The signs of the correct set were 138 positive and 152 negative.

An E Fourier synthesis revealed the position of all heavy atoms. The positional parameters of these 20 atoms with isotropic temperature factors of the form $T = \exp[-B(\sin \theta/\lambda)^2]$ were least-squares refined and resulted in an R index of 0.18 where R is defined as $\sum |F_o| - |F_c| / \sum |F_o|$. With anisotropic temperature factors the R index became 0.11.

A Fourier difference synthesis revealed the positions of the 16 hydrogen atoms, and when the parameters of these atoms were included in the least-squares refinement with isotropic temperature factors the R index became 0.058. At this stage of refinement a comparison between the observed and calculated intensities for the most intense reflections revealed that the observed values were less than the calculated ones. An extinction correction of the form $F_{\text{corr}} = SF[1 + (EF)I]F_o$ as suggested by Zachariasen (1963) was applied and led to a small, but significant, improvement between the

Table 1. Positional ($\times 10^4$) and thermal parameters (\AA^2) for *O*-methylobtusaquinone

Calculated standard deviations are in parentheses. The anisotropic temperature factor has the form $T = \exp[-\sum \sum (B_{ij}h_i h_j b_j / 4)]$ where h_i is the i th Miller index, b_i is the i th reciprocal axis length, and i and j are cycled 1 through 3. The isotropic temperature factor has the form $T = \exp[-B(\sin \theta/\lambda)^2]$. The hydrogen atom coordinates are $\times 10^3$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	1226 (2)	2159 (2)	1482 (2)	7.7 (1)	6.5 (1)	13.1 (2)	3.27 (8)	-0.5 (1)	0.7 (1)
O(2)	-2269 (2)	3947 (1)	-970 (1)	6.95 (9)	6.41 (9)	6.62 (9)	1.36 (7)	0.94 (7)	-0.68 (7)
O(3)	770 (2)	3712 (2)	2806 (2)	6.14 (9)	7.2 (1)	8.3 (1)	0.77 (8)	-1.03 (8)	1.57 (9)
C(1)	313 (3)	2931 (2)	1215 (2)	4.6 (1)	5.0 (1)	9.7 (2)	0.54 (9)	0.5 (1)	0.9 (1)
C(2)	-477 (3)	2985 (2)	221 (2)	5.4 (1)	4.7 (1)	8.6 (2)	0.46 (9)	1.5 (1)	-0.3 (1)
C(3)	-1494 (2)	3847 (2)	-60 (2)	4.9 (1)	4.54 (9)	6.6 (1)	0.04 (8)	1.10 (9)	0.11 (9)
C(4)	-1808 (2)	4755 (2)	613 (2)	4.11 (9)	4.60 (9)	6.3 (1)	0.22 (7)	0.91 (8)	0.65 (8)
C(5)	-1021 (2)	4710 (2)	1609 (2)	4.5 (1)	4.8 (1)	6.2 (1)	0.15 (8)	0.61 (8)	0.71 (9)
C(6)	-21 (2)	3854 (2)	1894 (2)	4.5 (1)	5.1 (1)	7.4 (1)	0.05 (8)	0.30 (9)	1.16 (9)
C(7)	-2011 (4)	3096 (3)	-1703 (2)	8.5 (2)	7.0 (2)	7.4 (2)	0.2 (1)	2.4 (2)	-1.4 (1)
C(8)	587 (5)	4602 (4)	3519 (3)	9.3 (2)	8.2 (2)	7.2 (2)	-0.5 (2)	-1.1 (2)	1.3 (2)
C(9)	-2834 (2)	5609 (2)	299 (2)	5.4 (1)	5.0 (1)	5.9 (1)	0.83 (9)	0.62 (9)	0.31 (9)
C(10)	-3255 (2)	6579 (2)	849 (2)	4.9 (1)	5.0 (1)	5.4 (1)	0.82 (8)	0.82 (8)	0.59 (9)
C(11)	-4353 (2)	7308 (2)	474 (2)	5.5 (1)	5.7 (1)	5.4 (1)	1.17 (9)	0.36 (9)	0.25 (9)
C(12)	-4907 (2)	8317 (2)	961 (2)	4.62 (9)	4.65 (9)	5.2 (1)	0.62 (8)	0.72 (8)	0.51 (8)
C(13)	-6028 (3)	8994 (2)	443 (2)	6.0 (1)	7.3 (1)	5.2 (1)	2.1 (1)	0.44 (9)	0.2 (1)
C(14)	-6574 (3)	9976 (3)	877 (2)	6.8 (1)	6.8 (1)	6.8 (1)	2.7 (1)	1.4 (1)	0.8 (1)
C(15)	-6004 (3)	10288 (2)	1802 (2)	7.5 (1)	5.7 (1)	6.8 (1)	1.5 (1)	1.9 (1)	-0.0 (1)
C(16)	-4908 (3)	9642 (2)	2324 (2)	7.2 (1)	6.6 (1)	6.1 (1)	0.2 (1)	0.8 (1)	-0.9 (1)
C(17)	-4346 (3)	8660 (2)	1914 (2)	5.5 (1)	5.3 (1)	5.7 (1)	0.48 (9)	-0.04 (9)	0.27 (9)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁
H(1)	-33 (2)	242 (2)	-27 (2)	5.0 (5)
H(2)	-121 (2)	535 (2)	209 (1)	4.3 (4)
H(3)	-103 (3)	325 (2)	-175 (2)	6.8 (7)
H(4)	-232 (2)	218 (2)	-150 (2)	5.8 (5)
H(5)	-270 (3)	327 (2)	-238 (2)	7.2 (7)
H(6)	84 (4)	535 (4)	332 (3)	9.4 (9)
H(7)	-46 (3)	478 (2)	365 (2)	7.2 (7)
H(8)	121 (4)	453 (3)	425 (3)	9.3 (8)
H(9)	-338 (3)	558 (2)	-46 (2)	6.3 (5)
H(10)	-278 (2)	669 (2)	154 (2)	5.1 (5)
H(11)	-460 (4)	727 (3)	-33 (2)	10.9 (9)
H(12)	-637 (3)	877 (2)	-26 (2)	7.3 (6)
H(13)	-748 (3)	1036 (2)	52 (2)	6.6 (6)
H(14)	-639 (3)	1096 (2)	203 (2)	6.8 (6)
H(15)	-454 (3)	992 (2)	300 (2)	7.2 (6)
H(16)	-352 (3)	817 (2)	229 (2)	5.7 (5)

observed and calculated *F*'s. In this expression SF is a scale factor, and EF the extinction parameter. By trial and error a value of 1×10^{-7} for the extinction parameter led to good agreement between observed and calculated *F*'s and gave a final *R* index of 0.051. This structure was used to calculate the positional and thermal parameters and their standard deviations listed in Table 1. The observed structure factors are given in Table 2.

Discussion of the structure

The molecular structure and numbering system used in this investigation are shown in Fig. 1. A stereoscopic drawing of the molecule made with the *ORTEP* program (Johnson, 1965) is shown in Fig. 2. This drawing

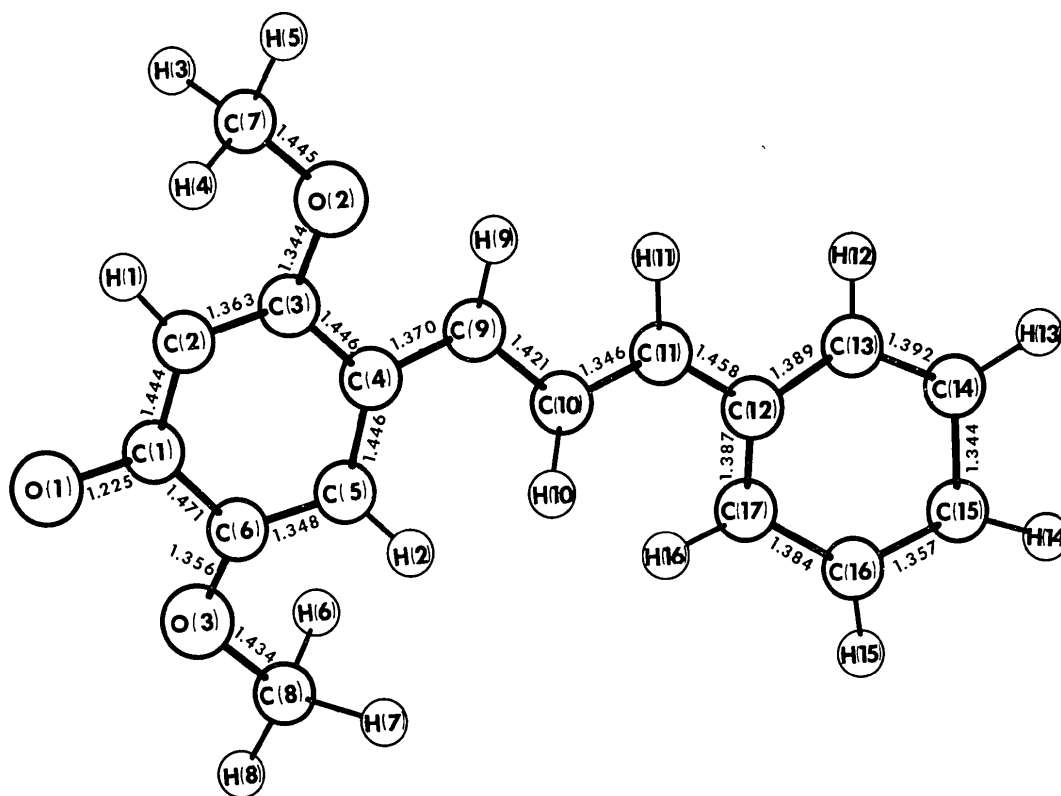


Fig. 1. The structure of *O*-methylobtusaquinone, the atom numbering system used in this investigation, and the interatomic distances between heavy atoms. E.s.d.'s are 0.005 Å.

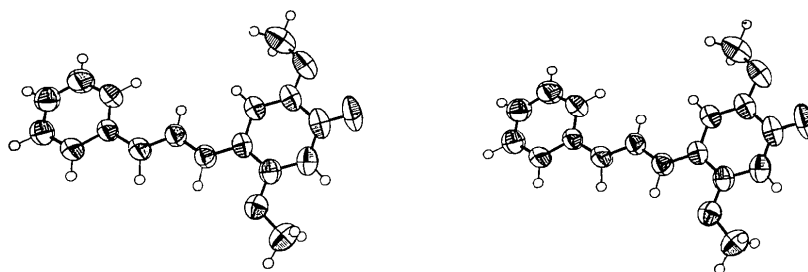
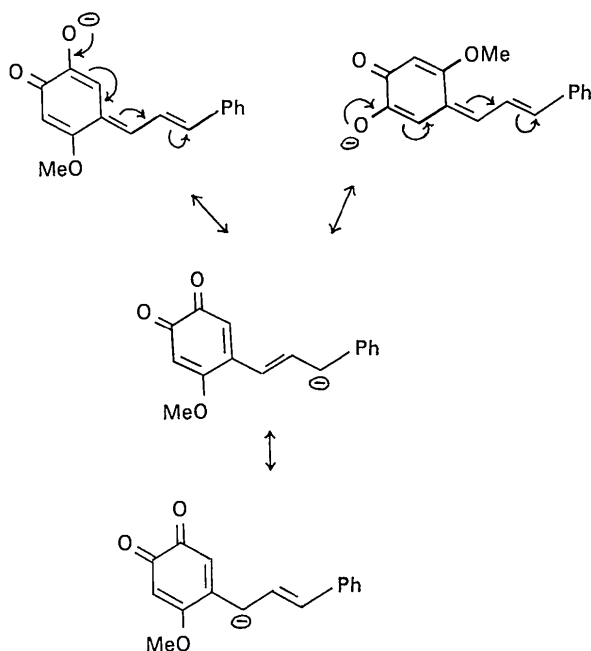


Fig. 2. A stereoscopic view of *O*-methylobtusaquinone. The thermal ellipses are drawn at the 50% probability level.

which place a double bond between carbons atoms (4) and(9).



The manner in which the *O*-methylobtusaquinone molecules are packed in the crystal is shown in Fig. 3. This stereoscopic view of the unit cell was made with the *ORTEP* program (Johnson, 1965). The direction of viewing is nearly parallel to *c* with *b* running left-to-right. This figure shows that the crystal consists of two parallel arrays of molecules and also illustrates the near planarity of the molecule, including the two methyl carbon atoms. Since there are no intermolecular hydrogen bonds between the molecules, the stability of the crystal (m.p. 169°) is probably due to a combination of π -orbital overlap, electrostatic attraction between dipolar resonance hybrids, and to the stiffness of the molecule due to resonance (Dauberry, Bunn & Brown, 1954). The shortest intermolecular distances between two heavy atoms and between a heavy atom and hydrogen are given in Table 3. These distances are compatible with the sum of their van der Waals radii.

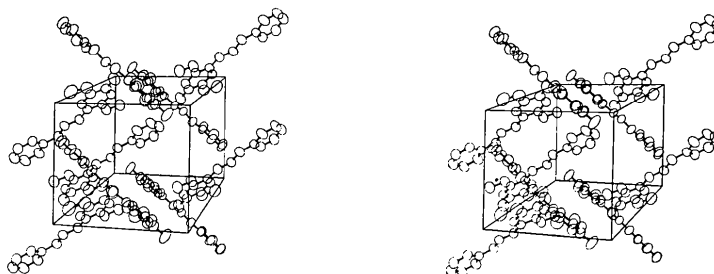


Fig. 3. A stereoscopic drawing of the unit cell of *O*-methylobtusaquinone. The structure as viewed down *c* with *b* horizontal. The thermal ellipsoids are scaled to include 50% probability.

Table 3. The intermolecular distances less than 3.50 Å between heavy atoms and less than 3.00 Å between a heavy atom and a hydrogen atom

O(1)···C(15')	3.324 Å	O(1)···H(14')	2.620 Å
O(1)···C(8'')	3.313	O(1)···H(16'')	2.748
O(1)···C(14')	3.418	O(1)···H(13')	2.824
O(2)···C(16''')	3.481	O(1)···H(10'')	2.915
C(3)···C(17'')	3.376	O(2)···H(15'')	2.674
C(13)···C(13''')	3.365	O(3)···H(16''')	2.735

Symmetry code

'	$1+x, y-1, z;$	'''	$x, \frac{3}{2}-y, \frac{1}{2}+z$
''	$\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z;$	iv	$1-x, \frac{3}{2}-y, \bar{z}.$

The distances between the heavy atoms are shown in Fig. 1; the angles are listed in Table 4. The bond lengths in the quinone ring and aliphatic chain show that the single bonds are slightly smaller, and the double bonds slightly larger, than would be expected for a non-resonating sp^2 - sp^2 system (Dewar & Schmeising, 1960). For the latter system these values are 1.479 and 1.338 Å, respectively. It is concluded, therefore, that ionized structures make only a small contribution to the resonance hybrid in *O*-methyl-obtusaquinone. Four of the benzene ring bond distances agree well with the expected value of 1.397 Å, but two of them, C(14)-C(15) and C(15)-C(16), are shorter than this value. The difference between the observed value for these two bonds and the normal value (~ 0.05 Å) is about ten standard deviations. There is, however, no obvious explanation for this discrepancy.

Table 4. Bond angles involving the heavy atoms

E.s.d.'s are 0.10°.			
O(1)-C(1)-C(2)	121.9°	C(1)-C(6)-O(3)	111.9°
O(1)-C(1)-C(6)	121.2	C(3)-O(2)-C(7)	118.4
C(1)-C(2)-C(3)	121.0	C(6)-O(3)-C(8)	116.7
C(2)-C(1)-C(6)	116.8	C(4)-C(9)-C(10)	127.4
C(2)-C(3)-C(4)	121.7	C(9)-C(10)-C(11)	121.6
C(2)-C(3)-O(2)	124.1	C(10)-C(11)-C(12)	127.2
C(3)-C(4)-C(5)	117.7	C(11)-C(12)-C(13)	119.0
C(4)-C(3)-O(2)	114.2	C(11)-C(12)-C(17)	123.2
C(3)-C(4)-C(9)	119.9	C(12)-C(13)-C(14)	120.8
C(4)-C(5)-C(6)	121.0	C(13)-C(12)-C(17)	117.8
C(5)-C(4)-C(9)	122.4	C(13)-C(14)-C(15)	120.1
C(5)-C(6)-C(1)	121.8	C(14)-C(15)-C(16)	120.4
C(5)-C(6)-O(3)	126.3	C(15)-C(16)-C(17)	120.9
		C(16)-C(17)-C(12)	120.1

Table 5. Distances and angles involving hydrogen atoms

E.s.d.'s are 0.1 Å and 3.0°.

H(1)—C(2)	0.96 Å	H(1)—C(2)—C(1)	122°	H(12)—C(13)—C(12)	117°
H(2)—C(5)	1.01	H(1)—C(2)—C(3)	117	H(12)—C(13)—C(14)	123
H(4)—C(7)	1.11	H(2)—C(5)—C(4)	119	H(13)—C(14)—C(13)	118
H(3)—C(7)	0.97	H(2)—C(5)—C(6)	120	H(13)—C(14)—C(15)	121
H(5)—C(7)	1.06	H(4)—C(7)—O(2)	108	H(14)—C(15)—C(14)	115
H(6)—C(8)	0.92	H(3)—C(7)—O(2)	104	H(14)—C(15)—C(16)	125
H(7)—C(8)	1.08	H(5)—C(7)—O(2)	110	H(15)—C(16)—C(15)	117
H(8)—C(8)	1.08	H(6)—C(8)—O(3)	109	H(15)—C(16)—C(17)	123
H(9)—C(9)	1.08	H(7)—C(8)—O(3)	119	H(16)—C(17)—C(16)	122
H(10)—C(10)	0.99	H(8)—C(8)—O(3)	119	H(16)—C(17)—C(12)	118
H(11)—C(11)	1.11	H(9)—C(9)—C(4)	118	H(3)—C(7)—H(4)	119
H(12)—C(13)	1.01	H(9)—C(9)—C(10)	115	H(3)—C(7)—H(5)	111
H(13)—C(14)	1.01	H(10)—C(10)—C(9)	119	H(4)—C(7)—H(5)	104
H(14)—C(15)	0.91	H(10)—C(10)—C(11)	119	H(6)—C(8)—H(7)	102
H(15)—C(16)	0.98	H(11)—C(11)—C(10)	111	H(6)—C(8)—H(8)	103
H(16)—C(17)	1.01	H(11)—C(11)—C(12)	119	H(7)—C(8)—H(8)	102

The bond angles for the two rings agree with literature values. Both the bond angles and bond distances found for the conjugated chain are in good agreement with those observed for the carotenoid chain (Bart & MacGillavry, 1968) and the conjugated chain in 11-*cis*-retinal (Gilardi, Karle & Karle, 1972).

The bond distances and angles involving the hydrogen atoms are given in Table 5. The estimated standard deviation for the distances and angles are 0.1 Å and 3.0°, respectively.

The molecule *O*-methylbtusaquinone is nearly planar. The out-of-plane distances of the plane forming atoms and the carbon atoms in the aliphatic chain from the plane of both the benzene and quinone rings are shown in Table 6. The out-of-plane distances of the

carbon and oxygen atoms of the two methoxyl groups from the plane of the quinone ring are also given in Table 6. The two methoxyl carbon atoms, C(7) and C(8), are only 0.018 and 0.050 Å, respectively, from the plane of the quinone ring.

The out-of-plane distances of C(9), C(10) and C(11) indicate that the molecule is slightly twisted. This twist results in a dihedral angle between the benzene and quinone rings of 4.86°.

The authors wish to thank Dr A. Zalkin for the use of his computer programs and both Professor David H. Templeton and Dr Zalkin for helpful discussions during the course of this investigation.

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Table 6. Deviation of atoms from the least-squares plane

The planes are of the form $AX+BY+CZ=D$ where X , Y , Z and D are in Å units relative to the axes a , b , and c .

Plane forming atoms and distance from plane	Distance from plane	Coefficients of the equation of the plane	
Benzene ring			
C(12) -0.002 Å	C(9) 0.067 Å	A	0.727
C(13) 0.003	C(10) 0.063	B	0.605
C(14) -0.004	C(11) 0.027	C	-0.464
C(15) 0.003		D	1.503 Å
C(16) -0.002			
C(17) 0.001			
Quinone ring			
C(1) -0.001 Å	C(9) -0.001 Å	A	0.757
C(2) 0.005	C(10) 0.038	B	0.604
C(3) -0.006	C(11) -0.068	C	-0.392
C(4) 0.003	O(1) 0.006	D	1.518 Å
C(5) 0.000	O(2) -0.003		
C(6) 0.000	O(3) -0.021		
	C(7) 0.018		
	C(8) 0.050		

Dihedral angle between benzene and quinone plane in 4.86°.

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