

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) B_{iso} for H atoms; $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$ for non-H atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/U_{\text{eq}}$
C1	0.7657 (1)	0.6578 (2)	0.0246 (1)	0.0326 (2)
C2	0.8682 (1)	0.5483 (2)	0.0287 (1)	0.0382 (2)
C3	0.8688 (1)	0.3406 (3)	0.0913 (1)	0.0425 (3)
C4	0.7672 (1)	0.3367 (2)	0.1196 (1)	0.0373 (2)
C5	0.7294 (1)	0.1765 (3)	0.1745 (1)	0.0489 (3)
C6	0.6332 (1)	0.1989 (3)	0.1932 (1)	0.0521 (3)
C7	0.5753 (1)	0.3823 (3)	0.1577 (1)	0.0489 (3)
C8	0.6123 (1)	0.5428 (2)	0.1027 (1)	0.0436 (3)
C9	0.7093 (1)	0.5208 (2)	0.0822 (1)	0.0336 (2)
H2A	0.9189 (10)	0.676 (3)	0.0427 (8)	4.0 (3)
H2B	0.8852 (10)	0.485 (3)	-0.0251 (8)	3.8 (3)
H3A	0.9177 (11)	0.374 (3)	0.1362 (9)	4.6 (4)
H3B	0.8853 (11)	0.177 (3)	0.0685 (9)	4.8 (4)
H5	0.7725 (11)	0.050 (3)	0.1986 (9)	5.3 (4)
H6	0.6052 (12)	0.087 (3)	0.2323 (10)	5.6 (4)
H7	0.5065 (11)	0.403 (3)	0.1723 (9)	4.3 (3)
H8	0.5700 (11)	0.670 (3)	0.0795 (10)	5.0 (4)

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.527 (2)	C2—H2A	0.999 (14)
C1—C9	1.473 (1)	C2—H2B	1.007 (14)
C1—C1 ⁱ	1.351 (1)	C3—H3A	1.002 (15)
C2—C3	1.538 (2)	C3—H3B	0.993 (15)
C3—C4	1.501 (2)	C5—H5	0.977 (16)
C4—C5	1.385 (2)	C6—H6	0.987 (17)
C4—C9	1.402 (2)	C7—H7	0.997 (15)
C5—C6	1.382 (2)	C8—H8	0.968 (16)
C6—C7	1.385 (2)		
C7—C8	1.384 (2)		
C8—C9	1.400 (2)		
C9—C1—C2	107.1 (1)	H2A—C2—C1	112.0 (8)
C1 ⁱ —C1—C2	125.2 (1)	H2B—C2—C1	110.3 (8)
C1 ⁱ —C1—C9	127.6 (1)	H2A—C2—C3	111.2 (8)
C3—C2—C1	106.5 (1)	H2B—C2—C3	112.2 (8)
C4—C3—C2	104.9 (1)	H2B—C2—H2A	104.7 (11)
C5—C4—C3	127.6 (1)	H3A—C3—C2	111.5 (9)
C9—C4—C3	111.3 (1)	H3B—C3—C2	112.1 (9)
C9—C4—C5	121.1 (1)	H3A—C3—C4	111.2 (9)
C6—C5—C4	119.7 (1)	H3B—C3—C4	110.3 (9)
C7—C6—C5	119.9 (1)	H3B—C3—H3A	107.0 (12)
C8—C7—C6	120.8 (1)	H5—C5—C4	118.1 (9)
C9—C8—C7	120.0 (1)	H5—C5—C6	122.2 (9)
C4—C9—C1	110.1 (1)	H6—C6—C5	120.7 (10)
C8—C9—C1	131.4 (1)	H6—C6—C7	119.3 (10)
C8—C9—C4	118.4 (1)	H7—C7—C6	120.3 (8)
		H7—C7—C8	118.8 (8)
		H8—C8—C7	118.5 (9)
		H8—C8—C9	121.5 (9)

Symmetry code: (i) $\frac{3}{2} - x, \frac{3}{2} - y, -z$.Table 3. Anisotropic displacement parameters (Å² × 10⁴)The form of the displacement factor is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	269 (4)	317 (5)	395 (6)	35 (4)	32 (4)	-38 (4)
C2	277 (5)	400 (6)	469 (6)	71 (4)	29 (4)	-5 (5)
C3	370 (6)	447 (6)	452 (7)	112 (5)	-26 (5)	13 (5)
C4	392 (5)	366 (5)	359 (6)	38 (4)	-8 (4)	-17 (4)
C5	574 (8)	459 (7)	431 (7)	48 (6)	2 (5)	78 (5)
C6	615 (8)	524 (8)	429 (7)	-66 (6)	81 (6)	67 (6)
C7	435 (6)	564 (8)	478 (7)	-43 (6)	121 (5)	19 (6)
C8	354 (6)	447 (6)	513 (7)	44 (5)	94 (5)	40 (5)
C9	323 (5)	318 (5)	369 (5)	24 (4)	23 (4)	-27 (4)

The structure was solved by *MULTAN88* (Debaerdemaeker *et al.*, 1988); all C atoms were found in the *E* map. Their positions and displacement parameters were refined and H

atoms were then introduced at calculated positions. After four cycles, the H-atom parameters (positional and displacement) were included in the refinement, along with a single scale factor and a secondary extinction parameter. All refinements proceeded smoothly and quickly.

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction, structure solution, structure refinement and preparation of material for publication: *CRYM* (Duchamp, 1964). Molecular graphics: *ORTEPII* (Johnson, 1976).

We thank Lawrence M. Henling for assistance in the data collection and in preparation of the manuscript.

Lists of structure factors have been deposited with the IUCr (Reference: CR1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Debaerdemaeker, T., Germain, G., Main, P., Refaai, L. S., Tate, C. & Woolfson, M. M. (1988). *MULTAN88. Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- Duchamp, D. J. (1964). American Crystallographic Association Meeting, Bozeman, Montana, paper B14, pp. 29–30.
- Frimer, A. A., Weiss, J. & Rosental, J. (1994). *J. Org. Chem.* **59**, 2516–2522.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.
- Larson, A. C. (1967). *Acta Cryst.* **23**, 644–665.

Acta Cryst. (1995). **C51**, 2366–2369

2-Bromo-4-[2-bromo-(*E*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one

SHIMING LI, KNUT LUNDQUIST AND NIKITA SOUBBOTIN

Department of Organic Chemistry, Chalmers University of Technology, S-41296 Göteborg, Sweden

ROLF STOMBERG

Department of Inorganic Chemistry, University of Göteborg, S-41296 Göteborg, Sweden

(Received 13 March 1995; accepted 12 May 1995)

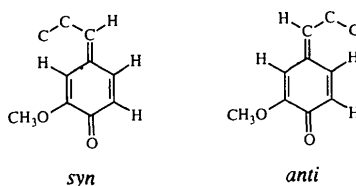
Abstract

The structure and stereochemistry of 2-bromo-4-[2-bromo-(*E*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one, C₁₀H₁₀Br₂O₂ (1), has been elucidated by X-ray crystallographic analysis. In chloroform or benzene

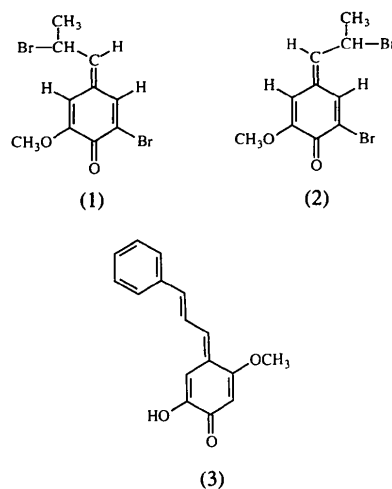
solution, (1) underwent partial isomerization to 2-bromo-4-[2-bromo-(*Z*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one, (2). NMR data for (1) and (2) are reported. The crystal investigated (at 173 K) contained 94% of (1) and 6% of (2) (solid solution).

Comment

Quinone methides play an important role in the biosynthesis of lignins and in lignin reactions occurring during certain types of pulping processes (Shevchenko & Apushkinskii, 1992). Lignin-related quinone methides are very reactive species and are usually not isolated but studied in solution. They are prone to undergo addition reactions leading to aromatic compounds. Lignin-related quinone methides of the 'guaiacyl type' exist as mixtures of *syn* and *anti* isomers (Ralph & Adams, 1983):



This type of isomerism has been studied by NMR spectroscopic methods (Ralph & Adams, 1983; Ralph & Ede, 1988; Ede, Main & Ralph, 1990). The results showed that the *syn* isomer is predominant (the ratio of *syn* isomer to *anti* isomer was found to be approximately 2:1). The quinone methides examined in this paper, 2-bromo-4-[2-bromo-(*E*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one, (1), and its *Z* isomer, (2), are closely related to the lignin-related quinone methides studied previously, but they differ from the latter compounds by having a bromo substituent on the ring. Our X-ray crystallographic study of the quinone methide prepared according to Zincke & Hahn (1903) demonstrates that it has structure (1). ^1H and ^{13}C NMR spectroscopic examinations (chloroform solution) were in agreement with this structure, but small amounts of the isomeric 2-bromo-4-[2-bromo-(*Z*)-propylidene]-6-methoxy-2,5-cyclohexadien-1-one, (2), were present in the solution. On standing in chloroform solution (or benzene solution) at room temperature, the amount of (2) slowly increased. In solutions kept overnight the ratio of *E* isomer to *Z* isomer, *i.e.* (1) to (2), was found to be 1.8:1. Evidently, (1) partially isomerizes to (2) in solution. Published ^1H and ^{13}C NMR spectral data for lignin-related quinone methides (Ralph & Adams, 1983; Ralph & Ede, 1988; Ede, Main & Ralph, 1990) provided a basis for the assignment of the signals from (1) and (2). Our X-ray crystallographic study of (1) strongly supports the assignment of *syn* and *anti* forms of quinone methides arrived at by NMR spectroscopic methods alone (Ede, Main & Ralph, 1990).



The distance between atoms H(C6) and H(C8) was found to be rather short (2.16 Å) and this supports the view (Ralph & Adams, 1983; Ede, Main & Ralph, 1990) that the location of the NMR signal from H(C6) is influenced by steric compression. This compression is also reflected in an enlargement of the angles C(6)—C(1)—C(7) [123.6 (5)°] and C(1)—C(7)—C(8) [125.5 (5)°].

Obtusaquinone is a naturally occurring quinone methide (Gregson, Ollis, Redman, Sutherland & Dietrichs, 1968) that may exist in stereoisomeric forms analogous to (1) and (2). X-ray crystallographic investigations have shown that obtusaquinone has structure (3) (Palmer, Wong & Jurd, 1973; Karle & Bultman, 1976).

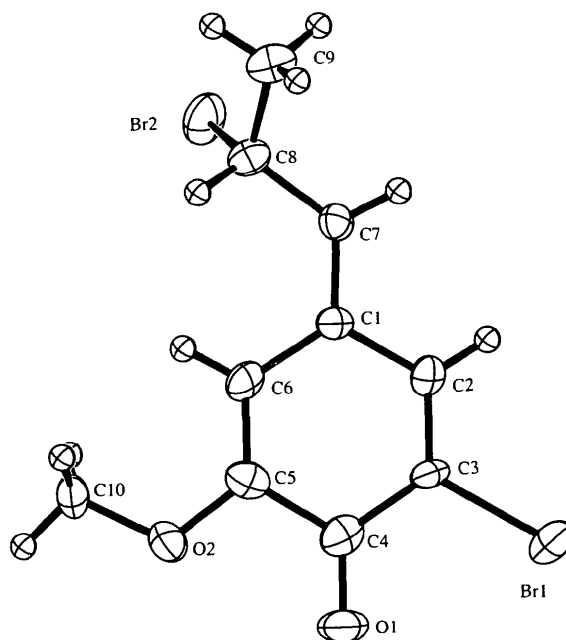


Fig. 1. A perspective drawing (ORTEP; Johnson, 1976) of (1) with displacement ellipsoids at the 50% level showing the numbering of the non-H atoms. H atoms are shown as small spheres of arbitrary radii.

A perspective view of molecule (1) is shown in Fig. 1. According to the structure analysis, the two crystals investigated, which were obtained from different batches, are solid solutions of (2) in (1) [the composition was determined as 94% of (1) to 6% of (2) in the experiment performed at 173 K]. Fig. 2 shows the position of (2) relative to (1). The plane of ring C(1A)–C(6A) in (2) forms an angle of 4° with the plane of ring C(1)–C(6) in (1). The shortest intermolecular distances are 2.26 [O(1)··H(C7)($\frac{3}{2}-x, -\frac{1}{2}+y, 1-z$)] and 2.22 Å [H(C2)··O(1A)($\frac{3}{2}-x, \frac{1}{2}+y, 1-z$)].

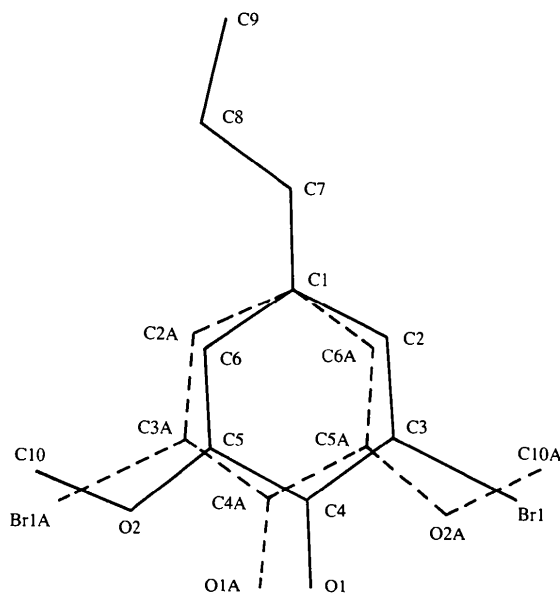


Fig. 2. The position of isomer (2) relative to (1). Only the C-atom skeleton, the O atoms and the Br atoms connected to the rings are shown. Solid lines represent isomer (1) and broken lines isomer (2).

The ring C(1)–C(6) is planar within 5 σ . Atom C(7) is located very near the ring plane [deviation 0.023 (8) Å]. The distance from the plane defined by the ring to atom C(9) is 0.832 Å. Atom O(1) is located 0.096 Å from the ring plane [on the same side as atom C(9)] and O(2) exhibits a similar deviation (0.117 Å), but in the opposite direction. As far as comparisons are possible, bond distances in the methylene quinone group of (1) agree with those observed in other compounds containing such a group (Palmer, Wong & Jurd, 1973; Karle & Bultman, 1976; Kutney *et al.*, 1992).

Experimental

Quinone methide (1) [and its stereoisomer (2)] was prepared starting from isoeugenol (Zincke & Hahn, 1903). It should be noted that the amount of bromine is too small in the description given by Zincke & Hahn (1903) for the preparation of the intermediate tribromo derivative of eugenol (*cf.* Hell & Portmann, 1895). Crystals of (1) suitable for X-ray

crystallographic analysis were obtained on recrystallization from benzene/hexane solution. The compound decomposed on long-term exposure to daylight. ¹H NMR spectrum of (1) (400 MHz, CDCl₃, 301 K, TMS): δ 1.93 (3H, *d*, *J* = 6.6 Hz, CH₃C), 3.86 (3H, *s*, OCH₃), 5.22 [1H, *dq*, *J* = 6.6 and 10.8 Hz, H(C8)], 6.33 [1H, *d*, *J* = 10.8 Hz, H(C7)], 6.51 [1H, *d*, *J* = 2.2 Hz, H(C6)], 7.49 p.p.m. [1H, *d*, *J* = 2.2 Hz, H(C2)]. ¹H NMR spectrum of (2) (400 MHz, CDCl₃, 301 K, TMS): δ 1.91 (3H, *d*, *J* = 6.4 Hz, CH₃C), 3.80 (3H, *s*, OCH₃), 5.26 [1H, *dq*, *J* = 6.4 and 11 Hz, H(C8)], 6.24 [1H, *d*, *J* = 2.0 Hz, H(C6)], 6.42 [1H, *d*, *J* = 11 Hz, H(C7)], 7.93 p.p.m. [1H, *d*, *J* = 2.0 Hz, H(C2)]. ¹³C NMR spectrum of (1) (100.6 MHz, CDCl₃, 301 K, TMS): δ 25.7 (C9), 41.4 (C8), 55.9 (OCH₃), 103.1 (C6), 124.8 (C3), 130.3 (C1), 142.3 (C2), 145.4 (C7), 152.7 (C5), 174.61 p.p.m. (CO). ¹³C NMR spectrum of (2) (100.6 MHz, CDCl₃, 301 K, TMS): δ 25.9 (C9), 41.5 (C8), 55.8 (OCH₃), 111.5 (C6), 127.0 (C3), 129.6 (C1), 133.2 (C2), 144.9 (C7), 152.3 (C5), 174.56 p.p.m. (CO).

Crystal data

C₁₀H₁₀Br₂O₂
M_r = 322.00
 Monoclinic
*P*2₁/*a*
a = 7.750 (4) Å
b = 13.131 (6) Å
c = 10.912 (3) Å
 β = 91.22 (3)°
V = 1110.1 (8) Å³
Z = 4
D_x = 1.926 Mg m⁻³

Mo K α radiation

λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 17.7–20.0°
 μ = 7.20 mm⁻¹
T = 173 K
 Prism
 0.46 × 0.18 × 0.18 mm
 Yellow

Data collection

Rigaku AFC-6R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2212 measured reflections
 2057 independent reflections
 1189 observed reflections
 [*I* > 3 σ (*I*)]
R_{int} = 0.021

θ_{\max} = 25.0°
h = 0 → 9
k = 0 → 15
l = -12 → 12
 3 standard reflections monitored every 150 reflections
 intensity decay: range 1.2–0.2%, average 0.4%

Refinement

Refinement on *F*
R = 0.029
wR = 0.031
S = 1.19
 1090 reflections
 140 parameters
 H-atom parameters not refined, atoms included in calculated positions

$w = 1/[\sigma^2(F_o) + 0.03(F_o)^2]$
 $(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	Occupancy†	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
C(1)	1.00	0.8405 (7)	0.0023 (4)	0.6562 (5)	1.8 (2)
C(2)	0.94	0.7594 (7)	0.0101 (5)	0.5348 (5)	1.9 (3)
C(3)	0.94	0.7651 (7)	-0.0684 (4)	0.4567 (5)	1.9 (3)

C(4)	0.94	0.8451 (7)	-0.1655 (5)	0.4867 (5)	2.4 (3)
C(5)	0.94	0.9170 (7)	-0.1735 (5)	0.6134 (5)	2.3 (3)
C(6)	0.94	0.9184 (7)	-0.0937 (5)	0.6913 (5)	2.2 (3)
C(7)	1.00	0.8355 (7)	0.0849 (4)	0.7313 (5)	2.0 (3)
C(8)	1.00	0.9115 (7)	0.0905 (4)	0.8568 (5)	2.4 (3)
C(9)	1.00	0.9774 (8)	0.1964 (5)	0.8902 (5)	3.1 (3)
C(10)	0.94	1.0325 (24)	-0.2887 (15)	0.7621 (5)	2.3 (5)
O(1)	0.94	0.8571 (6)	-0.2360 (3)	0.4147 (4)	3.3 (2)
O(2)	0.94	0.9770 (6)	-0.2687 (4)	0.6390 (4)	3.0 (3)
Br(1)	0.94	0.66228 (8)	-0.05707 (6)	0.29796 (5)	3.06 (3)
Br(2)	1.00	0.72330 (8)	0.05376 (6)	0.97247 (5)	3.44 (3)
O(2A)	0.06	0.73 (1)	-0.105 (6)	0.349 (7)	3.3 (8)
Br(1A)	0.06	1.017 (5)	-0.297 (3)	0.714 (2)	3 (1)
C(2A)	0.06	0.909	-0.091	0.716	1.9
C(3A)	0.06	0.922	-0.181	0.646	1.9
C(4A)	0.06	0.862	-0.187	0.525	2.3
C(5A)	0.06	0.785	-0.090	0.475	2.3
C(6A)	0.06	0.780	-0.005	0.540	2.2
C(10A)	0.06	0.662	-0.013	0.295	2.3
O(1A)	0.06	0.873	-0.267	0.468	3.3

† Atoms with an occupancy factor of 1.00 belong to both isomers, those with an occupancy factor of 0.94 belong to isomer (1) and those with an occupancy factor of 0.06 to isomer (2).

Table 2. Selected geometric parameters (Å, °)

C(1)—C(2)	1.458 (7)	C(4)—O(1)	1.219 (7)
C(1)—C(6)	1.446 (8)	C(5)—C(6)	1.349 (8)
C(1)—C(7)	1.361 (7)	C(5)—O(2)	1.361 (7)
C(2)—C(3)	1.339 (8)	C(7)—C(8)	1.481 (7)
C(3)—C(4)	1.452 (8)	C(8)—C(9)	1.523 (8)
C(3)—Br(1)	1.897 (5)	C(8)—Br(2)	2.008 (5)
C(4)—C(5)	1.483 (8)	C(10)—O(2)	1.427 (11)
C(2)—C(1)—C(6)	118.1 (5)	C(4)—C(5)—C(6)	122.0 (6)
C(2)—C(1)—C(7)	118.3 (5)	C(4)—C(5)—O(2)	112.1 (6)
C(6)—C(1)—C(7)	123.6 (5)	C(6)—C(5)—O(2)	125.9 (6)
C(1)—C(2)—C(3)	120.3 (5)	C(1)—C(6)—C(5)	120.8 (5)
C(2)—C(3)—C(4)	123.6 (5)	C(1)—C(7)—C(8)	125.5 (5)
C(2)—C(3)—Br(1)	120.1 (5)	C(7)—C(8)—C(9)	113.0 (5)
C(4)—C(3)—Br(1)	116.3 (4)	C(7)—C(8)—Br(2)	106.8 (4)
C(3)—C(4)—C(5)	115.0 (5)	C(9)—C(8)—Br(2)	108.3 (4)
C(3)—C(4)—O(1)	124.1 (5)	C(5)—O(2)—C(10)	117.2 (9)
C(5)—C(4)—O(1)	121.0 (6)		
C(1)—C(2)—C(3)—C(4)	1.9 (8)		
C(1)—C(2)—C(3)—Br(1)	-179.1 (4)		
C(1)—C(6)—C(5)—C(4)	3.5 (9)		
C(1)—C(6)—C(5)—O(2)	-175.9 (5)		
C(1)—C(7)—C(8)—C(9)	147.4 (5)		
C(1)—C(7)—C(8)—Br(2)	-93.7 (6)		
C(2)—C(1)—C(6)—C(5)	0.4 (8)		
C(2)—C(1)—C(7)—C(8)	-179.7 (5)		
C(2)—C(3)—C(4)—C(5)	1.8 (8)		
C(2)—C(3)—C(4)—O(1)	-176.9 (6)		
C(3)—C(2)—C(1)—C(6)	-3.1 (8)		
C(3)—C(2)—C(1)—C(7)	178.3 (5)		
C(3)—C(4)—C(5)—C(6)	-4.6 (8)		
C(4)—C(5)—O(2)—C(10)	-171.5 (10)		
O(1)—C(4)—C(5)—O(2)	-6.3 (8)		
O(1)—C(4)—C(3)—Br(1)	4.0 (8)		

Data were collected and reduced using *TEXSAN* (Molecular Structure Corporation, 1985), which was also used for cell refinement. One data set was collected at room temperature. It was observed that exposure of the crystal to Mo $K\alpha$ radiation resulted in a marked drop in intensity within one day and the crystal cracked. The data set was corrected for the decay. No absorption correction was applied as $\mu r \approx 0.8$; the resulting transmission factors indicate that the effects of absorption correction would be negligible. The structure was solved using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). *TEXSAN* was used for refinement. A structure with ordered molecules of (1) could be refined to $R = 0.046$. However, the crystal structure arrived at was

not completely satisfactory. The displacement parameter B_{iso} of C(10) (1.7 \AA^2) was unreasonably small (expected value $> 6 \text{ \AA}^2$) which indicates the presence of more electrons near C(10). Moreover, the calculated C(10)—O(2) bond distance [$1.11 (2) \text{ \AA}$] was far too short (expected value about 1.43 \AA). It was noticed that the presence of a Br atom, with a low occupation number, near the methoxy group position could explain the anomalies. A solution to these problems was achieved by assuming a model with small amounts of isomer (2) present in the crystal (Fig. 2). Due to overlap, only the positions of the non-H atoms of (1) and atoms Br(1A), C(10A) and O(1A) of (2) could be refined. All other atoms were included in calculated positions [with 90% of (1) and 10% of (2) R became 0.028, wR 0.031 and S 1.64]. With this model, the bond distances obtained became reasonable, but the errors were unacceptably large ($0.01\text{--}0.04 \text{ \AA}$). Therefore, data were collected for a second crystal (from another batch) at 173 K. There were no signs of deterioration of this crystal during the irradiation (duration 24 h). In this case, a structure with ordered molecules of (1) could be refined to $R = 0.035$. B_{iso} for C(10) became 1.6 \AA^2 and the bond distance C(10)—O(2) 1.28 \AA . The same model as above was applied. In the final cycles of the refinement the non-H atoms of molecule (1) and C(10A) and Br(1A) of (2) were refined. All other atoms were included in calculated positions. An occupation number of 0.06 for isomer (2) gave a minimum (0.029) R value and reasonable displacement parameters.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures - an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Ede, R. M., Main, L. & Ralph, J. (1990). *J. Wood Chem. Technol.* **10**, 101–110.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Gregson, M., Ollis, W. D., Redman, B. T., Sutherland, I. O. & Dietrichs, H. H. (1968). *Chem. Commun.* pp. 1395–1396.
- Hell, C. & Portmann, B. (1895). *Ber. Dtsch. Chem. Ges.* **28**, 2088–2093.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Karle, I. & Bultman, J. D. (1976). *Acta Cryst.* **B32**, 1963–1968.
- Kutney, J. P., Hewitt, G. M., Lee, G., Piotrowska, K., Roberts, M. & Rettig, S. J. (1992). *Can. J. Chem.* **70**, 1455–1480.
- Molecular Structure Corporation. (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Palmer, K. J., Wong, R. Y. & Jurd, L. (1973). *Acta Cryst.* **B29**, 1509–1514.
- Ralph, J. & Adams, B. R. (1983). *J. Wood Chem. Technol.* **3**, 183–194.
- Ralph, J. & Ede, R. M. (1988). *Holzforchung*, **42**, 337–338.
- Shevchenko, S. M. & Apushkinskii, A. G. (1992). *Russ. Chem. Rev.* **61**, 105–131.
- Zincke, Th. & Hahn, O. (1903). *Justus Liebigs Ann. Chem.* **329**, 1–36.