

[1.42 (2) Å] has the usual single-bond value (André, Fourme & Zechmeister, 1972; Jeffrey & Park, 1972), and the C(2)–O(3)–C(2<sup>1</sup>) angle of 117 (2)<sup>o</sup> is consistent with the observations reported for other ethers and is close to the value of 115<sup>o</sup> found in Na<sub>3</sub>[Yb(ODA)]<sub>3</sub>·2NaClO<sub>4</sub>·6H<sub>2</sub>O.

The C(1)–C(2)–O(3) angle has the expected tetrahedral value while the three angles subtended at C(1) are very close to 120<sup>o</sup>.

The oxygen–oxygen contact distances along the edges of the uranium coordination polyhedron are reported in Table 3.

Apart from the O(1<sup>ii</sup>)–O(1<sup>iii</sup>) contact of 3.33 Å, all distances between the coordinated oxygen atoms, except those belonging to the same ligand are in the range 2.83–2.99 Å, *i. e.* larger than twice the van der Waals radius of oxygen (1.4 Å).

However, the relatively small hindrance of the organic ligand, as well as the fact that each chemical unit is linked to four others, causes the structure to be very compact, so that there are relatively short U–U contacts of 5.46 and 6.03 Å.

Finally we point out that from the solution a three-dimensional polymeric covalent crystal has been obtained.

We thank Mrs M. Magnabosco and Mr F. Benetollo for their valuable assistance with the practical work.

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## An Improved Structure of *trans*-Stilbene\*

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The structure of *trans*-stilbene has been reinvestigated and an improved set of structure parameters determined. Cell constants of  $a=15.710$  (4),  $b=5.723$  (1),  $c=12.381$  (3) Å and  $\beta=111.89$  (4)<sup>o</sup> were measured and the space group  $P2_1/c$  with  $Z=4$  was confirmed. Least-squares refinement of all atoms including the hydrogen atoms converged to an  $R$  of 0.072. The molecule was found to be almost planar with the phenyl rings only slightly twisted from the general plane of the molecule. A disorder similar to that found for the isostructural compound, azobenzene, has been observed. Various parameters have been compared with those found in the earlier work.

### Introduction

There appeared in the literature (Robertson & Woodward, 1937) some time ago an X-ray structure determination of *trans*-stilbene (I). The analysis suffers from many of the problems which early crystallographers faced: comparatively inaccurate data collection methods, solution of structure in projection, poor e.s.d.'s, and limited computational facilities. However, this

structure has been used by numerous authors in the last few years as the basis for MO calculations (Ljunggren & Wettermark, 1970; Bromberg & Muszkat, 1972; Beringhelli, Gavezzotti & Simonetta, 1972), conclusions about u.v. geometries (Bernstein, 1972; Bürgi & Dunitz, 1971; Momicchioli, Baraldi & Bruni, 1972), and other results (Baughman, 1971; Frank, Myasnikova & Kitaigorodskii, 1971). We were in need of a better determination of the geometry of (I) for molecular mechanics work that is in progress (Allinger & Sprague, 1973) and consequently recollected the 3-D X-ray data and refined the structure of (I). We now report the findings of this study.

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### Experimental

The crystal used for data collection was prepared by trituration with 95% ethanol. No preliminary data were collected on film. The cell dimensions were determined from least-squares refinement of 28 accurately centered points using Cu  $K\bar{\alpha}$  radiation (1.5418 Å).  $a = 15.710$  (4),  $b = 5.723$  (1),  $c = 12.381$  (3) Å,  $\beta = 111.89$  (4)°,  $V = 1033$  Å<sup>3</sup>. For a formula weight of 180.25 (C<sub>14</sub>H<sub>12</sub>) and assuming  $Z = 4$ , the density calculated is 1.156 g cm<sup>-3</sup>. The literature value (*Handbook of Chemistry and Physics*, 1963) for the density of the solid is 1.164 g cm<sup>-3</sup>. The linear absorption coefficient,  $\mu(\text{Cu } K\bar{\alpha})$  is 5.005 cm<sup>-1</sup>. These data are in reasonable agreement with those of Robertson & Woodward (1937) who found  $a = 12.35$ ,  $b = 5.70$ ,  $c = 15.92$  Å,  $\beta = 114.0^\circ$  and  $V = 1023$  Å<sup>3</sup>. Their measured density was 1.159 g cm<sup>-3</sup> and the calculated density was 1.161 g cm<sup>-3</sup>. Systematic absences observed on the diffractometer confirm their space group assignment as  $P2_1/a$ . However, we have chosen to reassign the space group designation as the more standard designation  $P2_1/c$ .

All data were collected on a crystal of dimensions 0.3 × 0.4 × 0.4 mm on an Enraf-Nonius CAD-4 automated diffractometer which uses a graphite monochromator and Cu  $K\bar{\alpha}$  radiation with the  $\omega$ - $2\theta$  scan technique. A series of three standard reflections, measured after every 51 data points, indicated that no significant decomposition occurred during data collection. The data were then corrected for Lorentz-polarization effects by means of *DATRED* (Finder & Newton, 1972) but were not corrected for absorption. Out of a possible total of 2366 reflections, 1685 were collected with  $\sin \theta/\lambda < 0.619$  and  $I > 2\sigma$ . The reflections which had  $I < 2\sigma$  were not included in the final data set.

### Determination and refinement

The data were reduced to an absolute scale by the method of Wilson (1942), and  $E$  values obtained by use of *FAME* (Dewar, Stone & Fleischer, 1968). The structure was solved by direct methods with *MULTAN*

(Germain, Main & Woolfson, 1971) and the 218  $E$ 's  $> 1.5$ . The set of phases with the highest ABSFOM (1.19) led to a successful solution of the structure. An  $E$  map generated from this set of phases produced starting positions for all 14 non-hydrogen atoms which gave an initial conventional  $R = 0.401$ . After 5 cycles of full-matrix least-squares refinement with *UCLALS* (Gantzel, Sparks & Trueblood, 1961) with isotropic temperature factors and unit weights, the value of  $R$  dropped to 0.140. Use of anisotropic temperature factors and unit weights for 5 cycles lowered  $R$  to 0.119. A difference map at this stage of refinement revealed starting positions for the 12 hydrogen atoms. Fourteen cycles of full matrix least-squares refinement, treating carbon atoms anisotropically and hydrogen atoms isotropically and weights of  $1/\sigma(F_{\text{obs}})$ , produced a final unweighted, conventional  $R$  of 0.072.\*

### Results and discussion

Table 1 gives the positions and e.s.d.'s of all atoms along with the anisotropic temperature factors  $\beta$ 's obtained from the least-squares refinement. Because of the difference in relative cell lengths between  $a$  and  $b$ ,  $U$ 's were computed to facilitate comparisons of the anisotropic temperature factors. The results of these conversions are given in Table 2. An interesting observation originally reported by Robertson & Woodward (1937) has been confirmed by us. Although  $P2_1/c$  has four equivalent positions, and  $Z = 4$  for this cell, (I) has been found to occupy a center of inversion in the unit cell. The net result of this is to generate two unique non-attached halves per asymmetric unit (Fig. 1). These are referred to in the text as molecules 1 and 2. Further, as was previously observed, the two halves are very nearly related by a twofold screw axis parallel to  $a$ . Such a relation is, of course, not allowed by a

\* A table of observed and calculated  $F$ 's has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 30208, 13 pp., 1 microfiche. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final atomic positions and temperature factors ( $\times 10^5$ )

The anisotropic temperature factors are of the form:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
1C(1)	0.47677 (15)	0.40540 (45)	0.00215 (21)	495 (11)	3668 (85)	698 (18)	-167 (50)	548 (23)	-183 (64)
1C(2)	0.42390 (14)	0.36768 (41)	0.07662 (18)	404 (10)	3485 (77)	631 (17)	-3 (48)	381 (20)	170 (59)
1C(3)	0.42186 (16)	0.52690 (46)	0.16085 (20)	487 (11)	3528 (84)	726 (19)	-159 (52)	484 (23)	68 (64)
1C(4)	0.36899 (18)	0.48353 (52)	0.22683 (23)	601 (13)	4170 (99)	808 (21)	113 (60)	735 (27)	52 (74)
1C(5)	0.31809 (18)	0.28024 (52)	0.21068 (24)	540 (13)	4504 (104)	934 (24)	204 (60)	783 (29)	784 (78)
1C(6)	0.32023 (18)	0.11965 (31)	0.12937 (25)	559 (13)	3776 (93)	1049 (25)	-341 (60)	709 (30)	482 (77)
1C(7)	0.37302 (17)	0.16222 (46)	0.06339 (22)	533 (12)	3348 (84)	878 (22)	-303 (54)	606 (26)	-153 (68)
2C(1)	0.96937 (19)	0.07355 (57)	0.96884 (26)	592 (14)	4691 (113)	1034 (26)	123 (63)	718 (30)	314 (84)
2C(2)	0.91804 (15)	0.05886 (52)	0.84116 (22)	469 (12)	4568 (99)	825 (21)	-74 (58)	599 (26)	526 (74)
2C(3)	0.92455 (18)	-0.12134 (55)	0.76934 (26)	541 (13)	4492 (110)	1084 (27)	361 (64)	642 (31)	605 (86)
2C(4)	0.87412 (21)	-0.11838 (58)	0.65108 (28)	658 (16)	4650 (116)	1091 (28)	-136 (72)	828 (35)	-767 (94)
2C(5)	0.81588 (18)	0.06536 (61)	0.60207 (25)	504 (13)	5689 (126)	852 (24)	-79 (69)	469 (28)	461 (89)
2C(6)	0.80974 (20)	0.24514 (60)	0.67239 (28)	599 (15)	5204 (128)	1080 (28)	694 (74)	660 (33)	800 (98)
2C(7)	0.85933 (21)	0.24206 (56)	0.78958 (27)	658 (15)	4514 (110)	1022 (25)	376 (68)	816 (32)	57 (85)

Table 1 (cont.)

	$x/a$	$y/b$	$z/c$	$B_{iso} \times 10^2$
1C(1)H	0.4709 (20)	0.2807 (54)	-0.0578 (27)	337 (64)
1C(3)H	0.4580 (19)	0.6792 (53)	0.1713 (24)	291 (57)
1C(4)H	0.3633 (18)	0.5985 (52)	0.2810 (25)	278 (57)
1C(5)H	0.2843 (20)	0.2374 (54)	0.2552 (26)	315 (62)
1C(6)H	0.2880 (21)	-0.0303 (58)	0.1196 (26)	360 (64)
1C(7)H	0.3808 (18)	0.0406 (54)	0.0099 (25)	306 (59)
2C(1)H	0.9604 (26)	0.2149 (77)	1.0255 (36)	641 (98)
2C(3)H	0.9711 (25)	-0.2594 (69)	0.8045 (34)	600 (93)
2C(4)H	0.8803 (22)	-0.2425 (61)	0.6076 (31)	407 (72)
2C(5)H	0.7774 (20)	0.0784 (53)	0.5163 (28)	366 (65)
2C(6)H	0.7667 (20)	0.3907 (60)	0.6340 (26)	392 (69)
2C(7)H	0.8535 (20)	0.3757 (54)	0.8415 (27)	351 (64)

monoclinic space group with  $b$  unique. The halves are not quite symmetry related, but their near symmetry is apparent, even in the intensity data, where  $h00$  is systematically weak for  $h$  odd.

Table 2. Anisotropic temperature factors  $U_{ij} (\times 10^4 \text{ \AA}^2)^*$ 

	$U_{11}$		$U_{22}$		$U_{33}$	
	1	2	1	2	1	2
C(1)	533	637	609	779	467	691
C(2)	435	505	578	758	422	552
C(3)	524	582	586	746	485	725
C(4)	647	708	692	772	540	729
C(5)	581	543	748	944	625	570
C(6)	602	645	627	864	701	722
C(7)	574	708	556	749	587	683

\*  $U$  values are referred to crystal axes.

Tables 3 and 4 list the bond lengths and bond angles respectively. We were at first disturbed by the short 1-1' double bond, 1.318 Å in molecule 1 and 1.295 Å in molecule 2, since they appear to be significantly different from the 1.33 Å listed in *International Tables for X-ray Crystallography* (1962) for C=C bonds. As was observed by Wyckoff (1971) and Brown (1966a), *trans*-stilbene is isostructural with azobenzene in the solid state. Furthermore, Brown observed appreciably larger thermal parameters for molecule 2 than for molecule 1. Although Brown at first ascribed this to the greater volume occupied by molecule 2, after solution of the structure of azotoluene (Brown, 1966b) which has the same space group but only  $\frac{1}{2}$  molecule per asymmetric unit, he proposed a different explanation. The azotoluene structure was found to consist of two molecular

orientations randomly occupying the same sites in 1:1 fashion. This disorder led to the observed short bonds and abnormally large anisotropic temperature factors in azotoluene. Brown (1966a) postulated that the short N-N bond in azobenzene resulted from a similar disorder.

Table 3. Bond lengths (Å)

1C(1)-1C(1')	1.318 (3)*	1C(6)-1C(7)	1.386 (3)
2C(1)-2C(1')	1.295 (6)*	2C(6)-2C(7)	1.368 (4)
1C(1)-1C(2)	1.469 (3)	1C(1)-1C(1)H	1.00 (3)
2C(1)-2C(2)	1.485 (4)	2C(1)-2C(1)H	1.11 (4)
1C(2)-1C(3)	1.394 (3)	1C(7)-1C(7)H	1.00 (3)
2C(2)-2C(3)	1.390 (4)	2C(7)-2C(7)H	1.02 (3)
1C(2)-1C(7)	1.397 (3)	1C(3)-1C(3)H	1.02 (3)
2C(2)-2C(7)	1.385 (4)	2C(3)-2C(3)H	1.05 (4)
1C(3)-1C(4)	1.387 (3)	1C(4)-1C(4)H	0.97 (3)
2C(3)-2C(4)	1.381 (4)	2C(4)-2C(4)H	0.92 (3)
1C(4)-1C(5)	1.384 (4)	1C(5)-1C(5)H	0.93 (2)
2C(4)-2C(5)	1.377 (4)	2C(5)-2C(5)H	1.01 (3)
1C(5)-1C(6)	1.373 (4)	1C(6)-1C(6)H	0.98 (3)
2C(5)-2C(6)	1.375 (5)	2C(6)-2C(6)H	1.07 (3)

\* These  $\sigma$ 's, calculated from positional parameters related by an inversion center, have been corrected for correlation assuming a correlation coefficient of +1.

Table 4. Bond angles

Heavy atoms only	Molecule 1	Molecule 2
C(2)-C(1)-C(1')	126.7 (2)°	125.8 (3)°
C(1)-C(2)-C(3)	123.3 (2)	125.6 (2)
C(1)-C(2)-C(7)	118.9 (2)	116.9 (3)
C(3)-C(2)-C(7)	117.8 (2)	117.5 (2)
C(2)-C(3)-C(4)	120.6 (2)	121.3 (2)
C(3)-C(4)-C(5)	120.4 (2)	120.0 (3)
C(4)-C(5)-C(6)	119.9 (2)	119.0 (3)
C(5)-C(6)-C(7)	119.9 (2)	121.1 (3)
C(2)-C(7)-C(6)	121.4 (2)	121.1 (3)
Involving a hydrogen atom		
C(2)-C(1)-C(1)H	116.1 (14)	124.4 (20)
C(1')-C(1)-C(1)H	116.8 (14)	109.7 (20)
C(2)-C(3)-C(3)H	119.0 (14)	119.8 (21)
C(4)-C(3)-C(3)H	120.3 (14)	118.8 (21)
C(3)-C(4)-C(4)H	121.1 (14)	117.9 (21)
C(5)-C(4)-C(4)H	118.3 (14)	122.1 (21)
C(4)-C(5)-C(5)H	124.2 (19)	124.0 (16)
C(6)-C(5)-C(5)H	115.7 (19)	117.0 (16)
C(5)-C(6)-C(6)H	121.6 (16)	119.0 (17)
C(7)-C(6)-C(6)H	118.4 (16)	119.9 (17)
C(2)-C(7)-C(7)H	117.2 (13)	118.4 (17)
C(6)-C(7)-C(7)H	121.1 (14)	120.5 (17)
C(1)-C(1')-C(1')H	116.8 (14)	109.7 (20)

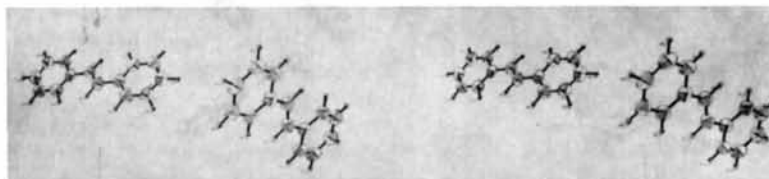


Fig. 1. Stereo drawing of *trans*-stilbene unique halves and the center of inversion related halves. Drawing made by ORTEP (Johnson, 1965).

It is not surprising that *trans*-stilbene possesses a similar disorder. The parallels in the temperature factors and in the short bonds are apparent. More weight is given to this hypothesis by the observation of an otherwise unexplained peak in the difference map at  $x=0.922$ ,  $y=-0.078$ , and  $z=0.947$  which is about a third more intense than the peak at  $2C(1)H$ . This peak is on the inside of the  $2C(1')-2C(1)-2C(2)$  angle at a position too close to  $2C(1')$ ,  $2C(1)$  and  $2C(2)$  to be chemically meaningful. This peak is most likely a result of a partial occupancy of this site by another molecule. On the basis of this evidence we conclude, as did Brown, that the data for molecule 1 is more accurate than that for molecule 2. Therefore, results based on molecule 2 will be significantly less reliable than those based on molecule 1, and molecule 1 will be used for comparison purposes unless otherwise stated.

The  $C(1)-C(1')$  double bond can, however, be compared with that found by Robertson & Woodward (1937) which was  $1.33 \pm 0.04$ . The average C-C bond in the benzene ring was  $1.39$  Å as compared to our  $1.385$  Å, and the single-bond values agree well with Robertson & Woodward's (1937)  $1.44$  Å and  $1.45$  Å which are  $\pm 0.02$ . The  $C(2)-C(1)-C(1')$  angle is observed to be smaller than Robertson & Woodward's (1937),  $126.7(2)^\circ$  as compared to  $128^\circ$ . This is not surprising as Robertson & Woodward do not place a great deal of reliability on their measured angle.

Of perhaps greater importance are the dihedral angles. Of those dihedral angles involving only heavy atoms, the greatest deviation from planarity is  $5^\circ$  and this is the twist angle of the phenyl from the vinyl group in molecule 1. The actual angle is  $4.98(35)^\circ$  in 1 and  $3.30(36)^\circ$  in 2. The e.s.d.'s for the dihedral angles are calculated by evaluation of the analytical derivatives and will be reported elsewhere (Finder & Newton,

1973). These data compare with Robertson & Woodward's (1937) observation of  $10^\circ$  and  $3^\circ$  respectively for this twist.

The near planarity of the molecule leads to other effects. The vinyl hydrogen is now squeezed between the *o* and *o'* hydrogens leading to a  $1C(1)H-1C(7)H$  distance of  $2.34$  Å and a  $1C(1)H-1C(3')H$  distance of only  $2.11$  Å. In molecule 2, the corresponding distances are  $2.45$  and  $1.99$  Å, respectively.

The benzene ring carbons and hydrogens are planar with an average deviation from planarity of only  $0.02$  Å. Although the near planarity of the entire molecule enforces some close intramolecular approaches, there are only a few close intermolecular approaches as can be seen in the unit-cell diagram (Fig. 2). In agreement with Robertson & Woodward (1937), there are no carbon-carbon intermolecular distances of less than  $3.5$  Å, and no carbon-hydrogen distances of less than  $2.96$  Å. There are only two intermolecular approaches which might be considered less than van der Waals radii, and these are symmetry related.  $2C(6)H$  is only  $2.49$  Å from  $1C(7)H$  of the molecule related by  $2_1$ , and translated one cell on  $x$ . The other is  $2C(6')H$  to  $1C(7')H$  related by  $2_1$ , and translated two cells on  $x$ , two cells on  $-y$  and one cell on  $z$ .

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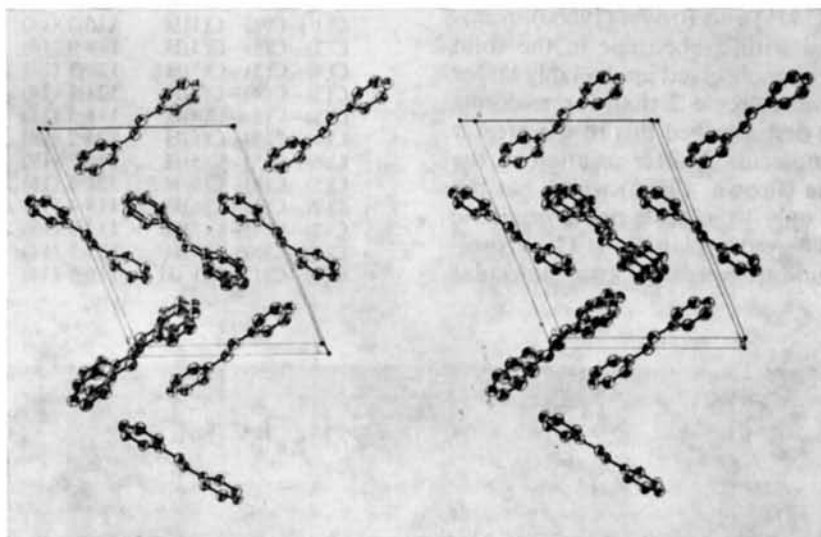


Fig. 2. Stereoscopic packing diagram of *trans*-stilbene. Drawing made by ORTEP (Johnson, 1965). View is down the unique  $b$  axis with  $c$  horizontal.

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## The Crystal Structure of Monobromodehydrobispulegone

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Crystals of monobromodehydrobispulegone,  $C_{20}H_{27}BrO$ , are orthorhombic, space group  $P2_12_12_1$ , with four molecules per unit cell. The lattice constants are:  $a = 11.656$  (2),  $b = 11.669$  (2),  $c = 12.766$  (2) Å. The crystal structure has been solved by the heavy-atom technique and refined by the full-matrix least-squares method. The final  $R$  index for 692 independent observed reflexions is 0.107. The molecule shows stress in the pentagonal ring. In the cyclohexane ring the oxygen and bromine substituents appear to be coplanar and the methyl substituent is in an axial position. The molecular packing shows no remarkable directional features.

### Introduction

The study of the crystal structure of monobromodehydrobispulegone, whose chemical formula appears in Fig. 1, was undertaken in order to determine some conformational aspects of the substances obtained from the reductive dimerization of the pulegone, and continues the work begun with the X-ray structure determination of the analogous compound, dibromodehydrobispulegone (Perales, Martínez-Carrera & García-Blanco, 1969). Extensive chemical studies of such a dimerization have already appeared in the literature (Camps, Esquefa, Ferrer, Magrans, Pascual & Sust, 1961; Bartual, Ferrer, Pascual & Vendrell, 1966; Bartual, Camps, Pares & Pascual, 1968; Bartual & Pascal, 1970; Bartual, Camps, Ferrer, Pascual & Roque, 1970; Font-Cistero, 1972). It was thought convenient to study the present compound by X-ray techniques in order to determine the cause of the stress on the C(8) atom (Fig. 1) and the conformation of the cyclohexane substituents.

### Experimental

Crystals of monobromodehydrobispulegone were kindly made available to us by Dr J. Pascual Vila (Departa-

mento de Química Orgánica, Universidad de Barcelona). The crystals are colourless prisms elongated along the  $c$  axis. The density was measured by flotation in aqueous potassium iodide solution. The lattice constants were determined by means of a four-circle automatic diffractometer and are shown in Table 1 with other physical constants.

Table 1. *Crystal data for monobromodehydrobispulegone*  
Standard deviations, given in parentheses, refer to the least significant digits.

Formula	$C_{20}H_{27}BrO$
Molecular weight	362.91
Wavelength (Cu $K\alpha$ )	1.5418 Å
$a$	11.656 (2) Å
$b$	11.669 (2)
$c$	12.766 (2)
$V$	1737.64 Å <sup>3</sup>
$Z$	4
$D_{\text{obs}}$ (flotation)	1.33 g cm <sup>-3</sup>
$D_{\text{cal}}$	1.39
$\mu$ (Cu $K\alpha$ )	32.66 cm <sup>-1</sup>
$F(000)$	760
Space group	$P2_12_12_1$

Intensity data were collected at room temperature with Ni-filtered Cu  $K\alpha$  radiation from multiple-film in-