

for anomalous dispersion. The final R was 0.066 for 1681 observed data.* Final positional parameters are given in Table 1, with estimated standard deviations in parentheses. Bond lengths and angles are in Table 2. The numbering system and stereochemistry are shown in Fig. 1.

Discussion. A rearrangement, different from that which formed the dibromide (II) (Sommerville & Laing, 1978*b*), has occurred yielding a 1,9-ether bridge and a double bond between C(1) and C(2). O(2) has reacted with the ethanol thus forming a ketal with O(1) of the vinyl bromide system of ring *A*. Ring *B* is forced into a boat conformation and two bromines have substituted α to C(9). The conformation of the substituents on ring *B* is: phenyl at C(7)-*endo* [torsion angle C(1)–C(6)–C(7)–C(18) 171°], *trans* to Br(3) at C(8)-*exo* [C(18)–C(7)–C(8)–Br(3) 97°]; phenyl at C(11)-*exo* [C(1)–C(6)–C(11)–C(12) 79°], *trans* to Br(2) at C(10)-*endo* [C(12)–C(11)–C(10)–Br(2) 95°]. If ring *B* were an ideal boat, the *endo*–*exo* torsion angle would be 120°; the value of about 95° found in (III) reflects a twisting about bonds C(7)–C(8) and C(10)–C(11) to relieve *endo*...*endo* strains between the Br at C(10) and the phenyl ring at C(7) [torsion angles C(6)–C(7)–C(8)–C(9) 8° and C(9)–C(10)–C(11)–C(6) 13°]. Thus the *endo* groups have moved out and away, while the *exo* groups have moved down and in.

The six-membered O-rings impose little strain on the molecule (as shown by the coplanarity of the atoms of

the vinyl system). A model shows that the framework is rigid, and only C(4) is movable to any extent. This mobility is evident in its *B* value which is considerably larger than the *B* of any other atom in the spiro skeleton. Ring *A* is best described as a 'sofa', C(1), C(2), C(6) and C(5) being coplanar within 0.01 Å with C(3) only 0.12 Å out of the plane. C(4) is 0.68 Å away from the plane. C(4) is bent towards the phenyl ring at C(11), presumably so that the H atom on C(5), *syn* to C(11), is bent down and away from C(12) of the phenyl ring. If ring *A* takes the alternative sofa conformation with C(4) folded away from the *exo* phenyl ring, the H atom on C(5) is forced close to C(12) thus generating intramolecular strain. It is possible that the particular 'sofa' conformation adopted by ring *A* is a result of the distortion of ring *B*. Examination of a Dreiding model of (III) shows that if Br(2) and C(18) are forced *inwards*, then the conformational strains resulting from torsion about the bonds C(10)–C(11) and C(7)–C(8) in ring *B* cause ring *A* to 'flip' so that C(4) now points away from the phenyl ring on C(11).

We thank the South African Council for Scientific and Industrial Research for generous financial support, Dr G. Gafner, National Physical Research Laboratory, CSIR, for collecting the intensities, and Dr L. P. L. Piacenza (University of Durban–Westville) for his interest and for supplying the sample.

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Acta Cryst. (1978). **B34**, 676–679

1,9-Epoxy-2,8,10-tribromo-9-methoxy-7,11-diphenylspiro[5.5]undec-1(2)-ene*

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(Received 13 July 1977; accepted 2 September 1977)

Abstract. C₂₄O₂H₂₃Br₃, $M_r = 583$, monoclinic, $P2_1/c$, $a = 8.58$ (1), $b = 15.84$ (2), $c = 16.62$ (2) Å, $\beta = 96.6$ (1)°, $V = 2244$ Å³, $D_c = 1.73$, $D_m = 1.71$ (2) g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 57.5$ cm⁻¹. $R = 0.054$ for

2007 observed data; three Br and 12 phenyl C atoms anisotropic, 20 H atoms included. This compound is the fourth product of the bromination of 7,11-diphenylspiro[5.5]undecane-1,9-dione and is the *O*-methyl analogue of the *O*-ethyl tribromo ketal compound described previously [Sommerville & Laing, *Acta*

* Bromides of a Diphenyl Spiro Diketone. IV.

Cryst. (1978), **B34**, 674–676], with which it is closely isostructural.

Introduction. When the spiro ketone 7,11-diphenylspiro[5.5]undecane-1,9-dione is brominated in pure chloroform, the products are isolated as a syrup. Crystallization can be achieved from methanol and CH_2Cl_2 , and needles of a compound (IV) different from those characterized previously (Sommerville & Laing,

1978*a,b,c*) can be isolated. Preliminary Weissenberg photographs showed that the crystal's unit-cell dimensions and *HOL*, *H1L* and *H2L* intensity distributions were similar to those of (III), one of the known compounds (Sommerville & Laing, 1978*c*), but the relationship between the two compounds was not clear. The crystal structure was therefore determined.

Data were collected from a crystal $0.2 \times 0.2 \times 0.5$ mm on a Philips four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) for θ between 3 and 22° . The ω - 2θ scan mode was used with a scan width of 1.0° ; each peak was counted for 30 s, and the background counting time was 30 s for each peak. Of the 2862 reflexions measured, 2007 were classed as observed with $I > 1.65\sigma(I)$. Three reflexions were used as standards, and their intensities measured every hour; no decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. It was evident that the compound was closely isostructural with one of the known compounds (III), and the three-dimensional Patterson map confirmed this. It too had three large peaks near the origin (one with $u, w \approx 0$) and a large peak on the Harker section at $v = \frac{1}{2}$. However, this peak had two maxima, one of 330 units and a second of 200

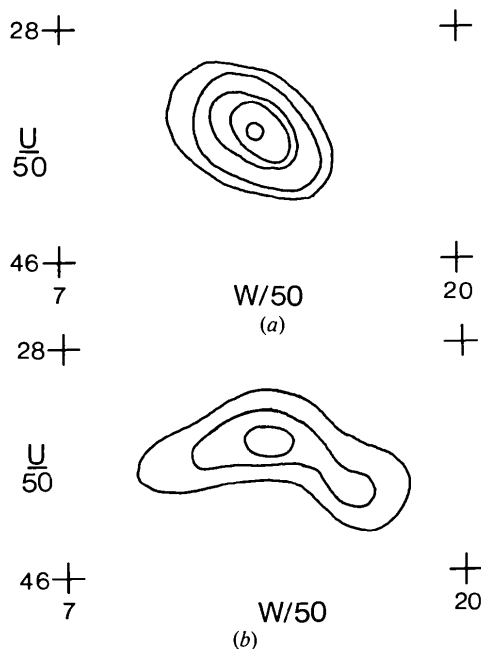


Fig. 1. The appearance of the Harker section $u\frac{1}{2}w$ of the Patterson maps of (a) (III) (Sommerville & Laing, 1978*c*) and (b) (IV). Contours are at intervals of 100 units starting at 100 relative to origin peaks of approximately 1800 units.

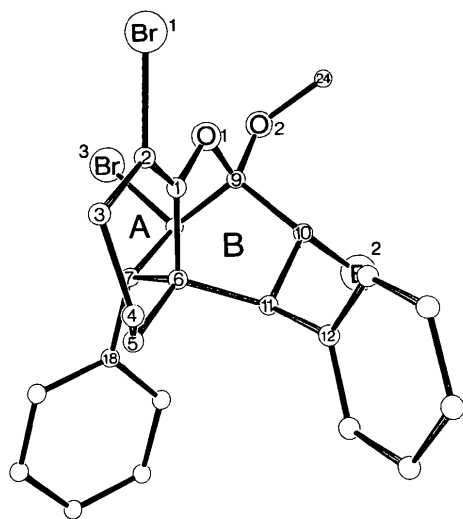


Fig. 2. A projection of the molecule showing the geometry and numbering system.

Table 1. Final fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters, with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Br(1)	8586 (1)	5950 (1)	3755 (1)	*
Br(2)	11443 (1)	3169 (1)	1040 (1)	*
Br(3)	6017 (2)	4382 (1)	831 (1)	*
O(1)	8927 (6)	4827 (4)	2323 (3)	3.52 (13)
O(2)	9429 (7)	4849 (4)	1000 (3)	4.02 (14)
C(1)	8679 (10)	4372 (5)	3014 (5)	2.88 (18)
C(2)	8478 (10)	4742 (5)	3688 (5)	3.14 (19)
C(3)	8110 (11)	4309 (6)	4439 (5)	4.20 (22)
C(4)	8616 (14)	3386 (8)	4404 (8)	8.41 (35)
C(5)	8145 (10)	2967 (6)	3621 (5)	4.28 (22)
C(6)	8583 (9)	3428 (5)	2869 (5)	2.78 (18)
C(7)	7244 (10)	3311 (5)	2153 (5)	3.20 (19)
C(8)	7776 (10)	3742 (5)	1402 (5)	3.62 (21)
C(9)	9193 (10)	4298 (6)	1641 (5)	3.65 (21)
C(10)	10621 (10)	3752 (5)	1938 (5)	3.35 (20)
C(11)	10159 (10)	3113 (5)	2580 (5)	3.19 (19)
C(12)	11494 (10)	2963 (5)	3251 (5)	*
C(13)	11879 (10)	2150 (6)	3496 (5)	*
C(14)	13032 (12)	2010 (6)	4152 (6)	*
C(15)	13818 (12)	2670 (7)	4567 (6)	*
C(16)	13429 (11)	3471 (7)	4314 (6)	*
C(17)	12310 (11)	3623 (6)	3666 (6)	*
C(18)	6714 (10)	2405 (5)	2018 (5)	*
C(19)	5452 (10)	2107 (6)	2404 (6)	*
C(20)	5019 (11)	1258 (6)	2370 (6)	*
C(21)	5796 (11)	708 (6)	1918 (6)	*
C(22)	7009 (11)	988 (6)	1509 (6)	*
C(23)	7486 (10)	1837 (5)	1563 (5)	*
C(24)	10830 (12)	5366 (6)	1094 (6)	4.95 (24)

* Anisotropic thermal parameters for these atoms have been deposited.

Table 2. *Interatomic distances (Å) and angles (°) and least-squares planes*(a) Selected intramolecular bond lengths (± 0.02 Å)

C(1)–C(2)	1.29	Br(1)–C(2)	1.92
C(2)–C(3)	1.49	Br(3)–C(8)	1.97
C(5)–C(6)	1.53	Br(2)–C(10)	1.95
C(6)–C(1)	1.52	C(9)–O(2)	1.41
C(6)–C(7)	1.57	O(2)–C(24)	1.45
C(7)–C(8)	1.54	C(7)–C(18)	1.51
C(8)–C(9)	1.52	C(11)–C(12)	1.52
C(9)–C(10)	1.53	O(1)–C(1)	1.39
C(10)–C(11)	1.56	O(1)–C(9)	1.45
C(11)–C(6)	1.57		

(b) Selected bond angles ($\pm 2^\circ$)

C(1)–C(2)–C(3)	125	C(10)–C(11)–C(6)	107
C(5)–C(6)–C(1)	111	C(11)–C(6)–C(7)	108
C(6)–C(1)–C(2)	125	C(6)–C(7)–C(18)	114
Br(1)–C(2)–C(1)	120	C(8)–C(7)–C(18)	114
Br(1)–C(2)–C(3)	115	C(6)–C(11)–C(12)	115
C(1)–O(1)–C(9)	114	C(10)–C(11)–C(12)	112
O(1)–C(1)–C(2)	122	Br(3)–C(8)–C(7)	110
O(1)–C(1)–C(6)	113	Br(3)–C(8)–C(9)	112
C(1)–C(6)–C(7)	105	Br(2)–C(10)–C(9)	111
C(1)–C(6)–C(11)	109	Br(2)–C(10)–C(11)	111
C(5)–C(6)–C(7)	110	O(2)–C(9)–C(8)	110
C(5)–C(6)–C(11)	114	O(2)–C(9)–C(10)	114
C(6)–C(7)–C(8)	108	O(1)–C(9)–O(2)	106
C(7)–C(8)–C(9)	110	O(1)–C(9)–C(8)	110
C(8)–C(9)–C(10)	110	O(1)–C(9)–C(10)	105
C(9)–C(10)–C(11)	109	C(9)–O(2)–C(24)	117

(c) Least-squares planes of the form $Ax + By + Cz = D$, where A , B and C are the direction cosines of the normal to the plane referred to the orthogonal axes a , b , c^* . The deviations in Å of the most relevant atoms from the planes are given in square brackets.

	A	B	C	D
Plane 1: C(6), C(7), C(8), C(9), C(10), C(11)				
	–0.125	0.836	0.534	5.72
[C(6) 0.50, C(7) –0.16, C(8) –0.33, C(9) 0.47, C(10) –0.13, C(11) –0.35, Br(2) –1.81, Br(3) 0.19, O(1) 1.82, O(2) 0.60, C(12) –0.08, C(18) –1.43]				
Plane 2: C(1), C(2), C(5), C(6)				
	0.941	–0.100	0.323	7.39
[C(1) –0.01, C(2) 0.01, C(5) 0.00, C(6) 0.01, C(3) 0.04, C(4) 0.59]				
Plane 3: C(1), C(2), C(3), C(6), Br(1), O(1)				
	0.956	–0.065	0.288	7.52
[C(1) 0.02, C(2) 0.02, C(3) –0.02, C(6) 0.00, Br(1) 0.00, O(1) –0.02, C(4) 0.48, C(5) –0.09]				

units relative to the origin peak of 1830 units. This splitting is a result of the differences between the pairs of x and z coordinates of the Br atoms not being as close to 0, 0.25 and 0.5 as they were in the *O*-ethyl analogue (see Fig. 1). The Fourier map, phased on the three Br atoms, gave the coordinates of the lighter atoms. The structure was refined by block-diagonal least squares with the three Br and 12 phenyl C atoms

anisotropic; all H atoms (except those of the *O*-methyl group) were included in the structure-factor calculations. Weighting was proportional to $1/\sigma(F)$. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of Br was corrected for anomalous dispersion. The final R was 0.054 for 2007 observed data.* Final positional parameters are given in Table 1, with estimated standard deviations in parentheses. Bond lengths and angles are in Table 2. The numbering system and molecular geometry are shown in Fig. 2.

Discussion. Compound (IV) is the *O*-methyl analogue of (III) which was described previously (Sommerville & Laing, 1978c), and the geometry of (IV) is for practical purposes identical with that of (III). The torsion angles involving the substituents on ring *B* are within 3° of the values found in (III): C(1)–C(6)–C(7)–C(18) 168° , C(1)–C(6)–C(11)–C(12) 81° , C(18)–C(7)–C(8)–Br(3) 95° , C(12)–C(11)–C(10)–Br(2) 93° . The dihedral angle between the planes of the phenyl rings is 86° [in (III) this angle is 89°]. It is thus evident that the conformation of the phenyl rings is largely unaffected by packing effects and, as was observed in (I) (Sommerville & Laing, 1978a), it is intramolecular H...H contacts which determine the relative orientation of the phenyl rings about their bonds to ring *B*. As was found in (III), ring *B* is distorted from the ideal boat conformation with torsion angles C(6)–C(7)–C(8)–C(9) 13° , and C(9)–C(10)–C(11)–C(6) 16° [both about 4° larger than in (III)].

A comparison of the mean effective volume per non-hydrogen atom in the crystals of each of the related compounds is instructive: (I) 19.40, (II) 19.22, (III) 19.09, (IV) 19.34 Å³ (Sommerville & Laing, 1978a,b,c). As may be expected, the values are similar for all compounds (Laing, 1975) but slightly larger than the commonly found value of 18 Å³. The difference in packing density between (II) and (III) shows up in the high thermal motion of the ethyl carbons in (II). The difference between the packing densities of (III) and (IV) is reflected in the increased flexibility of ring *A* in (IV). The large B value of C(4) is not an artefact because this atom too had the largest B of the C atoms of the spiro system in the *O*-ethyl analogue (III). The lower packing density in (IV) has removed some of the constraints on ring *A* thus allowing C(4) to have a larger vibration amplitude.

We thank the South African Council for Scientific and Industrial Research for generous financial support, Dr G. Gafner, National Physical Research Laboratory,

* Lists of structure factors, anisotropic thermal-motion parameters, and the fractional atomic coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32968 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

CSIR, for collecting the intensities, and Dr L. P. L. Piacenza (University of Durban-Westville) for his interest and for supplying the sample.

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Acta Cryst. (1978). **B34**, 679–680

α -Phényl- α -éthyl-acétate d' α -Phényl-éthylammonium *n*

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(Reçu le 21 juin 1977, accepté le 15 septembre 1977)

Abstract. [(+) $C_{10}O_2H_{11}$ ·(-) C_8NH_{12}], orthorhombic, space group $P2_12_12_1$, $a = 17.794$ (5), $b = 15.528$ (4), $c = 5.816$ (2) Å, $Z = 4$. The structure was solved by analogy with that of α -phenylethylammonium α -phenyl- α -methylacetate *n*. Full matrix least-squares refinement with identical weights converged at $R = 0.07$ for all 1605 observed reflexions. A secondary-extinction coefficient was introduced: $g = 1.1 \times 10^{-4}$. The molecules are linked by hydrogen bonds.

Introduction. L'étude du sel *n* d' α -phényl- α -éthyl-acétate d' α -phényl-éthylammonium, décrit dans cet article, s'inscrit dans le cadre de l'étude de la séparation des sels diastéréoisomères (Leclercq & Jacques, 1975; Brianso, 1976).

Les mesures d'intensité ont été effectuées sur diffractomètre Philips PW1100 en utilisant la radiation

Cu $K\alpha$ et en déduisant un fond continu théorique résultant d'une série unique de mesures effectuées en fonction de l'angle θ .

Les positions des atomes C, O et N ont été déterminées par analogie avec le sel d' α -phényl- α -méthyl-acétate d' α -phényl-éthylammonium *n* étudié précédemment (Brianso, 1976): paramètres cristallins voisins, groupe spatial identique. Une série de Fourier effectuée avec les phases du sel connu a permis de placer les 21 atomes de C, O et N, et une série différence les atomes H. Le facteur R étant resté fixé à 7%, le coefficient d'extinction

