2,2,10-Tribromo-7,11-diphenylspiro[5.5]undecane-1,9-dione–Methanol*

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Abstract. $C_{23}O_2H_{21}Br_3.CH_3OH$, $M_r = 569 + 32$ (solvent), monoclinic, $P2_1/n$, $a = 11.39$ (1), $b = 20.33$ (2), $c = 10.08$ (1) Å, $\beta = 94.3$ (1)°, $V = 2327$ Å³, $D_c = 1.72$, $D_m = 1.70$ (2) g cm⁻³, $Z = 4$, μ(Mo $K\alpha$) $= 55.5$ cm⁻¹. $R = 0.063$ for 2124 observed data; three Br and 12 phenyl C atoms anisotropic, 21 H atoms included. Both rings are distorted chairs; the conformations of the substituent groups are: phenyl at C(7), axial; Br at C(10), equatorial; phenyl at C(11), equatorial. O(1) of the keto group at C(1) is close to C(8) and C(10) of the other ring.

Introduction. As part of an investigation into the chemistry of naturally occurring sesquiterpenes with a spiro skeleton Dr L. P. L. Piacenza (University of Durban–Westville) studied the bromination of 7,11-diphenylspiro[5.5]undecane-1,9-dione (de Jongh, Gerhartl & Wynberg, 1965) under different conditions. A tribromide (I) was isolated from the reaction in glacial acetic acid. The positions of the Br atoms could not be deduced by chemical means, and because the configuration of the phenyl groups in the parent compound was also unknown, a crystallographic study of (I) was undertaken.

(I)
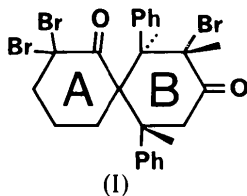
Suitable crystals were obtained from methanol and CH_2Cl_2. Data were collected from a crystal $0.2 \times 0.2 \times 0.2$ mm on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) for θ between 3 and 22°. The ω–2θ scan mode and a scan width of 0.6° were used; each peak was counted for 15 s, and the background counting time was 15 s for each peak. Of the 2955 reflexions measured, 2124 were classed as observed $[I > 1.65\sigma(I)]$. 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. A temperature-sharpened Patterson map

gave the coordinates of the three Br atoms and subsequent Fourier maps yielded the coordinates of the lighter atoms. A difference map showed that a molecule of methanol was present. The structure was refined by block-diagonal least squares with the three Br atoms and 12 phenyl C atoms anisotropic. All H atoms (excluding those of the methanol) 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*

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters for the non-hydrogen atoms*

Standard deviations are in parentheses.

	x	y	z	$B(\text{Å}^2)$
Br(1)	4137 (1)	1801 (1)	5772 (1)	*
Br(2)	6159 (1)	2027 (1)	3863 (1)	*
Br(3)	3384 (1)	5326 (1)	3656 (1)	*
O(1)	5055 (6)	3246 (3)	4775 (7)	3.66 (16)
O(2)	2886 (8)	4828 (4)	6325 (9)	5.96 (22)
C(1)	4288 (8)	2912 (5)	4209 (10)	2.61 (22)
C(2)	4490 (9)	2176 (5)	4062 (10)	3.14 (24)
C(3)	3796 (9)	1837 (5)	2915 (10)	3.41 (24)
C(4)	2517 (9)	2071 (5)	2786 (11)	3.50 (24)
C(5)	2491 (9)	2812 (5)	2571 (11)	3.04 (23)
C(6)	3092 (8)	3215 (5)	3725 (10)	2.40 (21)
C(7)	2330 (9)	3202 (5)	4960 (10)	3.01 (22)
C(8)	2864 (9)	3660 (5)	6079 (11)	3.34 (24)
C(9)	3097 (10)	4356 (5)	5629 (11)	3.94 (26)
C(10)	3655 (9)	4424 (5)	4322 (10)	3.09 (23)
C(11)	3236 (9)	3943 (5)	3225 (10)	3.10 (24)
C(12)	3986 (9)	3999 (4)	2018 (11)	*
C(13)	5207 (10)	4015 (6)	2184 (12)	*
C(14)	5818 (12)	4088 (6)	1039 (15)	*
C(15)	5283 (13)	4146 (6)	−166 (13)	*
C(16)	4090 (14)	4142 (6)	−354 (12)	*
C(17)	3450 (11)	4073 (6)	761 (12)	*
C(18)	1002 (9)	3328 (5)	4626 (10)	*
C(19)	256 (9)	2788 (6)	4576 (12)	*
C(20)	−907 (10)	2876 (7)	4311 (13)	*
C(21)	−1380 (10)	3484 (8)	4119 (13)	*
C(22)	−655 (11)	4032 (7)	4148 (14)	*
C(23)	546 (10)	3953 (6)	4410 (13)	*
O(3)	4482 (10)	14 (6)	3828 (11)	10.66 (34)
C(24)	5682 (13)	106 (7)	3909 (15)	7.68 (42)

* Anisotropic thermal parameters for these atoms have been deposited.

Table 2. *Interatomic distances* (Å) *and angles* (°) *and least-squares planes*

Selected intramolcular bond lengths (±0·02 Å)

C(1)–C(2)	1·52		C(10)–C(11)	1·53
C(2)–C(3)	1·52		C(11)–C(6)	1·58
C(3)–C(4)	1·53			
C(4)–C(5)	1·52		Br(1)–C(2)	1·95
C(5)–C(6)	1·54		Br(2)–C(2)	1·95
C(6)–C(1)	1·54		Br(3)–C(10)	1·97
C(6)–C(7)	1·57		C(1)–O(1)	1·21
C(7)–C(8)	1·55		C(9)–O(2)	1·22
C(8)–C(9)	1·52		C(7)–C(18)	1·55
C(9)–C(10)	1·51		C(11)–C(12)	1·54

Selected bond angles (±2°)

C(1)–C(2)–C(3)	116	C(5)–C(6)–C(7)	110
C(2)–C(3)–C(4)	111	C(5)–C(6)–C(11)	108
C(3)–C(4)–C(5)	109	C(6)–C(7)–C(8)	111
C(4)–C(5)–C(6)	115	C(7)–C(8)–C(9)	114
C(5)–C(6)–C(1)	111	C(8)–C(9)–C(10)	116
C(6)–C(1)–C(2)	120	C(9)–C(10)–C(11)	116
Br(1)–C(2)–Br(2)	107	C(10)–C(11)–C(6)	114
Br(1)–C(2)–C(1)	105	C(11)–C(6)–C(7)	110
Br(1)–C(2)–C(3)	111	C(6)–C(7)–C(18)	115
Br(2)–C(2)–C(1)	109	C(8)–C(7)–C(18)	113
Br(2)–C(2)–C(3)	108	O(2)–C(9)–C(8)	121
O(1)–C(1)–C(2)	119	O(2)–C(9)–C(10)	123
O(1)–C(1)–C(6)	121	Br(3)–C(10)–C(9)	108
C(1)–C(6)–C(7)	106	Br(3)–C(10)–C(11)	108
C(1)–C(6)–C(11)	112	C(6)–C(11)–C(12)	114
		C(10)–C(11)–C(12)	111

Atoms defining the least-squares planes and, in square brackets, deviations (Å) of atoms from them

Plane 1: C(6), C(7), C(8), C(9), C(10), C(11)

[C(6) 0·26, C(7) −0·26, C(8) 0·20, C(9) −0·13, C(10) 0·13, C(11) −0·19, Br(3) −0·90, O(2) −0·53, C(12) 0·29, C(18) −1·78]

Plane 2: C(1), C(2), C(5), C(6)

[C(1) −0·14, C(2) 0·08, C(5) −0·07, C(6) 0·14, C(3) −0·10, C(4) 0·56]

Crystallography, 1962); that of Br was corrected for anomalous dispersion. The final R was 0·063 for 2124 observed data.* Final positional parameters are given in Table 1. Some bond lengths and angles are given in Table 2. The numbering system and stereochemistry are shown in Fig. 1.

Discussion. Two of the three Br atoms have substituted α to C(1) on ring A while the third is on ring B between the keto group at C(9) and the phenyl group at C(11). Both rings are slightly distorted chairs; the conformations of the substituents on ring B are: phenyl at C(7),

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* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33054 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
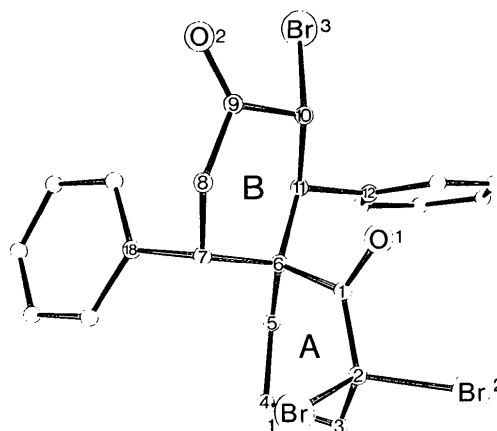

Fig. 1. A projection of the molecule showing the numbering system. Rings *A* and *B* are distorted chairs; pertinent torsion angles involving the ketone O atoms are Br(1)–C(2)–C(1)–O(1) 81; Br(2)–C(2)–C(1)–O(1) −33; Br(3)–C(10)–C(9)–O(2) −22°. The torsion angles between the equatorial Br atoms and keto O atoms thus differ by 10°, probably as a result of the constraint of the spiro system on the flexibility of the chairs *A* and *B*. The Br atoms do not eclipse the O atoms (Eliel, 1962; Newman, 1956).

axial [torsion angle C(1)–C(6)–C(7)–C(18) 166°]; phenyl at C(11), equatorial [C(1)–C(6)–C(11)–C(12) 62°]; Br at C(10), equatorial [C(12)–C(11)–C(10)–Br 65°]. O(1) is close to three C atoms of ring B: O(1)···C(8) 3·03, O(1)···C(9) 3·33, O(1)···C(10) 2·89 Å. These short separations suggest that, under the correct conditions, it may be possible for a chemical interaction to occur between O(1) and one of C(8), C(9) or C(10).

The thermal motion of the equatorial phenyl ring at C(11) is considerably larger than that of the axial ring at C(7). Examination of a model shows that neither ring can undergo free rotation about its bond to ring B and that the positioning of each phenyl ring is determined by intramolecular contacts between pairs of H atoms.

References

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