Structure of 2,5-Dibromotricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione, C$_{11}$H$_8$Br$_2$O$_2$

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Abstract. $M_r = 331\cdot99$, triclinic, $P\bar{1}$, $a = 6\cdot457$ (3), $b = 7\cdot668$ (3), $c = 11\cdot189$ (4) Å, $\alpha = 77\cdot32$ (3), $\beta = 81\cdot40$ (3), $\gamma = 71\cdot19$ (5)°, $V = 509\cdot8$ Å^3, $Z = 2$, $D_x = 2\cdot163$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 78\cdot5$ cm^{-1}, $F(000) = 320$, $T = 110$ (2) K, final $R = 0\cdot028$ for 1482 reflections with $I > 3\sigma(I)$. The title compound is an addition product of 2,5-dibromo-*p*-benzoquinone and cyclopentadiene. The two remaining double bonds are aligned parallel to each other with a separation of 3·67 (3) Å, a configuration which allows a further intramolecular cyclization. The molecules are held together by van der Waals forces.

Introduction. The present study is part of a series of structural investigations of adducts and precursors obtained in the process of synthesis aimed at obtaining substituted cubanes and homocubanes (Umrigar, Vaz, Kirschenheuter, Griffin, Majeste, Klein, Stevens, Gilbert, Alster, Sandus & Legendre, 1984). The title compound was synthesized *via* a [2 + 2] cycloaddition of 2,5-dibromo-*p*-benzoquinone and cyclopentadiene. The conformation and intramolecular distance between the C=C double bonds are of particular interest.

Experimental. Crystals obtained by recrystallization from ethanol, approximate dimensions 0·28 × 0·28 × 0·38 mm; Enraf–Nonius CAD-4 diffractometer, graphite crystal monochromator; cell dimensions from least-squares analysis of 25 reflections with $20 < 2\theta < 40°$ measured on diffractometer. Cell dimensions and lack of systematic absences indicated triclinic space group with $Z = 2$; successful determination of the structure confirmed $P\bar{1}$. Intensity data collected within range $2\cdot0 < 2\theta < 50°$, $-7 \le h \le 7$, $0 \le k \le 9$, $-13 \le l \le 13$; $\omega{:}2\theta$ scan mode; intensities of three standards measured every 2 h decayed by 2·8%, decay correction applied; crystal orientation checked every 200 reflections, 1802 unique I, of which 1482 treated as observed by $I > 3\sigma(I)$ [$\sigma(I)$ e.s.d. based on counting

statistics (c.s.)] and included in least-squares refinement; Lorentz–polarization and absorption corrections applied. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980; Frenz, 1982). Hydrogen atoms located from difference Fourier syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for non-H and isotropic for hydrogen atoms (which correspond to C atoms they are attached to), minimizing $\sum w(|F_o| - |F_c|)^2$, converged to $R = 0\cdot028$, $R_w = 0\cdot036$, $w = 1/\sigma^2(F)$, $\sigma^2(F^2) = \sigma^2_{c.s.} + (0\cdot03F^2)^2$, $S = 1\cdot69$, $(\Delta/\sigma) = 0\cdot01$. Difference Fourier map showed no significant electron density, max. 0·97 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All computer programs from the *SDP* system (Frenz, 1982) on a PDP 11/34 computer.

Discussion. Final atomic positional and equivalent isotropic thermal parameters are given in Table 1.† Bond angles, bond distances and selected torsion angles with their respective e.s.d.'s are listed in Table 2. The molecular conformation and atom labeling scheme are shown in an *ORTEP* plot (Johnson, 1976) in Fig. 1.

The conformation adopted by the molecule consists of a half-chair cyclopentadiene ring *cis*-fused in a [2 + 2] cycloaddition to a benzoquinone moiety. The geometry of the norbornene type of ring thus formed is in good agreement with similar structures (Destro, Filippini, Gramaccioli & Simonetta, 1969; Filippini, Gramaccioli, Rovere & Simonetta, 1972). The angle 94·2 (3)° for the C(7)–C(11)–C(10) bridgehead also corresponds to characteristic values found in similar environments (Bats, Bellinger & Ried, 1984). A least-squares plane through atoms C(7)–C(8)–C(9)–C(10) shows planarity within the standard deviation

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† Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39623 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3) \, [a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + 2ab(\cos\gamma)\beta_{1,2} + 2ac(\cos\beta)\beta_{1,3} + 2bc(\cos\alpha)\beta_{2,3}].$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Br(1)	0.33944 (7)	0.34822 (5)	0.09110 (3)	1.466 (9)
Br(2)	−0.08714 (7)	1.03739 (5)	0.29962 (4)	1.557 (9)
O(1)	−0.2484 (5)	0.9908 (4)	0.0509 (3)	1.51 (6)
O(2)	0.1172 (5)	0.3461 (4)	0.3453 (3)	1.66 (7)
C(1)	−0.1468 (6)	0.8608 (5)	0.1238 (4)	1.15 (8)
C(2)	0.0336 (7)	0.7073 (6)	0.0800 (4)	1.33 (9)
C(3)	0.1201 (6)	0.5460 (5)	0.1523 (3)	1.11 (8)
C(4)	0.0504 (6)	0.5014 (5)	0.2853 (4)	1.12 (8)
C(5)	−0.1073 (6)	0.6558 (5)	0.3445 (3)	1.08 (8)
C(6)	−0.2048 (7)	0.8491 (5)	0.2617 (4)	1.20 (8)
C(7)	−0.4542 (7)	0.8936 (6)	0.2973 (4)	1.37 (9)
C(8)	−0.5161 (7)	0.7583 (6)	0.2394 (4)	1.52 (9)
C(9)	−0.4359 (7)	0.5892 (6)	0.3023 (4)	1.44 (9)
C(10)	−0.3201 (7)	0.6050 (6)	0.4056 (4)	1.44 (9)
C(11)	−0.4605 (7)	0.7985 (6)	0.4319 (4)	1.61 (9)
H(2)	0.077 (6)	0.725 (5)	0.006 (3)	0.1 (7)*
H(7)	0.475 (7)	0.014 (5)	0.276 (4)	1.6 (9)*
H(10)	0.286 (6)	0.486 (6)	0.530 (3)	1.1 (9)*
H(5)	0.036 (6)	0.333 (5)	0.600 (3)	0.8†
H(8)	0.411 (6)	0.796 (5)	0.174 (3)	0.5 (8)*
H(9)	0.429 (6)	0.521 (5)	0.715 (3)	0.5 (8)*
H(11)	0.418 (7)	0.805 (6)	0.465 (4)	1.5 (9)*
H(11')	0.401 (7)	0.141 (6)	0.517 (4)	2.0 (9)*

* Atoms were refined isotropically.
† Thermal parameter not refined.

Table 2. *Bond lengths (Å) and angles and selected torsion angles (°), with e.s.d.'s in parentheses*

The e.s.d.'s of torsion angles are in the range 0.4 to 0.5°.

Br(1)–C(3)	1.886 (3)	Br(2)–C(6)	1.979 (3)
O(1)–C(1)	1.213 (4)	O(2)–C(4)	1.208 (4)
C(1)–C(2)	1.477 (5)	C(1)–C(6)	1.522 (4)
C(2)–C(3)	1.321 (5)	C(3)–C(4)	1.486 (4)
C(4)–C(5)	1.498 (4)	C(5)–C(6)	1.555 (5)
C(5)–C(10)	1.567 (5)	C(6)–C(7)	1.543 (5)
C(7)–C(8)	1.515 (5)	C(7)–C(11)	1.524 (5)
C(8)–C(9)	1.312 (5)	C(9)–C(10)	1.513 (5)
C(10)–C(11)	1.534 (5)		

O(1)–C(1)–C(2)	120.3 (3)	O(1)–C(1)–C(6)	121.2 (3)
C(2)–C(1)–C(6)	118.5 (3)	C(1)–C(2)–C(3)	122.8 (3)
Br(1)–C(3)–C(2)	121.6 (3)	Br(1)–C(3)–C(4)	114.4 (2)
C(2)–C(3)–C(4)	124.0 (3)	O(2)–C(4)–C(3)	121.9 (3)
O(2)–C(4)–C(5)	120.1 (3)	C(3)–C(4)–C(5)	118.0 (3)
C(4)–C(5)–C(6)	118.4 (3)	C(4)–C(5)–C(10)	111.9 (3)
C(6)–C(5)–C(10)	101.7 (3)	Br(2)–C(6)–C(1)	103.0 (3)
Br(2)–C(6)–C(5)	109.7 (2)	Br(2)–C(6)–C(7)	111.7 (2)
C(1)–C(6)–C(5)	116.6 (3)	C(1)–C(6)–C(7)	112.7 (3)
C(5)–C(6)–C(7)	103.4 (3)	C(6)–C(7)–C(8)	102.8 (3)
C(6)–C(7)–C(11)	101.7 (3)	C(8)–C(7)–C(11)	100.5 (3)
C(7)–C(8)–C(9)	107.8 (3)	C(8)–C(9)–C(10)	107.8 (3)
C(5)–C(10)–C(9)	106.5 (3)	C(5)–C(10)–C(11)	98.9 (3)
C(9)–C(10)–C(11)	100.6 (3)	C(7)–C(11)–C(10)	94.2 (3)

O(1)–C(1)–C(6)–Br(2)	−75.2	Br(2)–C(6)–C(7)–C(11)	−86.6
O(1)–C(1)–C(2)–C(3)	−166.1	Br(2)–C(6)–C(7)–C(8)	169.6
C(2)–C(1)–C(6)–C(7)	−133.2	C(3)–C(4)–C(5)–C(10)	123.0
O(1)–C(1)–C(6)–C(5)	164.7	O(2)–C(4)–C(5)–C(6)	−174.8
O(1)–C(1)–C(6)–C(7)	45.3	O(2)–C(4)–C(5)–C(10)	−57.0
Br(1)–C(3)–C(4)–C(5)	174.3	O(2)–C(4)–C(3)–C(2)	172.2
Br(1)–C(3)–C(4)–O(2)	−5.7	C(4)–C(5)–C(6)–Br(2)	−111.2
C(1)–C(6)–C(7)–C(11)	158.0	C(4)–C(5)–C(10)–C(11)	−168.9
C(4)–C(5)–C(6)–C(7)	129.5	C(1)–C(6)–C(5)–C(10)	−117.8

whereas the plane through atoms C(7)–C(6)–C(5)–C(10) deviates by as much as −0.043 (4) and +0.044 (4) Å for C(5) and C(6), respectively [dihedral angle = 70.0 (4)°]. The six-membered ring, C(1) to C(6), is slightly puckered such that the least-squares planes through atoms C(1)–C(2)–C(3)–C(4) and C(1)–C(6)–C(5)–C(4) form a dihedral angle of 10.1 (4)° with the double bond C(2)=C(3) deviating away from the double bond C(8)=C(9).

The C(6)-*exo*–Br(2) bond distance, 1.979 (3) Å, is much larger than the C(3)–Br(1) bond distance of 1.886 (3) Å; an effect which may be a consequence of both the hybridization of the carbon atom and C(11)···Br(2) steric repulsion [torsion angle Br(2)–C(6)–C(7)–C(11) = −86.6 (4)°]. A value of 1.981 (5) Å for a C-*exo*–Br bond distance has recently been reported (Olmstead, Hope, Sampath & Schore, 1984). For a 2,5-dibromobenzoquinone molecule C—Br and C=O distances of 1.873 (4) and 1.220 (4) Å have been found (Syed, Umrigar, Griffin, Stevens & Majeste, 1984).

The crystal packing of the molecules is shown in a stereodiagram (*ORTEP*; Johnson, 1976) in Fig. 2. The
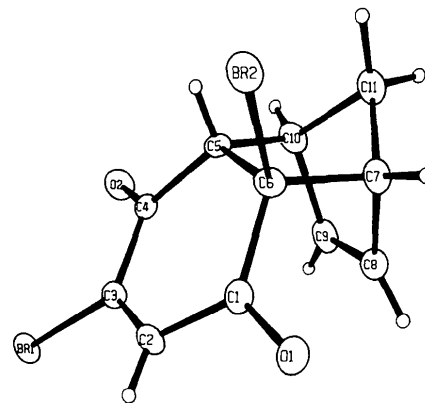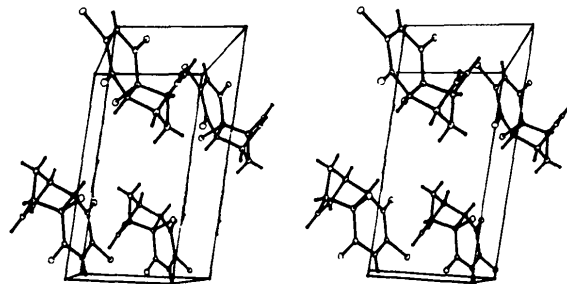

Fig. 1. *ORTEP* (Johnson, 1976) plot of the title compound showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. For clarity H atoms are given arbitrary radii.

Fig. 2. Stereoscopic view of the structure showing four molecules down the *b* axis with approximately horizontal *a* and vertical *c* axes.

crystal structure consists of discrete molecules packed in the unit cell by van der Waals forces. The intramolecular distances between C(2)=C(3) and C(8)=C(9) double bonds are C(2)···C(8) 3·668 (3) Å and C(3)···C(9) 3·674 (3) Å, which is close to the sum of the van der Waals radii. The structural study thus indicates the possibility of closing the ring to form a cage structure. Subsequently, intramolecular cyclization has been achieved (Umrigar & Griffin, 1984).

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The Structure of 1-tert-Butyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide, C$_{12}$H$_{25}$OP

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Abstract. $M_r = 216\cdot30$, monoclinic, $P2_1/m$, $a = 6\cdot137$ (2), $b = 12\cdot181$ (4), $c = 9\cdot005$ (3) Å, $\beta = 96\cdot24$ (3)°, $V = 669\cdot2$ (9) Å^3, $Z = 2$, $D_m = 1\cdot06$, $D_x = 1\cdot07$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot73$ cm^{-1}, $F(000) = 240$, $T = 295$ K, $R = 0\cdot052$, $R_w = 0\cdot051$, 1138 observed reflections. The single methyl group on C(3) is trans to the tert-butyl group on P. The four-membered ring is puckered with an angle of 19·2 (4)°, and the direction of ring puckering is such that the diaxial cross-ring interactions (CH$_3$ and O) between the substituents on P and C(3) are minimized.

Introduction. The structural analysis of 1-tert-butyl-2,2,3,4,4-pentamethylphosphetane 1-oxide (TPPO) was undertaken to confirm the stereochemistry, the direction and amount of puckering in the four-membered ring, and to compare the results with predictions based on previous results of similar compounds. The title compound was prepared by previously published methods (Gray & Cremer, 1972).

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