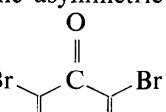# (Z, Z)-2,4-Dibromo-1,5-diphenylpenta-1,4-dien-3-one

By N. W. Alcock and J. F. Sawyer

Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL, England

Abstract. $C_{17}H_{12}OBr_2$, monoclinic, $P2_1/c$, $a=41\cdot080$ (11), $b=6\cdot527$ (2), $c=11\cdot118$ (3) Å, $\beta=97\cdot77$ (2)°, $V=2953$ (1) Å^3 at 18 °C, $Z=8$, $D_x=1\cdot76$ g cm^{-3}. There are two essentially identical molecules in the asymmetric unit both having approximately planar

$$Br\diagdown C\diagup Br$$
$$\text{(with } O \text{ above the central } C\text{)}$$

conformations with Br and O adjacent. Intramolecular repulsions result in substantial deviations from planarity.

Introduction. The title compound (m.p. 97–98 °C), recrystallized from ethanol, was prepared and supplied by Professor Shoppee. The crystals appear as chunky needles (needle axis c). Systematic absences $h0l$, $l\neq 2n$; $0k0$, $k\neq 2n$, indicate space group $P2_1/c$ with two independent molecules in the asymmetric unit. The crystals also display pseudo-absences $hk0$, $h\neq 2n$.

Data were collected on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation to $2\theta_{max}$ of 50° in two shells with $\omega/2\theta$ scans over the range $(K_{\alpha 1}-0\cdot 9)$–$(K_{\alpha 2}+0\cdot 8)$°. In the first shell (0° <

Table 1. *Atomic coordinates* ($\times 10^4$) *and anisotropic temperature factors* ($\times 10^4$) *with standard deviations in parentheses*

$$T=\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}.$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(11)	1573 (1)	−1534 (4)	3388 (3)	88 (2)	30 (2)	78 (2)	19 (2)	27 (2)	4 (2)
Br(12)	917 (1)	4886 (5)	5324 (2)	124 (3)	75 (2)	39 (1)	56 (2)	32 (2)	10 (2)
O(1)	1190 (4)	776 (24)	4988 (14)	74 (13)	29 (9)	42 (9)	1 (9)	18 (9)	10 (8)
C(11)	1581 (5)	2553 (34)	2564 (20)	18 (14)	26 (10)	39 (13)	6 (11)	−5 (11)	−15 (11)
C(12)	1449 (6)	1279 (39)	3262 (20)	20 (14)	50 (17)	42 (13)	12 (12)	−12 (11)	10 (13)
C(13)	1223 (6)	1899 (35)	4102 (20)	42 (15)	34 (13)	49 (14)	4 (12)	23 (12)	−32 (13)
C(14)	1024 (5)	3721 (30)	3849 (18)	23 (13)	20 (12)	28 (11)	16 (10)	8 (10)	−10 (10)
C(15)	894 (5)	4363 (32)	2773 (16)	40 (16)	31 (14)	11 (10)	0 (11)	14 (10)	14 (9)
C(111)	1825 (5)	2373 (39)	1725 (21)	4 (13)	53 (15)	51 (14)	12 (12)	1 (11)	−5 (14)
C(112)	2025 (7)	4138 (39)	1561 (21)	40 (18)	64 (16)	37 (14)	−8 (14)	−7 (13)	6 (12)
C(113)	2264 (9)	4079 (59)	701 (30)	65 (28)	113 (29)	60 (20)	4 (21)	14 (20)	−19 (20)
C(114)	2292 (7)	2315 (52)	94 (22)	55 (19)	76 (23)	41 (15)	−7 (17)	−1 (13)	−5 (16)
C(115)	2124 (7)	610 (39)	276 (23)	43 (19)	60 (16)	47 (15)	27 (14)	16 (15)	−6 (13)
C(116)	1894 (6)	575 (43)	1063 (22)	46 (18)	70 (20)	35 (14)	4 (14)	−4 (13)	−10 (14)
C(121)	660 (5)	6054 (33)	2421 (20)	7 (12)	42 (13)	38 (13)	6 (10)	−8 (10)	21 (11)
C(122)	445 (6)	5732 (40)	1282 (23)	43 (16)	56 (17)	53 (16)	10 (14)	18 (13)	25 (14)
C(123)	201 (8)	7149 (44)	922 (28)	45 (22)	53 (19)	67 (21)	5 (15)	23 (17)	15 (16)
C(124)	169 (6)	8876 (46)	1625 (29)	24 (16)	71 (20)	90 (22)	14 (13)	24 (16)	37 (18)
C(125)	395 (7)	9236 (42)	2716 (27)	57 (20)	61 (18)	66 (20)	13 (16)	28 (17)	23 (15)
C(126)	643 (7)	7840 (41)	3096 (21)	84 (24)	37 (17)	49 (14)	4 (15)	22 (14)	−10 (13)
Br(21)	4084 (1)	9898 (5)	4436 (2)	119 (3)	70 (2)	28 (1)	−46 (2)	1 (1)	−6 (2)
Br(22)	3445 (1)	3329 (4)	1931 (3)	96 (3)	35 (2)	69 (2)	−16 (2)	−9 (2)	7 (2)
O(2)	3804 (5)	5763 (24)	3900 (13)	107 (15)	34 (10)	31 (8)	−15 (9)	15 (9)	6 (7)
C(21)	4112 (6)	9277 (44)	1912 (23)	19 (19)	56 (20)	61 (16)	16 (14)	6 (14)	−24 (14)
C(22)	3970 (5)	8677 (34)	2892 (20)	10 (12)	48 (14)	37 (13)	13 (11)	1 (10)	−6 (12)
C(23)	3776 (6)	6793 (36)	2928 (21)	32 (14)	24 (12)	59 (15)	−4 (11)	13 (12)	−15 (13)
C(24)	3542 (6)	6133 (30)	1830 (22)	49 (18)	6 (10)	59 (15)	−9 (10)	26 (14)	−2 (11)
C(25)	3401 (6)	7260 (35)	1013 (20)	60 (20)	35 (12)	24 (12)	11 (12)	−4 (12)	−25 (12)
C(211)	4344 (6)	10955 (31)	1752 (20)	40 (16)	16 (11)	38 (12)	−22 (11)	−9 (12)	−6 (10)
C(212)	4549 (6)	10647 (38)	824 (19)	17 (14)	65 (16)	43 (12)	23 (13)	11 (11)	3 (12)
C(213)	4791 (7)	12076 (42)	697 (22)	39 (19)	68 (19)	46 (16)	−4 (15)	32 (14)	17 (15)
C(214)	4823 (8)	13850 (38)	1428 (23)	89 (25)	42 (16)	37 (16)	9 (14)	−14 (16)	24 (14)
C(215)	4593 (7)	14167 (39)	2339 (24)	53 (19)	35 (16)	75 (18)	−3 (14)	32 (15)	12 (13)
C(216)	4379 (6)	12745 (31)	2455 (18)	2 (12)	29 (13)	37 (12)	−5 (9)	−6 (10)	0 (10)
C(221)	3166 (6)	7070 (39)	−71 (19)	21 (14)	52 (19)	35 (13)	7 (12)	5 (11)	16 (13)
C(222)	2987 (7)	8737 (42)	−531 (27)	31 (19)	61 (19)	90 (22)	13 (14)	10 (17)	21 (16)
C(223)	2753 (7)	8807 (40)	−1569 (27)	50 (18)	56 (18)	80 (20)	10 (14)	−38 (17)	−9 (16)
C(224)	2701 (7)	6778 (62)	−2137 (23)	45 (20)	110 (29)	32 (15)	−16 (22)	−4 (14)	−17 (20)
C(225)	2896 (8)	5114 (44)	−1717 (25)	73 (21)	51 (17)	62 (17)	−44 (17)	−4 (16)	14 (17)
C(226)	3115 (8)	5260 (38)	−663 (28)	49 (22)	36 (15)	60 (22)	−15 (14)	−17 (18)	−2 (16)

$2\theta \le 35°$) all reflexions were collected; in the second ($35° < 2\theta \le 50°$) a reflexion was only collected if the intensity of an 8s preliminary count was greater than 40 c.p.s. A variable scan rate, $1\cdot0$–$29\cdot3°$ min^{-1} depending on the intensity of the preliminary count was used. Cell constants and errors were obtained by least-squares refinement of the positions of 15 reflexions (Mo $K\alpha$, $\lambda = 0\cdot71069$ Å).

The positions of the four Br atoms were located with *NORMAL* and *MULTAN* (Germain & Woolfson, 1968) applied to the 274 reflexions with $E > 1\cdot50$ in the first shell of data. Fourier and least-squares refinement with the 1865 observed [$I/\sigma(I) > 3\cdot0$] reflexions in both shells located the remaining non-hydrogen atoms. The final refinement was with Br, C and O with anisotropic temperature factors to an R of $0\cdot081$. Scattering factors were from Cromer & Mann (1968). The weighting scheme was $\sqrt{w} = 1\cdot0/(186 - 335 \sin \theta)$. H atoms were not included and no correction for absorption was performed. Computing was carried out with the X-RAY system (1972) on a CDC 7600 computer.

Fig. 1 shows the atomic numbering, bond lengths and angles; Fig. 2 gives views of the two molecules. Atomic coordinates and temperature factors are given in Table 1, and molecular planes in Table 2.*

Discussion. The primary aim of the investigation was to determine the conformation of the compound [regarded to have the Z,Z configuration (Shoppee & Cooke, 1973)]. There was also the possibility of intermolecular Br$\cdots$O secondary bonds (Alcock, 1972), important in many brominated steroids (Peck, Duax, Eger &

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31357 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Norton, 1970). The independent molecules are virtually identical. Both approximate to a planar
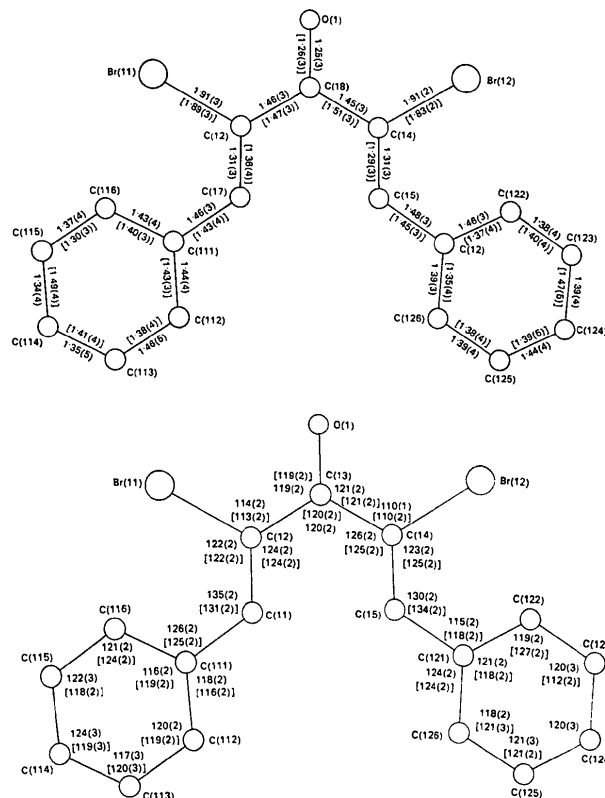

Fig. 1. Atomic numbering, bond lengths and angles (in square brackets for the second molecule) with standard deviations in parentheses. For the second molecule, the initial digit in each atom's number is (2) instead of (1).

Table 2. *Least-squares planes*

(a) Equations of the least-squares mean planes $PI + QJ + RK = S*$ in orthogonal space. Deviations of atoms forming these planes are insignificant and are not shown.

Plane	Defining atoms	P	Q	R	S
1	Br(11), C(11), C(12), C(13)	0·6583	0·2039	0·7246	6·4071
2	Br(12), C(13), C(14), C(15)	0·8072	0·5902	0·0119	4·3591
3	Br(21), C(21), C(22), C(23)	0·7768	−0·5879	0·2257	13·6357
4	Br(22), C(23), C(24), C(25)	0·8316	−0·1868	−0·5230	11·2415
5	C(12), C(13), C(14), O(1)	0·6604	0·5265	0·5354	5·9584
6	C(22), C(23), C(24), O(2)	0·7835	−0·5312	−0·3223	11·8726
7	C(111)–C(116)	0·6055	−0·2893	0·7414	5·3629
8	C(121)–C(126)	0·7137	0·4736	−0·5161	2·1855
9	C(211)–C(216)	0·5654	−0·4721	0·6764	10·9384
10	C(221)–C(226)	0·7973	0·2218	−0·5614	10·0034

(b) Angles (°) between planes or lines

(1)–(2)	48·7		(3)–(4)	50·4
(1)–(5)	21·6		(3)–(6)	32·0
(1)–(7)	28·7		(3)–(9)	29·6
(2)–(5)	31·8		(4)–(6)	23·2
(2)–(8)	31·8		(4)–(10)	23·8

* With the orthogonal unit vector I parallel to A, K perpendicular to A in the AC plane and J perpendicular to the AC plane.
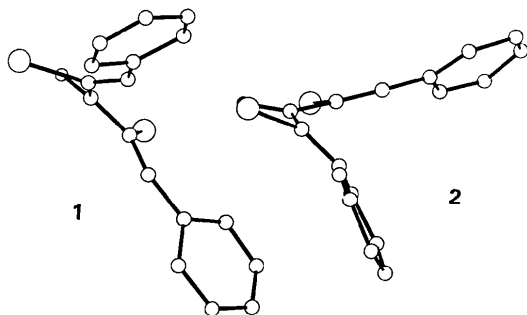
Fig. 2. Views of the two molecules showing the deviations from planarity.
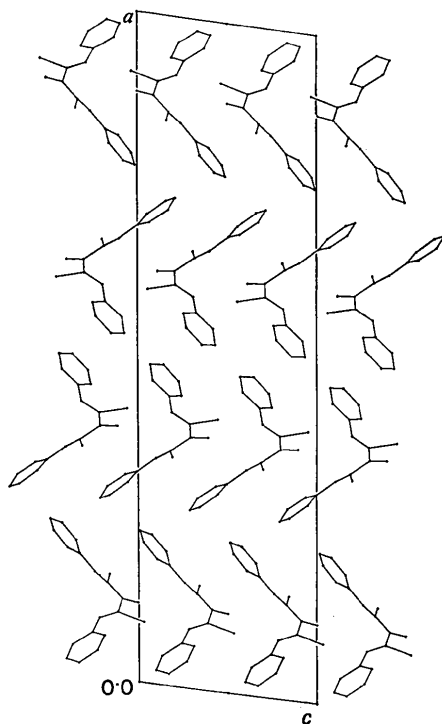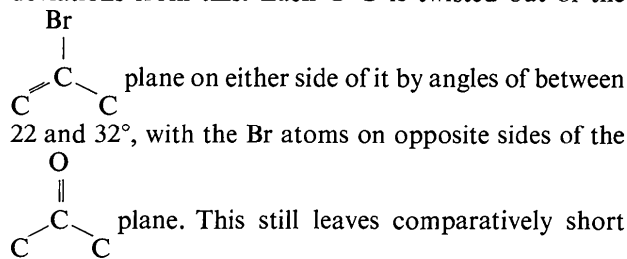

Fig. 3. Packing diagram, viewed down **b**. The rows contain respectively (from the bottom) molecules 1,2,1,2, those in each row being related by the glide plane.

conformation with Br and O adjacent. This probably arises because rotation by 180° about either C–C bond would lead to Br–H or Br–Br repulsion. Maximum π-

conjugation requires the molecule to be completely planar,* but intramolecular repulsions lead to large deviations from this. Each C=O is twisted out of the

$$\begin{array}{c} Br \\ | \\ {}_{\nearrow}C{}_{\searrow} \\ C \qquad C \end{array}$$ plane on either side of it by angles of between

22 and 32°, with the Br atoms on opposite sides of the

$$\begin{array}{c} O \\ \| \\ {}_{\nearrow}C{}_{\searrow} \\ C \qquad C \end{array}$$ plane. This still leaves comparatively short

O–Br contacts of 2·93–2·95 Å. Further, the phenyl rings are twisted out of plane by between 24 and 32° to increase the Br–H(*ortho*) contact distances resulting in values between 2·61 and 2·78 Å (H in calculated positions). The (Ph)C–C$^{\substack{C \\ \diagup}}$ angles are also substantially larger than expected, presumably for the same reason. Other bond lengths and angles have normal values.

The molecular packing (Fig. 3) proved not to be controlled by Br···O secondary bonds. Instead, the phenyl rings take up the typical herring-bone arrangement.

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* This is found in 1,5-diphenylpenta-1,4-dien-3-one itself [investigated as its uranyl complex (Alcock, Herron, Kemp & Shoppee, 1975)].

References

ALCOCK, N. W. (1972). *Advanc. Inorg. Radiochem.* **15**, 1–58.
ALCOCK, N. W., HERRON, N., KEMP, T. J. & SHOPPEE, C. W. (1975). To be published.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* B**24**, 91–96.
PECK, D. N., DUAX, W. L., EGER, C. & NORTON, D. A. (1970). *Amer. Cryst. Assoc. Abstracts*, Summer 1970, 71 (L6).
SHOPPEE, C. W. & COOKE, B. J. A. (1973). *J. Chem. Soc. Perkin* I, pp. 2197–2199.
X-RAY system (1972). Technical Report TR-192 of the Computer Science Center, Univ. of Maryland, June 1972.