

Table 4. The values of the geometrical parameters show that relief from overcrowding is achieved through a combination of factors: (i) extension of the C(4)–C(5) bond length, (ii) bond-angle deformations at C(4), C(5) and N(1), (iii) significant torsion around the C(2)–N(3) double bond, and (iv) slight (but possibly significant) deviation from planarity of the phenyl ring carrying the Br atom. All these distortions serve to reduce the intramolecular non-bonded interactions, among which of special note are C(7)···C(13), 2.972 (4); C(8)···C(13), 3.133 (4); C(8)···H(133), 2.56 (3) Å; and perhaps C(6)···C(15), 3.266 (4); N(1)···H(15), 2.56 (3); O(1)···H(203), 2.42 (3); and H(202)···H(212), 2.20 (4) Å.

There are no intermolecular contacts shorter than the sum of van der Waals radii, with the exception of C(16)···H(241) (at $\frac{1}{2} - x, \frac{1}{2} + y, z$), 2.68 (3) Å.

References

- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 STRADI, R. (1978). Private communication.
 WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.

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The Photoproduct from Bis(*p*-bromophenyl) Tetraketone

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Abstract. C₃₁H₁₆Br₄O₇, *M_r* = 820.15, triclinic, *P* $\bar{1}$, *a* = 13.682 (7), *b* = 15.078 (8), *c* = 7.796 (4) Å, α = 96.26 (2), β = 95.78 (2), γ = 113.70 (2)°, *Z* = 2, *D_x* = 1.885 Mg m⁻³, *V* = 1445.3 Å³. Four C atoms, out of the five present in the tricyclo moiety, are bonded to bromophenyl groups; three are bonded directly whilst the fourth is bonded through a diketone.

Introduction. Irradiation of bis(*p*-bromophenyl) tetraketone in benzene under nitrogen at $\lambda > 50.0$ Å proceeded with evolution of carbon monoxide (Rubin, Krochmal & Kaftory, 1979) and yielded yellow crystals. Attempts to obtain structural information by chemical and spectral methods led to an ambiguous result.

Intensities from a yellow crystal, 0.2 × 0.2 × 0.3 mm, were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo *K*α radiation ($\lambda = 0.71069$ Å) for θ between 3 and 23°. The ω –2 θ scan mode was used; the scan width was 1.3°, each peak was scanned for 26 s and the background was counted for 13 s on each side of the peak. 4468 reflexions were measured of which 123 were of zero net intensity.

The four Br atoms were located by *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The remaining heavy atoms were found by successive difference maps.

H atom positions were calculated from the heavy-atom positions, but not refined. The non-H atoms were refined by least-squares analysis in two separate blocks with *SHELX* (Sheldrick, 1976). Scattering factors for C, O were taken from Cromer & Mann (1968), for Br from Doyle & Turner (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965). 123 reflexions with zero net intensity and 307 with $\theta > 23^\circ$ were omitted.

For 4038 non-zero reflexions the final *R* = 0.093, *R_w* = 0.105. The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where *k* and *g* refined to 0.4178 and 0.0135 respectively. Final positional parameters are listed in Table 1.* Bond distances and angles involving non-H atoms are given in Fig. 1 and Table 2 respectively.

Discussion. In the tricyclononane skeleton the six-membered ring [C(3), C(4), O(3), C(5), O(5), C(6)] adopts the boat configuration, the three five-membered rings having an envelope shape; two rings [C(3), O(4), C(5), O(5), C(6) and C(3), O(4), C(5), O(3), C(4)] are

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34293 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates for non-hydrogen atoms ($\times 10^4$) and for H atoms ($\times 10^3$)*

E.s.d.'s are given in parentheses.

	x	y	z		x	y	z
Br(1)	3006 (2)	3223 (1)	-1881 (2)	C(14)	3855 (7)	5509 (6)	3199 (11)
Br(2)	8558 (1)	10443 (1)	10605 (1)	C(15)	3915 (9)	5800 (7)	1544 (12)
Br(3)	222 (1)	3125 (1)	189 (2)	C(16)	3683 (9)	5108 (8)	28 (13)
Br(4)	1199 (1)	11644 (1)	3335 (2)	C(21)	7099 (7)	9768 (7)	9520 (11)
O(1)	3978 (5)	5995 (5)	6222 (8)	C(22)	6529 (8)	10235 (6)	8735 (12)
O(2)	4871 (5)	7764 (4)	3929 (9)	C(23)	5469 (7)	9722 (6)	8043 (11)
O(3)	3185 (5)	8784 (4)	7264 (7)	C(24)	4940 (7)	8729 (6)	8113 (10)
O(4)	3265 (4)	8306 (4)	4520 (7)	C(25)	5509 (8)	8249 (7)	8878 (14)
O(5)	1708 (4)	7555 (4)	5441 (8)	C(26)	6579 (8)	8775 (7)	9543 (12)
O(6)	2223 (5)	6672 (5)	7314 (9)	C(31)	795 (8)	4276 (7)	1865 (18)
O(7)	3218 (7)	7351 (6)	9910 (11)	C(32)	834 (8)	4198 (7)	3607 (18)
C(1)	3998 (6)	6183 (6)	4715 (11)	C(33)	1282 (8)	5045 (7)	4853 (14)
C(2)	4156 (7)	7234 (6)	4598 (10)	C(34)	1664 (6)	5969 (6)	4246 (13)
C(3)	3410 (6)	7596 (5)	5463 (9)	C(35)	1588 (8)	6034 (7)	2509 (13)
C(4)	3749 (7)	8150 (6)	7387 (11)	C(36)	1161 (9)	5189 (8)	1269 (14)
C(5)	2569 (6)	8488 (6)	5571 (11)	C(41)	1588 (6)	10660 (6)	4086 (12)
C(6)	2221 (7)	6885 (6)	5589 (11)	C(42)	853 (7)	9693 (6)	3705 (12)
C(7)	3119 (8)	7384 (7)	8363 (11)	C(43)	1168 (7)	8968 (6)	4146 (11)
C(11)	3403 (9)	4133 (7)	183 (13)	C(44)	2219 (6)	9247 (6)	5087 (11)
C(12)	3352 (9)	3835 (7)	1807 (16)	C(45)	2916 (7)	10221 (6)	5478 (12)
C(13)	3575 (8)	4500 (6)	3264 (11)	C(46)	2597 (7)	10927 (6)	4976 (13)
H(12)	314	307	191	H(32)	52	348	400
H(13)	354	426	452	H(33)	134	501	623
H(15)	414	656	144	H(35)	186	674	210
H(16)	372	533	-124	H(36)	111	523	-11
H(22)	693	1101	865	H(42)	4	950	307
H(23)	503	1009	741	H(43)	62	820	378
H(25)	511	746	895	H(45)	372	1044	618
H(26)	703	841	1010	H(46)	315	1169	529

Table 2. *Bond angles ($^\circ$)*

The e.s.d.'s are typically 0.6-0.9 $^\circ$ (for atom numbering see Fig. 1).

C(4)-O(3)-C(5)	105.8	C(3)-C(4)-C(24)	119.2	C(12)-C(11)-C(16)	120.9	C(32)-C(31)-C(36)	122.7
C(3)-O(4)-C(5)	95.2	C(7)-C(4)-C(24)	116.5	C(11)-C(12)-C(13)	119.9	C(31)-C(32)-C(33)	119.4
C(5)-O(5)-C(6)	105.0	O(3)-C(5)-O(4)	103.3	C(12)-C(13)-C(14)	122.1	C(32)-C(33)-C(34)	117.8
C(6)-O(6)-C(7)	108.7	O(3)-C(5)-O(5)	110.4	C(1)-C(14)-C(13)	121.5	C(6)-C(34)-C(33)	117.8
O(1)-C(1)-C(2)	113.5	O(3)-C(5)-C(44)	110.9	C(1)-C(14)-C(15)	121.1	C(6)-C(34)-C(35)	120.0
O(1)-C(1)-C(14)	125.4	O(4)-C(5)-O(5)	103.4	C(13)-C(14)-C(15)	117.2	C(33)-C(34)-C(35)	122.1
C(2)-C(1)-C(14)	121.1	O(4)-C(5)-C(44)	114.6	C(14)-C(15)-C(16)	120.7	C(34)-C(35)-C(36)	120.1
O(2)-C(2)-C(1)	121.3	O(5)-C(5)-C(44)	113.5	C(11)-C(16)-C(15)	119.1	C(31)-C(36)-C(35)	117.9
O(2)-C(2)-C(3)	121.5	O(5)-C(6)-O(6)	107.9	Br(2)-C(21)-C(26)	118.5	Br(4)-C(41)-C(42)	119.6
C(1)-C(2)-C(3)	117.1	O(5)-C(6)-C(3)	99.4	C(22)-C(21)-C(26)	118.9	Br(4)-C(41)-C(46)	119.0
C(2)-C(3)-O(4)	108.2	O(5)-C(6)-C(34)	111.6	C(21)-C(22)-C(23)	120.1	C(42)-C(41)-C(46)	121.4
C(2)-C(3)-C(4)	120.7	O(6)-C(6)-C(3)	106.8	C(22)-C(23)-C(24)	120.9	C(41)-C(42)-C(43)	119.4
C(2)-C(3)-C(6)	121.7	O(6)-C(6)-C(34)	111.9	C(4)-C(24)-C(23)	121.6	C(42)-C(43)-C(44)	119.2
O(4)-C(3)-C(4)	102.4	C(3)-C(6)-C(34)	118.2	C(4)-C(24)-C(25)	118.9	C(5)-C(44)-C(43)	120.0
O(4)-C(3)-C(6)	102.9	O(6)-C(7)-O(7)	117.7	C(23)-C(24)-C(25)	119.5	C(5)-C(44)-C(45)	120.5
C(4)-C(3)-C(6)	98.2	O(6)-C(7)-C(4)	111.6	C(24)-C(25)-C(26)	118.7	C(43)-C(44)-C(45)	119.5
O(3)-C(4)-C(3)	98.9	O(7)-C(7)-C(4)	130.3	C(21)-C(26)-C(25)	121.9	C(44)-C(45)-C(46)	120.4
O(3)-C(4)-C(7)	105.7	Br(1)-C(11)-C(12)	121.3	Br(3)-C(31)-C(32)	119.1	C(41)-C(46)-C(45)	120.1
O(3)-C(4)-C(24)	111.9	Br(1)-C(11)-C(16)	117.6	Br(3)-C(31)-C(36)	118.2	Br(2)-C(21)-C(22)	122.6
C(3)-C(4)-C(7)	102.4						

slightly distorted mirror images (Fig. 2 and torsion angles in Table 3) and the third [C(3), C(4), C(7), O(6), C(6)] is almost symmetrical.

It has been noted that as the number of O atoms attached to the same C atom increases, the C-O

distance tends to become shorter (Jeffrey, Pople & Radom, 1972; Lehn, Wipff & Bürgi, 1974; Banyard & Dunitz, 1976). Our present results support this suggestion; the mean value of the three C(5)-O lengths of 1.410 Å (1.405-1.413 Å) agrees well with the mean

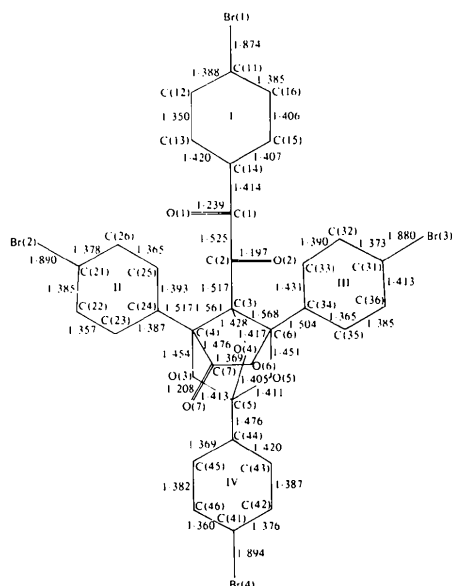


Fig. 1. Bond distances (Å). The e.s.d.'s of bond distances are typically 0.008–0.014 Å.

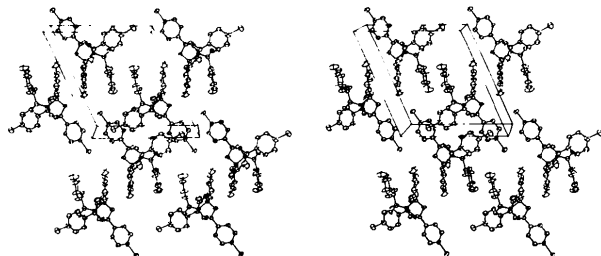


Fig. 2. Packing of molecules in the unit cell. The origin is at the lower left-hand corner; *a* is horizontal, *b* is up the page and *c* towards the reader (Johnson, 1965).

C–O length of 1.412 Å obtained in other *ortho*-ester moieties (Heitmann, Richards & Schroeder, 1974; Banyard & Dunitz, 1976). The lengths of the three outer C–O bonds [C(3)–O(4), C(4)–O(3), C(6)–O(5)] are markedly longer (1.428–1.451 Å) and agree well with the values obtained by Banyard & Dunitz (1976) (1.437–1.446 Å).

The tricyclic moiety has four pendant groups, each of which terminates in a bromophenyl group (three bromophenyl groups are bonded directly, while one is bonded through a diketone). In the crystal structure the interactions between the pendant groups govern the packing (Fig. 2). Parallel bromophenyl groups (I) and (III) (Fig. 1) are running along the [100] direction with

Table 3. Torsion angles (°) (for atom numbering see Fig. 1)

The e.s.d.'s are typically 0.9–1.1°.

C(4)–O(3)–C(5)–O(4)	–40	C(6)–O(5)–C(5)–O(4)	43
O(3)–C(5)–O(4)–C(3)	57	O(5)–C(5)–O(4)–C(3)	–58
C(5)–O(4)–C(3)–C(4)	–52	C(5)–O(4)–C(3)–C(6)	50
O(4)–C(3)–C(4)–O(3)	29	O(4)–C(3)–C(6)–O(5)	–25
C(3)–C(4)–O(3)–C(5)	6	C(3)–C(6)–O(5)–C(5)	–10
C(7)–O(6)–C(6)–C(3)	20	C(4)–O(3)–C(5)–O(5)	70
O(6)–C(6)–C(3)–C(4)	–33	O(3)–C(5)–O(5)–C(6)	–67
C(6)–C(3)–C(4)–C(7)	32	C(5)–O(5)–C(6)–C(3)	–10
C(3)–C(4)–C(7)–O(6)	–24	O(5)–C(6)–C(3)–C(4)	80
C(4)–C(7)–O(6)–C(6)	3	C(6)–C(3)–C(4)–O(3)	–76
C(4)–O(3)–C(5)–O(5)	70	C(3)–C(4)–O(3)–C(5)	6
O(3)–C(5)–O(5)–C(6)	–67	C(6)–O(6)–C(7)–C(4)	3
C(5)–O(5)–C(6)–O(6)	101	O(6)–C(7)–C(4)–O(3)	79
O(5)–C(6)–O(6)–C(7)	–86	C(7)–C(4)–O(3)–C(5)	–100

an array of approximately linear Br atoms. The other two groups (II, IV) of one molecule overlap with those of another related by the center of inversion at $(\frac{1}{2}, 0, \frac{1}{2})$.

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References

- BANYARD, S. H. & DUNITZ, J. D. (1976). *Acta Cryst.* B32, 318–320.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390–397.
- HEITMANN, J. A., RICHARDS, G. F. & SCHROEDER, L. R. (1974). *Acta Cryst.* B30, 2322–2328.
- JEFFREY, G. A., POPLER, J. A. & RADOM, L. (1972). *Carbohydr. Res.* 25, 107–116.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LEHN, J. M., WIPFF, G. & BÜRGI, H. B. (1974). *Helv. Chim. Acta*, 57, 493–496.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- RUBIN, M. B., KROCHMAL, E. C. JR & KAFTORY, M. (1979). To be published.
- SHELDRIK, G. M. (1976). Private communication.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.