C(16)–H(161)···O(4^{ii}) = 155°; with symmetry codes (i) $1-x$, $\frac{1}{2}+y$, $2-z$; (ii) $x-1$, y, z. However, the lack of electron-withdrawing groups in the close neighbourhood of C(6) and C(16) does not allow us to consider this contact as a hydrogen bond (Taylor & Kennard, 1982).

References

BARTON, D. H. R. & HOLNES, N. J. (1952). *J. Chem. Soc.* pp. 78–92.

CAMPSTEYN, H., DUPONT, L., LAMOTTE, J., DIDEBERG, O. & VERMEIRE, M. (1977). *Acta Cryst.* B**33**, 3443–3448.

COREY, E. J. & URSPRUNG, J. J. (1956). *J. Am. Chem. Soc.* **78**, 183–188.

DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure.* New York: Plenum.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JASKÓLSKI, M. (1982). Fourth Symp. Org. Cryst. Chem., Poznań, September 1982. Coll. Abstr. edited by Z. KALUSKI, pp. 70–71.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

ROQUES, R., DECLERCQ, J. P. & GERMAIN, G. (1978). *Acta Cryst.* B**34**, 2367–2370.

RUZICKA, L., COHEN, S. L., FURTER, M. & SLUYS-VEER, F. C. (1938). *Helv. Chim. Acta,* **21**, 1735–1756.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SPIRLET, M. R., DUPONT, L., DIDEBERG, O. & KAPUNDU, M. (1980). *Acta Cryst.* B**36**, 1593–1598.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Acta Cryst. (1986). C**42**, 1862–1868

Structures of 4,5,15,16-Tetraacetoxy[2.2]paracyclophane and Two Bis(crown-6)[2.2]-paracyclophanes*

BY CAROLYN B. KNOBLER, EMILY F. MAVERICK, KEITH M. PARKER, KENNETH N. TRUEBLOOD,† ROBERT L. WEISS, DONALD J. CRAM AND ROGER C. HELGESON

J. D. McCullough Laboratory for X-ray Crystallography, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, *USA*

(*Received* 10 *June* 1986; *accepted* 10 *July* 1986)

Abstract. (1): 4,5,15,16-Tetraacetoxy[2.2]paracyclophane, $C_{24}H_{24}O_8$, $M_r = 440{\cdot}4$, orthorhombic, *Pbca*, $a = 13{\cdot}543$ (2), $b = 9{\cdot}411$ (1), $c = 16{\cdot}997$ (1) Å, $V = 2166{\cdot}3$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}350$, $D_m = 1{\cdot}322$ (4) g cm^{-3} (flotation), λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8{\cdot}09$ cm^{-1}, $F(000) = 928$, $T = 295$ K, $R = 0{\cdot}0363$ for 1765 reflections with $I > 3\sigma(I)$. (2): 4,7,13,16-Bis(22-crown-6)[2.2]paracyclophane, $C_{36}H_{52}O_{12}$, $M_r = 676{\cdot}8$, monoclinic, $P2_1/c$, $T = 115$ K, $a = 9{\cdot}049$ (3), $b = 24{\cdot}760$ (11), $c = 15{\cdot}617$ (4) Å, $\beta = 104{\cdot}14$ (2)°, $V = 3393$ Å^3, $Z = 4$, $D_x = 1{\cdot}325$ (at 115 K), $D_m = 1{\cdot}286$ (5) (at 296 K) g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}60$ cm^{-1}, $F(000) = 1456$, $R = 0{\cdot}070$ for 3782 reflections with $|F| > 3\sigma(F)$. (3): 4,5,15,16-Bis(18-crown-6)[2.2]paracyclophane, $C_{36}H_{52}O_{12}$, $M_r = 676{\cdot}8$, orthorhombic, *Pbca*, $T = 296$ K, $a = 8{\cdot}347$ (4), $b = 16{\cdot}939$ (9), $c = 24{\cdot}330$ (20) Å, $V = 3440$ Å^3, $Z = 4$, $D_x = 1{\cdot}306$, $D_m = 1{\cdot}305$ (4) g cm^{-3} (flotation), λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}15$ cm^{-1}, $F(000) = 1456$, $R = 0{\cdot}074$ for 2336 reflections with $I > 2{\cdot}5\sigma(I)$. The molecules of (1) and (3), unlike those of (2), are centrosymmetric in the crystal. The geometry of the cyclophane moieties is typical of [2.2]paracyclophane units in other structures; the aromatic rings are characteristically bent into a boat shape. The O atoms attached to these rings are, in each structure, displaced from the planes of the four approximately coplanar aromatic C atoms. In (1) and (3), in which O atoms are bonded *ortho* to one another, these displacements average more than 0·1 Å and are uniformly in the direction of the bending of the aromatic rings, toward the bridging methylene groups. In (2), where the polyether rings join the two aromatic rings in pseudo-geminal positions, the oxygen atoms are displaced about 0·06 Å in the opposite direction. The polyether (crown-6) rings in (3) are disordered in two regions; the disorder persists at low temperature. In (2), on the other

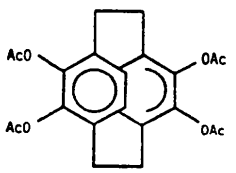
* [2.2]Paracyclophane = tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,-13,15-hexaene. 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

† To whom correspondence should be addressed.

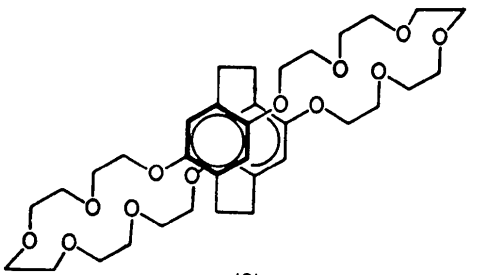
0108-2701/86/121862-07$01.50

hand, the polyether rings are not appreciably disordered at 115 K, although there is evidence of some disorder at room temperature.

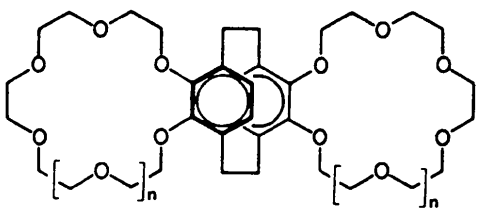
Introduction. The rigid layered structure of [2.2]-paracyclophane, with its 16 substitutable sites, offers possibilities for shaping host compounds for molecular complexation studies (Helgeson, Tarnowski, Timko & Cram, 1977; Cram & Trueblood, 1981). The two present cyclophane crown compounds proved to be less effective complexers than many other hosts, however, with (2) distinctly poorer than (3) for most ions tested (Helgeson *et al.*, 1977); this effect can be understood in terms of their molecular structures, reported here. We also report the structure of a non-crown compound (1) that in some ways serves as a control. The results are compared with those from some of the many other structural studies of [2.2]paracyclophane derivatives, to be found in Keehn's detailed review (Keehn, 1983) and in the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979). A preliminary account of the structure of (3) has appeared (Parker, Helgeson, Maverick & Trueblood, 1973).



(1)



(2)



(3), $n = 1$

Experimental. The preparation of (1), (2) and (3) has been described (Helgeson *et al.*, 1977). Crystals of (1) were grown from chloroform/ethyl acetate, those of (2) and (3) from CH_2Cl_2/heptane. Weissenberg and precession photographs of (1) and (3) show systematic absences $l = 2n+1$ for $h0l$ reflections, $k = 2n+1$ for $0kl$ reflections, and $h = 2n+1$ for $hk0$ reflections; photographs of (2) show systematic absences $k = 2n+1$ for $0k0$ reflections and $l = 2n+1$ for $h0l$ reflections; each forms colorless crystals; dimensions of crystal used for (1), 0·2 × 0·2 × 0·2 mm [those for (2) and (3) were comparable, but the crystals were lost before precise measurements were made]. Syntex $P\bar{1}$ diffractometer with graphite monochromator and variable temperature device (Strouse, 1976) for (1) and (2), Cu $K\alpha$ for (1), Mo $K\alpha$ for (2); orientation matrices and unit-cell dimensions by least-squares refinement of 15 reflections for (1) and (2) [100–113° in 2θ for (1), 28–39° for (2)]. Picker FACS-1 diffractometer for (3), Ni-filtered Cu $K\alpha$ radiation, orientation matrix and cell parameters by least-squares refinement of 14 reflections (45–61° in 2θ). Intensities of three standard reflections checked after every 97 or 98 reflections; < 3% average variation of intensity for each crystal, with no significant trend during data collection for (1) and (3) and a drop of about 3% for (2); 2·0° min^{-1} in 2θ for (1) and (2), 1·0° min^{-1} for (3), from 1·0–1·2° below $K\alpha_1$ to 1·0–1·2° above $K\alpha_2$. Intensities measured for (1), for $2\theta < 115°$, θ–2θ scan, and $115 < 2\theta < 158°$, parallel mode, $h = 0$ to 14, $k = 0$ to 11, $l = 0$ to 21; for (2), $2\theta < 50°$, θ–2θ scan, $h = 0$ to 10, $k = 0$ to 29, $l = -18$ to 18; for (3), for $2\theta < 125°$, θ–2θ scan, $h = 0$ to 9, $k = 0$ to 19, $l = 0$ to 27; for (1) and (2), counts for background were taken for half the scan time at each end of the scan range; for (3), background counted for 10 s at each end of the scan range; for (1), total of 2094 independent reflections, 1765 with $I > 3\sigma(I)$ used in structure solution and refinement; for (2), 6017 unique reflections (5197 with $|F| > 0$), 3782 with $|F| > 3\sigma(F)$ used in refinement; for (3), 3149 unique reflections, 2337 with $I > 2{\cdot}5\sigma(I)$ used in refinement; no absorption corrections; for (1), isotropic correction for extinction; (1) solved with *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier maps; (2) and (3) solved with Long's direct-methods program (Long, 1965); all H atoms readily found except a few in disordered regions of (3).

Hydrogen atoms of methylene and methyl groups (but *not* aromatic hydrogen atoms) were kept in geometrically reasonable positions with C–H = 1·08 Å and [for (1)] with fixed displacement* parameters based on those of the attached carbon atom. H atoms attached to aromatic C atoms were allowed to refine freely under the constraint that the C–H distance remained close to 1·08 Å. Refined by least-squares on $|F|$, $w = 1/\sigma^2(F_o)$. For (1), refinement of 158

* Heretofore commonly called 'vibration parameters' or 'temperature factor parameters'.

parameters converged to $wR = 0.0470$, $S = 2.90$,* ratio in final cycle of maximum least-squares shift to e.s.d. was 0·14 in a displacement parameter and 0·19 in a position parameter, maxima and minima on a final difference electron density map corresponded to 0·2 e Å^{-3}. For (2), refinement of 485 parameters (in 2 blocks) converged to $wR = 0.056$, $S = 1.44$,† with maxima and minima in final difference map = 0·39 and −0·42 e Å^{-3}. Structure (2) was also refined with a room-temperature‡ data set to give substantially the same structure, although there was evidence of disorder in one portion of one of the crown rings. For (3), refinement of 281 parameters converged to $wR = 0.106$, $S = 3.57$, with maxima and minima in final difference map = 0·68 and −0·44 e Å^{-3}. C—O and C—C distances involving the disordered atoms C(14), O(15), C(22) and C(23) were constrained to be near 1·42 and 1·48 Å respectively. Hydrogen atoms attached to C(14), C(22) and C(23) were placed in calculated, geometrically reasonable positions after the final refinement of all other atoms. Two sets of disordered atoms (designated *A* and *B*) were used in refining the pairs C(14)—O(15) and C(22)—C(23); for each pair the occupancies of the *A* and *B* sets were constrained so that their sum was 1·00. The atoms C(14*A*), O(15*A*) and C(22*A*), C(23*A*) refined to occupancies of about 0·52 and 0·60 respectively; in the final cycles their occupancies were fixed at 0·50. In the last cycle, the maximum ratio of least-squares shift to e.s.d. was 0·39 in the 'ordered' region and 0·90 in the disordered region, for non-H atoms. (3) was also studied at low temperature,§ but the disorder persisted at 115 K and the structure was almost identical to that at room temperature.

Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Calculations were performed on DEC VAX 11/750 and VAX 11/780 computers using the *UCLA Crystallographic Package* (1984) (locally edited versions of *CARESS*, *PROFILE*, *MULTAN*80 and *ORFLS*), *PLUTO* (Motherwell & Clegg, 1978), *SHELX*76 (Sheldrick, 1976), *GAVEZ* [locally edited version of *OPEC* (Gavezzotti, 1983)], and local molecular geometry and thermal motion programs, *MG*84 and *THMA* 10.

Discussion. Atomic coordinates and isotropic displacement parameters of the refined atoms are listed in Table 1. Some features of the molecular geometry, especially of the cyclophane portions of the molecules, are given in Tables 2* and 3; Fig. 1 should be used in conjunction with the tables in considering the geometry and distortions of the cyclophane moieties. *PLUTO* (Motherwell & Clegg, 1978) or *ORTEP* (Johnson, 1965) stereo drawings of the three molecules are shown in Figs. 2, 3 and 4.

The cyclophane groups are quite similar to each other and to the parent hydrocarbon, [2.2]paracyclophane (4). As indicated in Tables 2 and 3 (see also Fig. 1), the aromatic rings are bent in the usual way, with the four-atom planes (not including the *para* C atoms) parallel to each other [deviation 0·5° in (2), which has no center of symmetry]. There is, in addition, a sidewise parallel displacement of these rings relative to one another in each structure, varying from less than 0·1 Å in (3) to about 0·3 Å in (1) and more than 0·5 Å in (2). This effect is particularly evident in Fig. 3; one consequence is that the perpendicular interplanar spacing in each of these molecules, and especially in (2), is distinctly smaller than in the parent compound [2·94 Å in (2), 3·09 Å in (4)], although the larger α and β angles in (4) accentuate the difference. There is a small butterflying of the ring in (2), presumably as a result of the pseudo-geminal linking of the polyether rings. The C atoms to which the ether O atoms are linked are displaced out of the plane by about 0·017 (4) Å *away* from the center of the molecule and their attached O atoms are displaced even more in the same direction, about 0·06 Å. In (1) and (3), on the other hand, the four C atoms are coplanar within the precision of the data, and the *ortho* O atoms are displaced 0·09 to 0·17 Å *towards* the molecular center. The aromatic H atoms in these structures are, on the average, displaced slightly towards the molecular centers, as observed in other paracyclophanes, although the effect is scarcely significant, averaging about 0·05 (2) Å. The bridging $-CH_2-CH_2-$ bond length ranges from 1·564 to 1·590 Å, showing the significant extension characteristic of cyclophanes (Keehn, 1983) from the usual value of about 1·53 Å. There is a

* When displacement parameters for H atoms of (1) were refined and $I > 1.5\sigma(I)$ data were included (1890 reflections, 170 parameters, $R = 0.039$, $wR = 0.047$, $S = 2.79$) these $\langle u^2 \rangle$ values did not differ greatly from the fixed values: H on ring 0·05 Å^2 [0·054, 0·064 (5)], H on bridge C 0·07 [0·062–0·076 (6)], H of methyl group 0·10 [0·11–0·15 (1)].

† For all 6017 reflections, $R = 0.139$, $wR = 0.064$, $S = 1.29$; for the 2901 reflections with $I > 3\sigma(I)$, $R = 0.048$, $wR = 0.044$, $S = 1.40$.

‡ At 296 K, $a = 9.178$ (3), $b = 24.926$ (9), $c = 15.714$ (5) Å, $\beta = 104.92°$, $D_x = 1.294$, $D_m = 1.286$ (5) g cm^{-3}; at convergence, with Mo $K\alpha$ data, $R = 0.074$, $wR = 0.079$, $S = 2.7$ for 3485 reflections with $|F| > 3\sigma(F)$.

§ At 115 K, $a = 8.259$ (1), $b = 16.760$ (3), $c = 24.062$ (4) Å, $D_x = 1.264$ g cm^{-3}; Syntex $P\bar{1}$; at convergence, with Cu $K\alpha$ data, $R = 0.142$, $wR = 0.205$, $S = 6.93$ for 3130 reflections with $|F| > 3\sigma(F)$; 319 parameters were refined; data were collected to 156° in 2θ (from 112 to 156° in parallel mode).

* Lists of anisotropic displacement parameters, bond distances, bond and torsion angles, hydrogen-atom parameters and observed and calculated structure factors, and a few additional *ORTEP* stereoviews of (1), (2) and (3), have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43231 (65 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Position and displacement parameters for the title compounds*

Displacement parameters are commonly called vibration parameters. Units of $\langle U^2 \rangle$ are Å^2. Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter. An asterisk denotes an atom refined isotropically. Other isotropic values are $1/8\pi^2$ times the 'equivalent B value' for an anisotropic atom, as defined by Hamilton (1959).

	x	y	z	$\langle U^2 \rangle$
4,5,15,16-Tetraacetoxy[2.2]paracyclophane				
O(1)	0·07050 (9)	0·51372 (11)	0·33789 (6)	0·043
O(2)	0·04573 (12)	0·34060 (15)	0·24860 (7)	0·070
O(3)	0·20865 (8)	0·47980 (12)	0·45055 (6)	0·045
O(4)	0·25391 (11)	0·34520 (15)	0·34722 (8)	0·069
C(1)	−0·05066 (12)	0·38101 (15)	0·41358 (8)	0·040
C(2)	0·04595 (12)	0·42475 (15)	0·40074 (8)	0·038
C(3)	0·11784 (11)	0·40937 (14)	0·45815 (8)	0·038
C(4)	0·09523 (12)	0·35114 (15)	0·53121 (8)	0·041
C(5)	0·00460 (13)	0·28236 (15)	0·53763 (9)	0·044
C(6)	−0·06654 (13)	0·29580 (16)	0·47966 (9)	0·044
C(7)	−0·13637 (13)	0·44894 (18)	0·37078 (9)	0·048
C(8)	0·15431 (14)	0·39116 (18)	0·60351 (9)	0·049
C(9)	0·07269 (13)	0·45831 (19)	0·26385 (9)	0·047
C(10)	0·11114 (16)	0·56577 (24)	0·20786 (11)	0·064
C(11)	0·27060 (13)	0·44124 (17)	0·39101 (10)	0·047
C(12)	0·35887 (14)	0·53543 (20)	0·38895 (14)	0·063
H(5)	−0·0136 (12)	0·2277 (15)	0·5916 (5)	0·050
H(6)	−0·1405 (5)	0·2573 (17)	0·4900 (10)	0·050
4,7,13,16-Bis(22-crown-6)[2.2]paracyclophane at 115 K				
C(1)	0·0792 (4)	0·3734 (1)	0·0652 (2)	0·018
C(2)	0·1638 (4)	0·3301 (1)	0·0459 (2)	0·019
C(3)	0·3210 (4)	0·3357 (2)	0·0566 (2)	0·020
C(4)	0·3934 (4)	0·3848 (1)	0·0826 (2)	0·019
C(5)	0·3019 (4)	0·4302 (1)	0·0799 (2)	0·019
C(6)	0·1467 (4)	0·4243 (2)	0·0734 (2)	0·018
C(7)	0·5600 (4)	0·3875 (2)	0·1311 (2)	0·020
C(8)	0·5834 (4)	0·3951 (2)	0·2349 (2)	0·021
C(9)	0·4375 (4)	0·3867 (1)	0·2645 (2)	0·017
C(10)	0·3686 (4)	0·3364 (2)	0·2554 (2)	0·017
C(11)	0·2138 (4)	0·3303 (1)	0·2489 (2)	0·017
C(12)	0·1226 (4)	0·3757 (1)	0·2472 (2)	0·017
C(13)	0·1957 (4)	0·4247 (2)	0·2729 (2)	0·018
C(14)	0·3538 (4)	0·4303 (1)	0·2845 (2)	0·019
C(15)	−0·0432 (4)	0·3736 (1)	0·1984 (2)	0·019
C(16)	−0·0669 (4)	0·3647 (2)	0·0956 (2)	0·021
O(17)	0·0889 (3)	0·2813 (1)	0·0246 (2)	0·023
C(18)	0·1693 (4)	0·2421 (1)	−0·0148 (2)	0·024
C(19)	0·0627 (4)	0·1975 (2)	−0·0538 (2)	0·026
O(20)	0·0405 (3)	0·1621 (1)	0·0141 (2)	0·026
C(21)	−0·0377 (5)	0·1147 (1)	−0·0223 (3)	0·028
C(22)	−0·0330 (4)	0·0744 (2)	0·0504 (3)	0·028
O(23)	0·1186 (3)	0·0528 (1)	0·0758 (2)	0·031
C(24)	0·1355 (5)	0·0107 (2)	0·1401 (3)	0·030
C(25)	0·1764 (4)	0·0315 (2)	0·2332 (3)	0·029
O(26)	0·0505 (3)	0·0609 (1)	0·2483 (2)	0·028
C(27)	0·0761 (5)	0·0846 (2)	0·3346 (2)	0·027
C(28)	−0·0017 (4)	0·1383 (1)	0·3279 (3)	0·025
O(29)	0·0924 (3)	0·1824 (1)	0·3153 (2)	0·029
C(30)	0·1285 (4)	0·1851 (1)	0·2311 (2)	0·024
C(31)	0·2271 (4)	0·2342 (1)	0·2328 (2)	0·022
O(32)	0·1380 (3)	0·2815 (1)	0·2336 (2)	0·021
O(33)	0·3786 (3)	0·4784 (1)	0·0945 (2)	0·024
C(34)	0·2922 (4)	0·5261 (1)	0·0967 (3)	0·022
C(35)	0·4041 (4)	0·5720 (1)	0·1059 (3)	0·023
O(36)	0·3233 (3)	0·6198 (1)	0·1133 (2)	0·027
C(37)	0·4137 (4)	0·6676 (2)	0·1176 (3)	0·028
C(38)	0·3403 (4)	0·7117 (2)	0·1591 (2)	0·027
O(39)	0·3598 (3)	0·6997 (1)	0·2494 (2)	0·031
C(40)	0·2768 (4)	0·7353 (2)	0·2930 (3)	0·028
C(41)	0·2818 (4)	0·7133 (2)	0·3830 (3)	0·030
O(42)	0·4329 (3)	0·7211 (1)	0·4383 (2)	0·033
C(43)	0·4732 (5)	0·6837 (1)	0·5092 (3)	0·026
C(44)	0·5417 (5)	0·6322 (2)	0·4843 (3)	0·031
O(45)	0·4246 (3)	0·5974 (1)	0·4358 (2)	0·029
C(46)	0·4864 (4)	0·5563 (2)	0·3923 (3)	0·028
C(47)	0·3601 (4)	0·5180 (2)	0·3510 (3)	0·027
O(48)	0·4280 (3)	0·4792 (1)	0·3047 (2)	0·025
H(3)	0·392 (3)	0·301 (1)	0·056 (2)	0·03 (1)*
H(6)	0·079 (2)	0·458 (1)	0·084 (2)	0·01 (1)*
H(10)	0·433 (2)	0·302 (1)	0·245 (2)	0·01 (1)*
H(13)	0·132 (3)	0·461 (1)	0·276 (2)	0·04 (1)*

Table 1 (*cont.*)

	x	y	z	$\langle U^2 \rangle$
4,5,15,16-Bis(18-crown-6)[2.2]paracyclophane				
C(1)	−0·1267 (4)	−0·0968 (2)	−0·0139 (1)	0·047
C(2)	−0·2066 (4)	−0·0522 (2)	0·0257 (1)	0·041
C(3)	−0·2286 (4)	0·0291 (2)	0·0188 (1)	0·044
C(4)	−0·1724 (4)	0·0665 (2)	−0·0282 (2)	0·052
C(5)	−0·1239 (4)	0·0190 (3)	−0·0718 (2)	0·059
C(6)	−0·1013 (4)	−0·0611 (2)	−0·0651 (1)	0·054
C(7)	−0·0360 (5)	−0·1709 (2)	0·0008 (2)	0·063
C(8)	−0·1304 (5)	0·1535 (2)	−0·0278 (2)	0·074
O(9)	−0·2402 (3)	−0·0845 (1)	0·0766 (1)	0·052
C(10)	−0·3716 (5)	−0·1394 (2)	0·0760 (2)	0·066
C(11)	−0·3893 (6)	−0·1757 (3)	0·1312 (2)	0·079
O(12)	−0·4444 (4)	−0·1249 (2)	0·1720 (1)	0·092
C(13)	−0·6058 (6)	−0·1168 (3)	0·1772 (2)	0·082
C(16)	−0·6613 (6)	0·0212 (3)	0·2903 (2)	0·090
C(17)	−0·5807 (6)	0·1001 (4)	0·2898 (2)	0·090
O(18)	−0·6051 (4)	0·1353 (2)	0·2370 (1)	0·086
C(19)	−0·5172 (6)	0·2070 (3)	0·2296 (2)	0·091
C(20)	−0·5311 (6)	0·2329 (3)	0·1709 (2)	0·083
O(21)	−0·4372 (3)	0·1887 (2)	0·1339 (1)	0·082
O(24)	−0·2789 (3)	0·0744 (1)	0·0624 (1)	0·061
C(14*A*)	−0·6547 (17)	−0·0843 (6)	0·2312 (4)	0·089
C(14*B*)	−0·6696 (15)	−0·0503 (6)	0·2100 (3)	0·074
O(15*A*)	−0·5768 (10)	−0·0123 (5)	0·2446 (3)	0·082
O(15*B*)	−0·5995 (11)	−0·0476 (4)	0·2632 (2)	0·072
C(22*A*)	−0·4957 (14)	0·1131 (4)	0·1218 (4)	0·054
C(22*B*)	−0·5194 (15)	0·1313 (5)	0·1031 (6)	0·070
C(23*A*)	−0·4446 (6)	0·0912 (6)	0·0657 (4)	0·047
C(23*B*)	−0·4403 (8)	0·0615 (6)	0·0782 (7)	0·078
H(5)	−0·099 (4)	0·052 (2)	−0·109 (1)	0·08 (1)*
H(6)	−0·049 (3)	−0·098 (1)	−0·096 (1)	0·05 (1)*

possibility that this bond in (3) may be slightly foreshortened by a twisting motion of the rings about their normal comparable to that observed in (4) and its octafluoro derivative (Hope, Bernstein & Trueblood, 1972), but the displacement parameters are not precise enough to provide clear evidence.

The torsion angles in the polyether rings in (2) and (3) necessarily depart in places from the 'ideal' *ap* for C—O and *sc* for C—C bonds because of the ring-closure constraints. The two halves of (2) have distinctly different conformations in the outer portions of the rings, evident in Fig. 3, but in each crown ring the torsion angles about the C_{arom}—O bonds are not far from 0 or 180° (average deviation from these values about 13°), quite in contrast to the approximately 90° anticipated before the structure was determined (Helgeson *et al.*, 1977). This seems to be a consequence of the pseudo-geminal linking of the crown ring to the cyclophane. One result of it is that the four O atoms attached to the aromatic rings are oriented with their electron pairs pointing away from the region occupied by the other four O atoms, so it is not surprising that (2) is a much poorer complexer than many other crown-6 hosts. (3), on the other hand, is comparable in complexing power to 2,3-naphtho-18-crown-6; Fig. 4 shows that the O atoms of (3) are, at least potentially, in a position for cooperative interaction with cation guests. In the O(17) to O(32) ring of (2), the absolute values of the C—C torsion angles vary from 68 to 91°, while in the other crown ring, the two C—C torsion bonds nearest the cyclophane unit both

Table 2. *Selected average distances and angles*

The units of distances are Å and of angles °. Values in parentheses are representative e.s.d.'s; e.s.d.'s for the angles average about 0·2°. Corrections for thermal motion are smaller than the e.s.d.'s for all but the parent hydrocarbon, (4); corrected values for it are given in square brackets. Symbols in the left-hand column refer to Fig. 1(*a*).

	(1)	(2)	(3)	(4)
b	1·586 (2)	1·590 (5)	1·564 (6)	1·562 (2) [1·569*]
a	1·513 (2)	1·515 (5)	1·512 (5)	1·510 (2) [1·514]
e,g	1·392 (2)	1·393 (5)	1·395 (5)	1·384 (2) [1·394]
f	1·385 (2)	1·398 (5)	1·389 (6)‡	1·386 (2) [1·394]
p	2·76	2·77	2·75	2·78
q	3·04	3·06†	3·03	3·09
α	11·2	12·0	11·2	12·6
β	12·0	11·4	12·0	11·2
γ	112·5	112·6	113·0	113·7
Distances in polyether rings:				
C_{arom}–O		1·380 (4)	1·380 (4)	
C_{tetr}–O		1·426 (5)	1·414 (8)§	
C–C		1·502 (6)	1·488 (8)	

* When the bridging C–C distance in (4) is corrected for the molecular twisting motion, it becomes 1·593 Å (Hope *et al.*, 1972).

† The inter-ring distances between nominally eclipsed atoms in (2) vary from 3·02 to 3·11 Å because of the ring buckling caused by the pseudo-geminal attachment of the crown ring (see text).

‡ For (3), the *f* distances were 1·399 (5) C(2)–C(3), flanked by *ortho* O atoms, and 1·378 for C(5)–C(6), flanked by H atoms. A similar effect has been observed in other benzo crown derivatives (Bush & Truter, 1972; Mallinson & Truter, 1972; Hanson, 1978; Momany, Clinger, Hackert & Poonia, 1986; Sheldrick & Poonia, 1986).

§ The average for the C_{tetr}–O distances in (3) is 1·424 Å if distances involving O(12) are omitted (1·391, 1·360 Å). There is clearly some disorder in the region of O(12)–C(13) (see text).

Table 3. *Further information about deformation of aromatic rings*

The plane is the least-squares plane of atoms C(2), C(3), C(5) and C(6); for (2), the second line is the plane of C(10), C(11), C(13), C(14). Positive deviations are towards the center of the molecule.

	Distances in Å of atoms from the plane						Interplanar distance (Å)
Molecule	C(2)	C(3)	C(5)	C(6)	H (ave)	O (ave)	
(1)	0·005	−0·005	0·006	−0·006	0·04	0·142	3·02
(2)	−0·015	0·017	−0·015	0·016	0·09	−0·065	2·94
	−0·019	0·020	−0·018	0·021	0·09	−0·057	
(3)	−0·001	0·001	−0·002	0·002	0·00	0·104	3·03
(4)	(0)	(0)	(0)	(0)	0·04	–	3·09

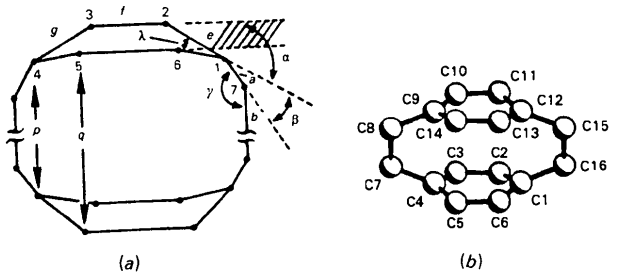


Fig. 1. (*a*) Schematic drawing of a [2.2]paracyclophane molecule (adapted from Keehn, 1983). We have used the same atom-numbering scheme for (1) and (3), with atom C(8) attached to C(4); the symbols given here are used in Table 2 for identifying certain (average) distances and angles. (*b*) The atom-numbering scheme for the cyclophane unit of (2). O(17) is attached to C(2), O(32) to C(11), O(33) to C(5) and O(48) to C(14) (see also Fig. 3).

have the *ap* conformation (−177, 177°), with the other three being *sc*. Each ring has at least one C–O bond that is *sc* rather than *ap*. In (3), the five C–C torsion angles (using average values in the disordered regions) are all *sc*, ranging from 52 to 75°. Of the ten C–O torsion angles, seven are *ap* (155–175°); the values for C(11)–O(12), O(15)–C(16) and C(20)–O(21) are 86, 132 and 88° respectively. These values would doubtless change when this host formed a complex and the need for turning $-CH_2-$ groups inwards to fill the 'hole' was removed.

Although the displacement parameters in these analyses of (2) and (3) are not of high quality, as judged by Hirshfeld's (1976) 'rigid-bond test', those for (2) are sufficiently good to suggest by the 'rigid-molecule test' (Rosenfield, Trueblood & Dunitz, 1978) that (2) shows no marked disorder at 115 K but that at room temperature there is appreciable disorder in the neighbourhood of O(23) to C(27), which was also apparent from the distances involving those atoms in the room-temperature refinement. In (3), the rigid-molecule test provides clear evidence of incipient disorder in the region of O(12) and C(13), as well as in the regions where disorder was specifically allowed for

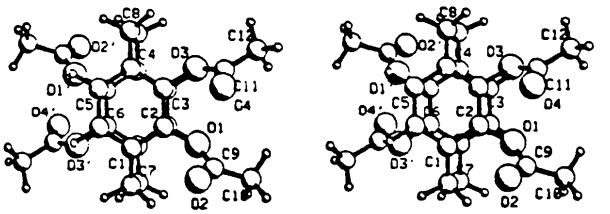


Fig. 2. *PLUTO* stereoview of the molecule of (1).

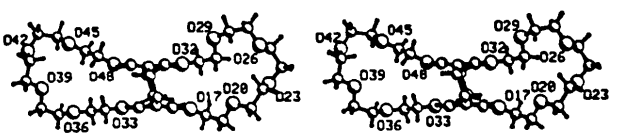


Fig. 3. *PLUTO* stereoview of the molecule of (2) along an axis through the approximate midpoints of the methylene bridges of the [2.2]paracyclophane unit. The difference in conformation of the two polyether rings and the sidewise mutual displacement of the two aromatic rings are evident.

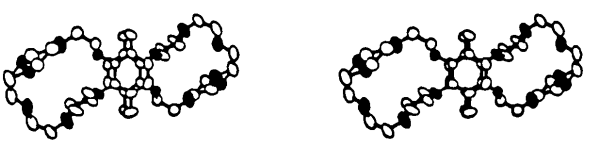


Fig. 4. *ORTEP* stereoview of the molecule of (3), looking down on the cyclophane rings (O atoms darkened). The disorder in two regions of the crown ring [near C(14)–O(15) and C(22)–C(23)] is represented by showing both '*A*' and '*B*' atoms.

during the refinement. It is not surprising that the largest peak in the final difference map for (3) (0·68 e Å^{-3}) is near O(12) and C(13).

The acetoxy geometry and the accompanying internal angle at the substituted C in the aromatic ring in (1) resemble these features found in other recent studies of aromatic acetoxy derivatives (Roszak, Borowiak & Gawron, 1984; Roszak & Borowiak, 1986). Atoms of the acetoxy groups are coplanar within 0·005 (2) and 0·002 (2) Å, the angle between the normals to these planes is 41·3° and the angles between normals to each plane and the plane through C(2)–C(3)–C(5)–C(6) are 60 and 55°. The atomic displacement parameters, which are quite good according to the Hirshfeld test, suggest that the acetoxy groups are librating about the bonds attaching them to the aromatic ring with almost equal (r.m.s.) amplitudes, a little more than 10° (Trueblood, 1978); the overall r.m.s. molecular libration in these directions is less than 2·5° (Schomaker & Trueblood, 1968, 1984).

The closest approach between molecules in (1) is between the carbonyl O atoms and the methyls of acetoxy groups in symmetry-related positions: O(4)···C(12) ($\frac{1}{2}-x$, $y-\frac{1}{2}$, z) 3·367, O(2)···C(10) ($-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) 3·428 Å, and O(4)···H(12*C*), 2·33, O(2)···H(10*C*), 2·39 Å. These C(sp^3)–H···O contacts, in each of which the C–H···O angle is 160°, might be considered to indicate weak hydrogen bonding similar to that found in acetamide (C–H···O = 3·45 Å) or acetic acid (C–H···O = 3·43 Å) (Berkovitch-Yellin & Leiserowitz, 1984). There are no unusually close intermolecular contacts in the structure of (2). The shortest C···O distance is between C(18) and O(29) at (x, $\frac{1}{2}-y$, $z-\frac{1}{2}$), 3·178 (3) Å, and the shortest H···O distance is here as well, H(18*A*) to this same O(29), 2·36 Å. The C–H···O angle is 131°, and this 'contact' might also be regarded as a weak hydrogen bond. There are three H···H contacts of about 2·25 Å, all involving the molecule at ($1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$): H(7) to H(40*A*), H(10) to H(38*B*) and H(25*A*) to H(35*B*).

The non-bonded distances in (3) were studied in an attempt to rationalize the disorder in the molecule. Across the crown ring, the shortest non-bonded distances are four H···H of 2·19 to 2·43 Å and three H···O of 2·49 to 2·64 Å (C–H···O angles 106 to 124°), all involving H atoms in the disordered region. The shortest intermolecular distances are six H···H of 2·24 to 2·41 Å, three of which involve atoms in the disordered region, and six H···O of 2·58 to 2·69 Å, four of which also involve disordered atoms, with C–H···O angles of 146 to 176°. None of these 'contacts' is unusually short, but the packing energy (Gavezzotti, 1983) depends to some extent on the modeling of the disorder. Let the symbol '*AA*' stand for the molecule with atoms C(14), O(15) in their *A* positions and C(22), C(23) also in their *A* positions. Then if the crystallographic molecular center of symmetry is retained, the van der Waals energy of '*AA*' is −113·3, '*BB*' is −113·9, '*BA*' is −112·8 and '*AB*' is −114·5 kcal mol^{-1}.* If the center of symmetry is removed (space group $P2_12_12_1$), the energies of '*AA,BB*' and '*BA,AB*' are the same, −113·7 kcal mol^{-1}. We take this, and the fact that the disorder persists at 115 K, to indicate that at least this portion of the structure has lower symmetry than *Pbca* in order to provide the best packing within the crown ring and also between molecules. Refinement in $Pbc2_1$ or in $P2_12_12_1$ was not successful since most of the atoms fit *Pbca* very well. Not surprisingly, statistical tests indicated strongly that the structure has a center of symmetry.

This work was supported in part by National Science Foundation Grant CHE82-05803 and earlier grants.

* 1 kcal mol^{-1} ≡ 4·18 kJ mol^{-1}.

References

ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B**35**, 2331–2339.

BERKOVITCH-YELLIN, Z. & LEISEROWITZ, L. (1984). *Acta Cryst.* B**40**, 159–165.

BUSH, M. A. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 341–344, 345–350.

CRAM, D. J. & TRUEBLOOD, K. N. (1981). *Top. Curr. Chem.* **98**, 43–106.

GAVEZZOTTI, A. (1983). *J. Am. Chem. Soc.* **105**, 5220–5225.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HANSON, I. R. (1978). *Acta Cryst.* B**34**, 1026–1028.

HELGESON, R. C., TARNOWSKI, T. L., TIMKO, J. M. & CRAM, D. J. (1977). *J. Am. Chem. Soc.* **99**, 6411–6418.

HIRSHFELD, F. L. (1976). *Acta Cryst.* A**32**, 239–244.

HOPE, H., BERNSTEIN, J. & TRUEBLOOD, K. N. (1972). *Acta Cryst.* B**28**, 1733–1743.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KEEHN, P. M. (1983). *Cyclophanes*. Vol. 1, pp. 69–238. New York: Academic Press.

LONG, R. E. (1965). PhD Dissertation, Univ. of California, Los Angeles.

MALLINSON, P. R. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1818–1823.

MOMANY, C., CLINGER, K., HACKERT, M. L. & POONIA, N. S. (1986). *J. Inclusion Phenom.* **4**, 61–67.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

PARKER, K., HELGESON, R. C., MAVERICK, E. & TRUEBLOOD, K. N. (1973). *Am. Crystallogr. Assoc. Abstr.*, winter meeting, p. 49.

ROSENFIELD, R. E., TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* A**34**, 828–829.

ROSZAK, A. & BOROWIAK, T. (1986). *Acta Cryst.* C**42**, 343–347.

ROSZAK, A., BOROWIAK, T. & GAWRON, M. (1984). *Acta Cryst.* A**40**, C-100.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1984). *Acta Cryst.* A**40**, C-339.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, W. S. & POONIA, N. S. (1986). *J. Inclusion Phenom.***4**, 93–98.
STROUSE, C. E. (1976). *Rev. Sci. Instrum.* **47**, 871–876.
TRUEBLOOD, K. N. (1978). *Acta Cryst.* A**34**, 950–954.
UCLA Crystallographic Package (1984). Univ. of California, Los Angeles.

Acta Cryst. (1986). C**42**, 1868–1870

Structure d'un β-Bloquant. Le (Hydroxy-2 isopropylamino-3 propoxy)-2 Benzonitrile

PAR M. COTRAIT

Laboratoire de Cristallographie et de Physique Cristalline, UA 144 *du CNRS, Université de Bordeaux* I, 351 *Cours de la Libération,* 33405 *Talence CEDEX, France*

ET G. PASTOR ET L. GIRAL

*Laboratoire de Chimie Organique et Structurale, Université des Science et Techniques du Languedoc, Place Eugène Bataillon, F*34060 *Montpellier CEDEX, France*

(*Reçu le* 26 *mars* 1986, *accepté le* 10 *juillet* 1986)

Abstract. $C_{13}H_{19}N_2O_2$, a new β-adrenergic compound, $M_r = 235{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}302$ (1), $b = 13{\cdot}412$ (2), $c = 13{\cdot}578$ (3) Å, $V = 1329{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}16$ (flotation), $D_x = 1{\cdot}175$ g cm^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}8$ cm^{-1}, $F(000) = 508$, $T = 298$ K, final $R = 0{\cdot}048$ for 1204 independent observed reflections. The isopropylaminopropanol is in a fully extended *trans* configuration. Crystal cohesion is assumed to be due to a large number of weak van der Waals interactions.

Introduction. De nombreuses études effectuées sur les aryloxypropanol-amines (Crowther & Smith, 1968; Howe, 1969, 1970; Howe, Crowther, Stephenson, Rao & Smith, 1968; Howe, McLoughlin, Rao, Smith & Chodnekar, 1968; Howe & Rao, 1968), il ressort que la chaîne oxypropanolamine joue un rôle prépondérant vis-à-vis de l'activité β-bloquante de ces composés.

Parmi les divers groupements aryles (naphtyle, phényle) nous nous sommes intéressés plus particulièrement au groupement phényle *ortho*-substitué. Afin de mieux apprécier l'influence des groupements placés en position *ortho* du cycle benzénique sur l'activité β-bloquante des molécules correspondantes, nous avons synthétisé une série de composés diversement substitués (Pastor, 1980; Pastor, Bompart, Giral & Alvart, 1986).

Afin de tenter d'interpréter la réactivité de ces composés nous avons entrepris l'étude conformationnelle de ces molécules en faisant appel à la RMN et la diffraction des rayons X. Nous présentons ici l'étude cristallographique du composé comportant le substituant $E = -CN$ qui présente une activité analogue à celle du propanolol, composé de référence.

Partie expérimentale. Plaquettes incolores, 0,6 × 0,3 × 0,1 mm; diffractomètre Enraf–Nonius CAD-4, monochromateur en graphite; 19 réflexions pour la détermination des paramètres; $h_{max} = 8$, $k_{max} = 15$, $l_{max} = 15$; balayage ω–2θ, $\Delta\theta = (1{,}0 + 0{,}15 \text{ tg } \theta)°$, ouverture du détecteur: $(1{,}4 + 0{,}6 \text{ tg } \theta)$ mm, $2\theta < 130°$, $\frac{1}{2}$ Ewald sphère; correction Lp, absorption négligée, pas de décroissance des intensités de référence (231 et $\bar{2}21$) avec le temps; 1344 réflexions indépendantes mesurées dont 1204 avec $I > 3\sigma(I)$; méthodes directes, programme *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982); affinement B_i puis β_{ij} des atomes C,N,O par moindres carrés, minimisation de $\sum w(|F_o| - |F_c|)^2$ avec $w = 1$ si $F_o < p$ et $w = p^2/F_o$ si $F_o > p$ où $p = (F_{o,max}/10)^{1/2}$; facteur de diffusion de Cromer & Waber (1974) pour C,N,O, de Stewart, Davidson & Simpson (1965) pour les hydrogènes; densité résiduelle $\Delta\rho$ de 0,3 et −0,2 e Å^{-3}, $(\Delta/\sigma)_{max} = 0{,}25$; affinement jusqu'à $R = 0{,}048$, $wR = 0{,}058$ et $S = 1{,}41$.

Discussion. Les coordonnées atomiques sont rassemblées dans le Tableau 1.* La Fig. 1 est une projection de la structure le long de l'axe *Ox*, et la Fig. 2 est une representation de la molécule, projetée sur le plan du cycle phényle. Les longueurs de liaison et angles de valence (Tableau 2) sont en bon accord avec ceux

* Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des paramètres des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 43234: 11 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

0108-2701/86/121868-03$01.50