

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
Cl	0.3794	0.291	0.3211	6.09 (3)
O(1)	-0.0046 (4)	0.4789 (5)	0.2688 (1)	5.75 (7)
C(2)	-0.1342 (4)	0.3599 (5)	0.2777 (1)	4.11 (7)
C(1)	-0.1220 (7)	0.1946 (7)	0.2524 (1)	5.7 (1)
C(3)	-0.1297 (4)	0.2992 (4)	0.3177 (1)	3.35 (6)
N(1)	-0.2615 (4)	0.2610 (4)	0.33960 (8)	3.44 (5)
C(4)	-0.2095 (4)	0.1951 (4)	0.37343 (9)	3.15 (6)
C(5)	-0.0389 (4)	0.1995 (4)	0.37054 (9)	3.28 (6)
N(2)	0.0050 (4)	0.2663 (4)	0.33539 (8)	3.48 (5)
C(6)	0.0511 (4)	0.1377 (5)	0.3995 (1)	3.77 (6)
C(7)	-0.0358 (4)	0.0697 (5)	0.43021 (9)	3.75 (6)
C(8)	-0.2093 (4)	0.0651 (4)	0.43320 (9)	3.34 (6)
C(9)	-0.2970 (4)	0.1300 (4)	0.40424 (9)	3.27 (6)
C(10)	-0.2929 (4)	-0.0182 (5)	0.4679 (1)	4.02 (7)
C(11)	-0.4716 (4)	0.0220 (5)	0.4752 (1)	3.90 (7)
C(12)	-0.5418 (4)	-0.0697 (5)	0.5105 (1)	3.94 (7)
C(13)	-0.7222 (5)	-0.0309 (6)	0.5191 (1)	4.19 (7)
C(14)	-0.7927 (4)	-0.1267 (6)	0.5538 (1)	4.01 (7)
C(15)	-0.9724 (4)	-0.0827 (5)	0.5629 (1)	4.21 (7)
C(16)	-1.0433 (5)	-0.1813 (6)	0.5971 (1)	4.11 (7)
C(17)	-1.2224 (5)	-0.1370 (6)	0.6067 (1)	4.34 (7)
C(18)	-1.2919 (5)	-0.2365 (6)	0.6410 (1)	4.36 (7)
C(19)	-1.4695 (5)	-0.1901 (6)	0.6513 (1)	4.64 (8)
C(20)	-1.5382 (6)	-0.2896 (7)	0.6855 (1)	5.3 (1)
C(21)	-1.7161 (7)	-0.2448 (8)	0.6955 (2)	6.3 (1)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(2)	1.389 (5)	C(8)—C(10)	1.518 (5)
C(2)—C(1)	1.506 (6)	C(10)—C(11)	1.499 (5)
C(2)—C(3)	1.511 (5)	C(11)—C(12)	1.523 (5)
C(3)—N(1)	1.331 (4)	C(12)—C(13)	1.517 (5)
C(3)—N(2)	1.324 (5)	C(13)—C(14)	1.518 (5)
N(1)—C(4)	1.398 (4)	C(14)—C(15)	1.522 (5)
C(4)—C(5)	1.394 (4)	C(15)—C(16)	1.516 (5)
C(4)—C(9)	1.374 (4)	C(16)—C(17)	1.520 (5)
C(5)—N(2)	1.387 (4)	C(17)—C(18)	1.516 (6)
C(5)—C(6)	1.383 (5)	C(18)—C(19)	1.517 (6)
C(6)—C(7)	1.377 (5)	C(19)—C(20)	1.511 (6)
C(7)—C(8)	1.417 (5)	C(20)—C(21)	1.515 (7)
C(8)—C(9)	1.381 (5)		
O(1)—C(2)—C(1)	109.0 (3)	C(7)—C(8)—C(9)	119.5 (3)
O(1)—C(2)—C(3)	110.1 (3)	C(7)—C(8)—C(10)	118.5 (3)
C(1)—C(2)—C(3)	110.3 (3)	C(9)—C(8)—C(10)	122.0 (3)
C(2)—C(3)—N(1)	124.6 (3)	C(4)—C(9)—C(8)	117.4 (3)
C(2)—C(3)—N(2)	125.2 (3)	C(8)—C(10)—C(11)	117.4 (3)
N(1)—C(3)—N(2)	110.1 (3)	C(10)—C(11)—C(12)	112.6 (3)
C(3)—N(1)—C(4)	108.4 (3)	C(11)—C(12)—C(13)	114.2 (3)
N(1)—C(4)—C(5)	106.0 (3)	C(12)—C(13)—C(14)	113.9 (3)
N(1)—C(4)—C(9)	130.9 (3)	C(13)—C(14)—C(15)	113.7 (3)
C(5)—C(4)—C(9)	123.0 (3)	C(14)—C(15)—C(16)	113.6 (3)
C(4)—C(5)—N(2)	106.6 (3)	C(15)—C(16)—C(17)	114.1 (3)
C(4)—C(5)—C(6)	120.4 (3)	C(16)—C(17)—C(18)	113.6 (3)
N(2)—C(5)—C(6)	132.9 (3)	C(17)—C(18)—C(19)	114.1 (3)
C(3)—N(2)—C(5)	108.8 (3)	C(18)—C(19)—C(20)	113.9 (4)
C(5)—C(6)—C(7)	116.9 (3)	C(19)—C(20)—C(21)	113.9 (4)
C(6)—C(7)—C(8)	122.8 (3)		

Program used to solve structure: *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Molecular graphics: *ORTEP* (Johnson, 1965). Full-matrix least-squares refinement: *SHELXS86* (Sheldrick, 1990). Following recommendations by Taylor & Kennard (1983), the H atoms of the N—H groups were placed at 1.03 Å from their N atoms in the direction obtained by refinement.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octaanisyl Cavitanes and a Related Caviplex

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Abstract

The macrocyclic host 41,42,43,44,45,46,47,48-octamethoxy-4,9,14,19,24,29,34,39-octamethylnonacyclo-[35.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}.1^{22,26}.1^{27,31}.1^{32,36}]octa-tetraconta-1(41),2,4,6(42),7,9,11(43),12,14,16(44),17,-19,21(45),22,24,26(46),27,29,31(47),32,34,36(48),37,-39-tetracosane [(I), C₆₄H₆₄O₈] contains a cavity lined with eight O atoms. This 'cavitand' complexes a caesium ion more strongly than any other alkali-metal ion, as expected from molecular models. The structure of a CH₂Cl₂ solvate of (I) [which we term (Ia)] was determined at 113 K. The conformation of the macrocycle appears to be stabilized by the intrusion of a 4-methyl group from a neighboring molecule. This conclusion was reinforced by the determination, at 115 K, of the structure of the ethanol solvate (Ib)

of the same host, and by the fact that a similar mutual orientation of a 4-methyl group of a neighboring molecule and the host ring was found. The structure of the caesium complex (Ic) of the same host was determined at 115 K; the ion makes the host much more symmetrical, with site symmetry *m* (molecular symmetry nearly *mm*2). The crystal structure of 41,42,43,44,45,46,47,48-octamethoxynonacyclo-[35.3.1.1^{2,6}.1^{7,11}.1^{12,16}.1^{17,21}.1^{22,26}.1^{27,31}.1^{32,36}]octatetraconta-1(41),2,4,6(42),7,9,11(43),12,14,16(44),17,19,21(45),22,24,26(46),27,29,31(47),32,34,36(48),37,39-tetracosane [(II), C₅₆H₄₈O₈], which lacks the eight 4-methyl groups of (I), was determined at room temperature; one methoxy group is disordered. No suitable crystals of a caesium complex of (II) could be grown.

Comment

These cavitands (Cram *et al.*, 1987) are eight-membered analogs of the prototype spherand (or cavitand) that contains six 4-methylanyl groups linked in the 2- and 6-positions (III) (Trueblood *et al.*, 1981; Trueblood, Maverick & Knobler, 1991). The original spherand was designed to undergo at most minimal conformational reorganization upon complexation; the molecule complexes only lithium and sodium ions. Molecular models of the present hosts suggested that the cavities would be larger and more flexible and that optimal complex-

ing of alkali-metal ions would occur with caesium, as was indeed found (Cram *et al.*, 1987). The models suggested also that the methyl of each methoxy group could either converge on, or diverge from, the cavity; in the six-membered analog, these methyls can only diverge. The present structures were determined to check these inferences. The atomic numbering in the first ring of the hosts (I) and (II) is indicated in Fig. 1; atoms in the other seven rings are numbered in a similar fashion, modulo 9 for (Ia), (Ib) and (Ic) [with allowance for the fact that in (Ic) atoms in the first and fifth rings lie on a mirror plane normal to *z*] and modulo 8 in (II).

The structure of (Ia) (Figs. 2 and 3) shows that there is a close interaction of each macrocycle with a 4-methyl group from a neighboring macrocycle. The geometry of this quite symmetrical interaction, evident in Figs. 2 and 3, is summarized in Table 5. Close examination of Fig. 3 shows that the H atoms of the intruding CH₃ lie closer to the mean molecular plane than do the C atoms of the four outward-directed methoxy CH₃ groups. This situation is impossible in the analogous hexameric anisyl derivatives (III) (Trueblood *et al.*, 1991), where the methoxy CH₃ groups are tightly packed together. Calculations confirm this visual impression (see Table 5). There seem to be no unusually close contacts of the macrocycle with the disordered solvent in (Ia); one H atom (H73A) does approach one aromatic ring of the host (Table 5 and Fig. 3). Our models for the disorder of

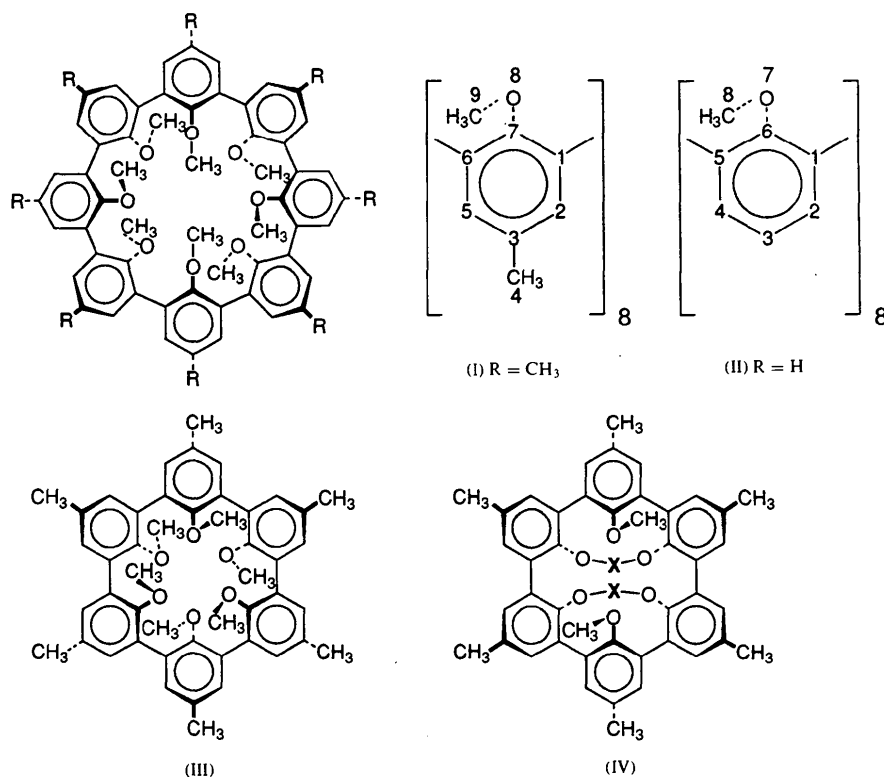


Fig. 1. Structural diagrams of compounds (I)-(IV).

the solvent in this structure, as well as in those of (Ib) and (Ic), are not entirely satisfactory, leaving residual peaks in the final difference maps of $0.5 e \text{ \AA}^{-3}$ [in (Ia)] to nearly $1.0 e \text{ \AA}^{-3}$ [in (Ib) and (Ic)].

Crystals of (Ib) contain disordered ethanol, but the host is ordered, as in (Ia), and again each macrocycle has a close interaction with a 4-methyl group from a neighboring macrocycle (Figs. 4 and 5, and Table 5). The approach of this CH₃ is neither as close nor as symmetrical as that in (Ia) because of interference by the (presumably) hydrogen-bonded CH₃CH₂OH. Packing calculations (Gavezzotti, 1983) indicated that a single molecule of ethanol cannot fill the available free space effectively; *e.g.* there could be essentially free rotation about the C—O bond of the major ethanol occupant.

Fig. 6 shows that Cs⁺ confers near-*mm*2 symmetry upon the macrocycle, and examination of the parameters (transformed to the axial system of the least-squares

plane) confirms this. The Cs⁺ has coordination number 10, with approximate *D*_{4d} symmetry (Table 6 and Fig. 6). The perchlorate ion has nearly ideal tetrahedral geometry.

The first of the present structures determined was that of (II); only a single crystal was obtained (grown fortuitously in an NMR tube), and it was lost before low-temperature data could be collected. The room-temperature structure of (II) is of low precision, as is evident upon inspection of the agreement factors, the *ORTEP* drawings, the *e.s.d.*'s of atomic coordinates and displacement parameters, and the matrix of differences in mean-square displacement amplitudes along bonds (Hirshfeld, 1976). Some of the 'vibration ellipsoids' are large, especially in the region C17—C24. There is evident disorder in the O—CH₃ portion of this anisyl moiety; in the final model, two O23—C24 groups are included, with occupancies 0.66 and 0.34, respectively. The major

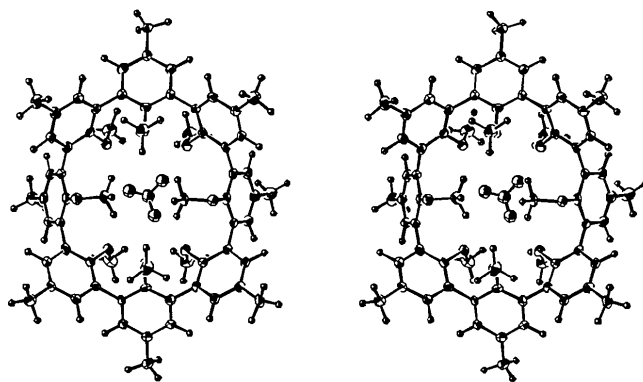


Fig. 2. *ORTEP* (Johnson, 1976) stereo drawing of (Ia); the solvent is not shown. Ellipsoids are drawn at 50% probability level in all figures. One 4-methyl group of a neighboring molecule (Table 5) is drawn with spheres of radius 0.2 Å. It helps to fill the cavity and thereby stabilize the conformation.

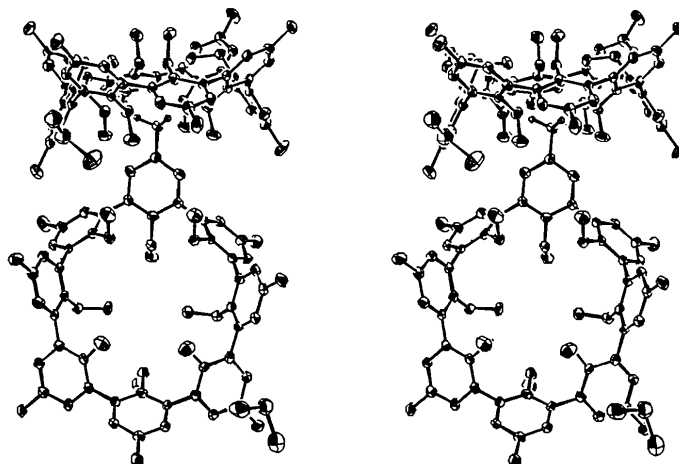


Fig. 3. *ORTEP* stereo drawing of part of the packing of (Ia), showing the approach of C40 of one macrocycle to a nearby macrocycle. The H atoms of this CH₃ (the only H atoms shown here) are closer to the mean plane of the second macrocycle than are the C atoms of the four straddling outward-directed methoxy methyls. The C and two Cl atoms of the (major occupancy) methylene chloride of solvation are shown, to illustrate the interaction described in Table 5.

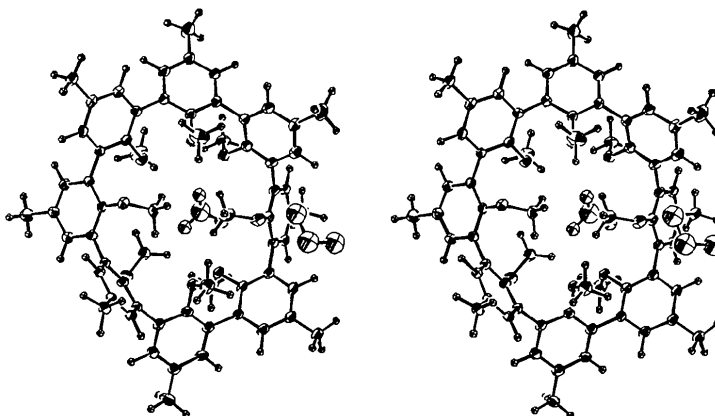


Fig. 4. *ORTEP* stereo drawing of (1b). The C—C—O atoms of the predominant disordered ethanol molecule are represented by spheres of radius 0.3 Å. The —OH of ethanol is presumably hydrogen bonded to a methoxy O atom (Table 5). Two methoxy methyls turn inward on the side facing the viewer, as in (1a). On the opposite side the conformation is stabilized by a third inward OCH₃ and a 4-methyl group of a neighboring molecule (shown as spheres of radius 0.2 Å).

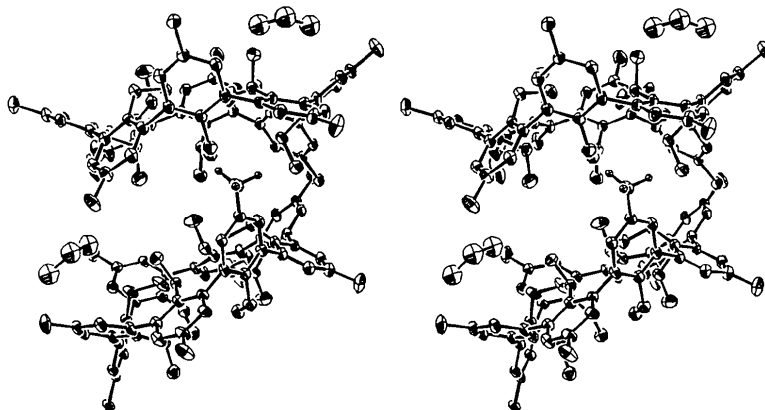


Fig. 5. *ORTEP* stereo drawing of (1b) showing the approach of a methyl group (C40) of one macrocycle to a nearby macrocycle. This approach is partly hindered by the conformational changes induced by the ethanol of solvation. As in Fig. 3, the only H atoms shown are those of this methyl.

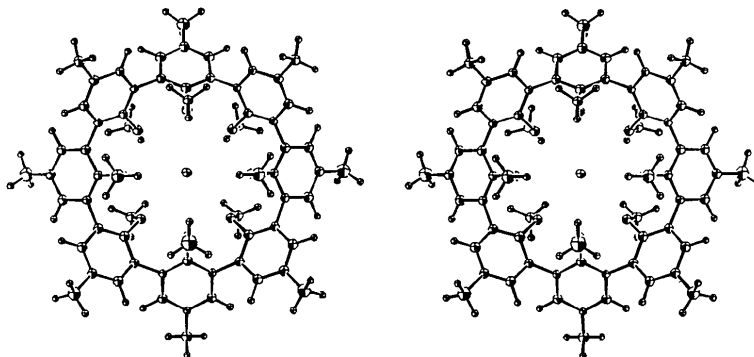


Fig. 6. *ORTEP* stereo drawing of (1c). The Cs⁺ ion is in the center of the cavity; the perchlorate ion and the solvent have been omitted.

conformer (Fig. 7) has four methyl groups turned 'in' (toward the center of the macrocycle), including C24A; in the minor conformer, C24B is 'out'. The disorder is not adequately described by the simple model used, but we were unable to improve it with our room-temperature data. The only close intermolecular interactions (Table 5) involve H···O contacts.

We believe that disorder is found in the macrocycle of (II), but not in those of (Ia) or (Ib), because (II) lacks the 4-methyl groups that seem to stabilize the macrocycle in (I) when no complexing ion is present. Four methoxy methyls turn inward to fill the cavity in the major conformer of (II), two on each side of the macrocycle. In (Ia), a 4-methyl group of a neighboring molecule approaches one side of the ring so symmetrically that there is no room for inward-turning methoxy methyls on that side; only the two on the other side remain in the 'inward' position. In (Ib), the presence of the (presumably) hydrogen-bonded ethanol is accompanied by a decreased tilt of the adjacent ring. This change in conformation and packing may be responsible for the fact that the 4-methyl of a neighboring molecule does not approach as symmetrically as in (Ia), with the consequence that there is room for an inward-turning methoxy methyl on this same side of the ring, evident in Fig. 4. No methoxy methyls turn inward in (Ic), because the Cs⁺ fills the cavity very effectively. Interaction of CH₃ groups in neighboring molecules with macrocycles containing O atoms has been reported frequently (*e.g.* Goldberg, 1975).

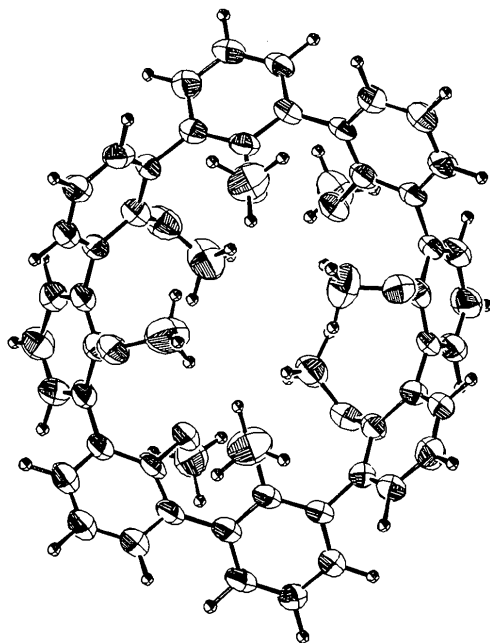


Fig. 7. ORTEP drawing of the major conformer of (II). The disordered methoxy group is at about 9 o'clock.

Table 7 summarizes the average geometry of the host macrocycles in the present structures, and compares them with the related hexaanisyl hosts. The greater conformational freedom and diminished overcrowding of the present molecules is evident in the lesser folding of, and departures from the planes of, the aromatic rings, and in the greater interplanar angles. The hexaanisyl spherand hosts and the bridged spherand hosts (final two columns of Table 7) release some strain upon complexation; (I) and (II) have no appreciable strain.

The precision of the displacement parameters for the atoms in these structures is not high, as evidenced both by their e.s.d.'s and by the fit to the Hirshfeld (1976) test (Dunitz, Maverick & Trueblood, 1988). Nonetheless, these parameters are more than adequate to establish that the host molecules show at most an overall librational amplitude of only about 2° in the crystal, even for (II) at room temperature (details are included with the Supplementary Material). The methoxy groups in (Ia), (Ib) and (II) are, however, undergoing appreciable torsional oscillation about the C—O bonds, with r.m.s. amplitudes averaging close to 7° in (Ia) and (Ib) (at about 114 K), and nearly 11° in (II) (at room temperature). Although the comparison is between different structures, with different degrees of intra- and intermolecular interaction, the fact that the mean-square amplitudes for these groups vary approximately in accord with the absolute temperature suggests that they do indeed represent actual motion, and not static displacement. Corrections to bond lengths in the host molecules are negligible except for the O—CH₃ bonds, for which they average 0.019 Å in (II) and 0.008 Å in (Ia) and (Ib). The perchlorate ion in (Ic) shows apparent librational amplitudes of about 6° in two directions; whether these are static or dynamic is unclear, but in any event, they lead to bond-length corrections of 0.010–0.013 Å.

The U^{ij} values for structure (Ib) are the most precise, with a mean e.s.d. of about 0.0020 Å². The average difference in mean-square displacement amplitudes for bonded pairs along the bonding direction (the Hirshfeld test) is 0.0017 Å², indicating that within the precision of the data, that criterion is met. One striking observation is that U^{11} for C13 of structure (Ib) is much the highest U^{ii} of any of the *p*-methyl groups in any of these structures, some 0.20 Å², corresponding to an r.m.s. amplitude of 0.45 Å. It seems particularly significant that the direction of this displacement is almost exactly that of the unusually short (2.89 Å) vector from C13 to C81 (Table 5); C81 is the methyl group of the lowest-occupancy ethanol molecule postulated in our model for the disorder. It seems reasonable that the occurrence of such a short contact approximately 25% of the time might lead to a large (static) displacement of C13.

These structures demonstrate clearly the reason why the standard free energy of complexation (Cram *et al.*,

1987) of Cs⁺ by (I) and (II) is less negative than that of Li⁺ and Na⁺ by (III) and (IV) (Cram & Lein, 1985): (I) and (II) are much more flexible than (III) and (IV), and must reorganize to complex Cs⁺, even though when in an appropriate conformation, they are highly complementary to Cs⁺. Furthermore, the O atoms in the present hosts must be desolvated before complexation; those in (III) and (IV) are not accessible to solvent.

Experimental

Compound (Ia)

Crystal data

C₆₄H₆₄O₈·0.7CH₂Cl₂

M_r = 1022

Monoclinic

*P*2₁/*n*

a = 14.936 (4) Å

b = 15.088 (4) Å

c = 25.727 (6) Å

β = 92.44 (2)°

V = 5792 (3) Å³

Z = 4

D_x = 1.173 Mg m⁻³

Cu *K*α radiation

λ = 1.54184 Å

Cell parameters from 15 reflections

θ = 50–60°

μ = 1.35 mm⁻¹

T = 113 K

Clear, chunky

0.55 × 0.43 × 0.41 mm

Colorless

Crystal source: Cram *et al.* (1987)

Data collection

Syntex *P*1̄ diffractometer

θ/2θ scans

Absorption correction: none

6624 measured reflections

5816 independent reflections

5140 observed reflections

[*F* > 4σ(*F*)]

θ_{max} = 75°

h = 0 → 14

k = 0 → 18

l = -25 → 29

3 standard reflections

monitored every 97

reflections

intensity decay: 0.2%

Refinement

Refinement on *F*

R = 0.070

wR = 0.076

S = 2.85

5140 reflections

727 parameters

H riding on attached C, or as part of rigid CH₃ group, C—H 1.08 Å, ⟨*u*_H²⟩ fixed

Weighting scheme based on measured e.s.d.'s

(Δ/σ)_{max} = 0.62

Δρ_{max} = 0.51 e Å⁻³

Δρ_{min} = -0.47 e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (Ib)

Crystal data

C₆₄H₆₄O₈·C₂H₆O

M_r = 1007

Monoclinic

*P*2₁/*n*

a = 14.117 (6) Å

b = 27.796 (9) Å

c = 14.845 (4) Å

β = 94.29 (3)°

Cu *K*α radiation

λ = 1.54184 Å

Cell parameters from 15 reflections

θ = 50–70°

μ = 0.53 mm⁻¹

T = 115 K

Clear, chunky

V = 5809 (4) Å³

Z = 4

D_x = 1.151 Mg m⁻³

Data collection

Syntex *P*1̄ diffractometer

θ/2θ scans

Absorption correction: none

11 032 measured reflections

8217 independent reflections

7590 observed reflections

[*F* > 3σ(*F*)]

*R*_{int} = 0.05

Refinement

Refinement on *F*

R = 0.082

wR = 0.085

S = 3.53

8209 reflections

733 parameters

H riding on attached C, or as part of rigid CH₃ group, C—H 1.08 Å, ⟨*u*_H²⟩ fixed

0.44 × 0.25 × 0.21 mm

Colorless

Crystal source: Cram *et al.* (1987)

θ_{max} = 75°

h = 0 → 16

k = 0 → 34

l = -17 → 17

3 standard reflections

monitored every 97

reflections

intensity decay: <1%

Weighting scheme based on measured e.s.d.'s

(Δ/σ)_{max} = 1.1

Δρ_{max} = 1.0 e Å⁻³

Δρ_{min} = -0.32 e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Compound (Ic)

Crystal data

C₆₄H₆₄O₈·1.04CH₂Cl₂·Cs⁺·ClO₄⁻

M_r = 1283

Orthorhombic

Pnam

a = 17.088 (5) Å

b = 19.691 (6) Å

c = 20.392 (6) Å

V = 6861 (4) Å³

Z = 4

D_x = 1.242 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 15 reflections

θ = 7.4–10.4°

μ = 0.65 mm⁻¹

T = 115 K

Prismatic needle

0.45 × 0.22 × 0.12 mm

Colorless

Crystal source: Cram *et al.* (1987)

Data collection

Syntex *P*1̄ diffractometer

θ/2θ scans

Absorption correction: by integration from crystal shape

*T*_{min} = 0.872, *T*_{max} =

0.925

6698 measured reflections

5072 independent reflections

3064 observed reflections

[*F* > 4σ(*F*)]

θ_{max} = 25°

h = 0 → 20

k = 0 → 23

l = 0 → 24

3 standard reflections

monitored every 97

reflections

intensity decay: <1%

Refinement

Refinement on *F*

R = 0.091

wR = 0.079

S = 1.83

(Δ/σ)_{max} = 0.16

Δρ_{max} = 0.92 e Å⁻³

Δρ_{min} = -0.99 e Å⁻³

Extinction correction: none

3064 reflections
207 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s

Compound (II)*Crystal data*C₅₆H₄₈O₈ $M_r = 849.0$

Triclinic

 $P\bar{1}$ $a = 7.924 (2) \text{ \AA}$ $b = 11.433 (3) \text{ \AA}$ $c = 25.541 (6) \text{ \AA}$ $\alpha = 79.12 (2)^\circ$ $\beta = 83.61 (2)^\circ$ $\gamma = 87.60 (2)^\circ$ $V = 2257.6 (10) \text{ \AA}^3$ $Z = 2$ $D_x = 1.249 \text{ Mg m}^{-3}$ *Data collection*Syntex $P\bar{1}$ diffractometer $\theta/2\theta$ scansAbsorption correction:
none

8012 measured reflections

8012 independent reflections

4918 observed reflections

 $[F > 2\sigma(F)]$ *Refinement*Refinement on F $R = 0.112$ $wR = 0.096$ $S = 1.49$

4918 reflections

606 parameters

H riding on attached C,
or as part of rigid CH₃
group, C—H 1.08 Å, $\langle u_{\text{H}}^2 \rangle$
fixed at U_{eq} (attached C) +
0.01 Å²Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Table
2.2B)Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ Cell parameters from 15
reflections $\theta = 9-11^\circ$ $\mu = 0.047 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Plates and prisms

 $0.44 \times 0.24 \times 0.15 \text{ mm}$

Colorless

Crystal source: Cram *et al.*
(1987) $\theta_{\text{max}} = 25.0^\circ$ $h = 0 \rightarrow 9$ $k = -13 \rightarrow 13$ $l = -29 \rightarrow 30$

3 standard reflections

monitored every 97

reflections

intensity decay: 0.5%

 $w = 1/[\sigma^2(F) + 0.0002F^2]$ $(\Delta/\sigma)_{\text{max}} = 0.14$ $\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (Ia)*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.8528 (3)	-0.0330 (3)	0.3549 (2)	0.024 (2)
C2	0.8479 (3)	-0.1242 (3)	0.3619 (2)	0.028 (2)
C3	0.8325 (3)	-0.1815 (3)	0.3198 (2)	0.031 (2)
C4	0.8274 (4)	-0.2801 (3)	0.3284 (2)	0.042 (2)
C5	0.8251 (3)	-0.1441 (3)	0.2703 (2)	0.030 (2)
C6	0.8292 (3)	-0.0542 (3)	0.2614 (2)	0.023 (2)
C7	0.8421 (3)	0.0019 (3)	0.3047 (2)	0.026 (2)
O8	0.8448 (2)	0.0925 (2)	0.2972 (1)	0.030 (1)
C9	0.7606 (4)	0.1336 (4)	0.3053 (2)	0.043 (2)
C10	0.8216 (3)	-0.0163 (3)	0.2076 (2)	0.025 (2)
C11	0.7441 (3)	-0.0278 (3)	0.1767 (2)	0.027 (2)
C12	0.7352 (3)	0.0073 (3)	0.1265 (2)	0.028 (2)
C13	0.6487 (4)	-0.0024 (4)	0.0946 (2)	0.042 (2)
C14	0.8068 (3)	0.0542 (3)	0.1083 (2)	0.029 (2)
C15	0.8867 (3)	0.0659 (3)	0.1377 (2)	0.027 (2)
C16	0.8933 (3)	0.0295 (3)	0.1873 (2)	0.024 (2)
O17	0.9716 (2)	0.0423 (2)	0.2166 (1)	0.030 (1)
C18	1.0281 (4)	-0.0330 (4)	0.2196 (2)	0.046 (2)
C19	0.9634 (3)	0.1158 (3)	0.1160 (2)	0.024 (2)
C20	1.0271 (3)	0.0697 (3)	0.0884 (2)	0.030 (2)
C21	1.1006 (3)	0.1135 (3)	0.0681 (2)	0.029 (2)
C22	1.1697 (4)	0.0622 (4)	0.0393 (2)	0.040 (2)
C23	1.1079 (4)	0.2035 (4)	0.0766 (2)	0.032 (2)
C24	1.0442 (4)	0.2513 (3)	0.1034 (2)	0.029 (2)
C25	0.9725 (3)	0.2050 (3)	0.1232 (2)	0.025 (2)
O26	0.9057 (2)	0.2514 (2)	0.1470 (1)	0.030 (1)
C27	0.9237 (4)	0.2670 (3)	0.2015 (2)	0.034 (2)
C28	1.0510 (3)	0.3497 (3)	0.1099 (2)	0.028 (2)
C29	0.9984 (3)	0.4053 (3)	0.0796 (2)	0.032 (2)
C30	1.0028 (3)	0.4967 (3)	0.0836 (2)	0.032 (2)
C31	0.9431 (4)	0.5572 (4)	0.0506 (2)	0.043 (2)
C32	1.0629 (3)	0.5317 (3)	0.1213 (2)	0.030 (2)
C33	1.1152 (3)	0.4785 (3)	0.1543 (2)	0.025 (2)
C34	1.1104 (3)	0.3878 (3)	0.1473 (2)	0.025 (2)
O35	1.1578 (2)	0.3301 (2)	0.1803 (1)	0.032 (1)
C36	1.2523 (3)	0.3311 (4)	0.1775 (2)	0.043 (2)
C37	1.1663 (3)	0.5200 (3)	0.1989 (2)	0.025 (2)
C38	1.2373 (3)	0.5781 (3)	0.1915 (2)	0.028 (2)
C39	1.2854 (3)	0.6167 (3)	0.2335 (2)	0.026 (2)
C40	1.3649 (3)	0.6758 (3)	0.2249 (2)	0.029 (2)
C41	1.2597 (3)	0.5962 (3)	0.2837 (2)	0.027 (2)
C42	1.1875 (3)	0.5402 (3)	0.2918 (2)	0.025 (2)
C43	1.1412 (3)	0.5036 (3)	0.2494 (2)	0.027 (2)
O44	1.0672 (2)	0.4502 (2)	0.2570 (1)	0.031 (1)
C45	0.9857 (4)	0.4985 (4)	0.2560 (2)	0.043 (2)
C46	1.1562 (3)	0.5228 (3)	0.3453 (2)	0.026 (2)
C47	1.1250 (3)	0.5911 (3)	0.3755 (2)	0.029 (2)
C48	1.0901 (4)	0.5764 (3)	0.4238 (2)	0.033 (2)
C49	1.0560 (4)	0.6518 (4)	0.4551 (2)	0.050 (2)
C50	1.0888 (3)	0.4899 (3)	0.4419 (2)	0.027 (2)
C51	1.1203 (3)	0.4202 (3)	0.4139 (2)	0.023 (2)
C52	1.1555 (3)	0.4369 (3)	0.3656 (2)	0.026 (2)
O53	1.1847 (2)	0.3660 (2)	0.3369 (1)	0.032 (1)
C54	1.2800 (4)	0.3566 (4)	0.3373 (2)	0.048 (2)
C55	1.1221 (3)	0.3280 (3)	0.4356 (2)	0.025 (2)
C56	1.1988 (3)	0.2968 (3)	0.4627 (2)	0.031 (2)
C57	1.2035 (4)	0.2132 (3)	0.4844 (2)	0.034 (2)
C58	1.2898 (3)	0.1828 (4)	0.5127 (2)	0.050 (2)
C59	1.1283 (3)	0.1589 (3)	0.4790 (2)	0.032 (2)
C60	1.0508 (3)	0.1861 (3)	0.4522 (2)	0.022 (2)
C61	1.0489 (3)	0.2719 (3)	0.4302 (2)	0.024 (2)
O62	0.9705 (2)	0.3018 (2)	0.4062 (1)	0.027 (1)
C63	0.9638 (3)	0.2894 (3)	0.3504 (2)	0.031 (2)
C64	0.9699 (3)	0.1300 (3)	0.4482 (2)	0.024 (2)
C65	0.9081 (3)	0.1322 (3)	0.4877 (2)	0.025 (2)
C66	0.8291 (3)	0.0839 (3)	0.4845 (2)	0.028 (2)
C67	0.7620 (3)	0.0897 (4)	0.5273 (2)	0.034 (2)
C68	0.8108 (3)	0.0312 (3)	0.4405 (2)	0.025 (2)
C69	0.8716 (3)	0.0258 (3)	0.4009 (2)	0.024 (2)
C70	0.9507 (3)	0.0751 (3)	0.4052 (2)	0.023 (2)
O71	1.0113 (2)	0.0706 (2)	0.3662 (1)	0.029 (1)

All unique intensity data out to 50° in θ were collected for (Ia) and (Ib); a limited number of additional data were collected to 75°, in parallel mode. Negative values of k for intensities measured in parallel mode were changed to positive values, without checking to be sure that Friedel's law was obeyed. All measurements at low temperature were made with a device of Strouse (1976).

For all compounds, data collection: Syntex $P\bar{1}$ software; cell refinement: Syntex $P\bar{1}$ software; data reduction: CARESS (UCLA Crystallographic Package, 1984); program(s) used to solve structure: MULTAN78 (Main *et al.*, 1978); program(s) used to refine structure: SHELX76 (Sheldrick, 1976); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: local programs. In addition, the program UCLA FMLS (UCLA Crystallographic Package, 1984) was used in the refinement of structure (II).

C72	1.0693 (4)	-0.0049 (4)	0.3713 (2)	0.043 (2)	C59	0.3222 (3)	0.02095 (10)	0.3482 (2)	0.0305 (10)
C11†	0.2233 (2)	0.2277 (1)	0.9243 (1)	0.066 (1)	C60	0.2807 (3)	0.06619 (10)	0.3323 (2)	0.0264 (9)
C12‡	0.0615 (2)	0.2374 (2)	0.8599 (1)	0.071 (1)	C61	0.2653 (3)	0.09560 (10)	0.4059 (2)	0.0266 (9)
C73‡	0.1206 (6)	0.1773 (6)	0.9092 (3)	0.057 (2)*	O62	0.21596 (19)	0.13879 (7)	0.39135 (16)	0.0281 (7)
C13§	0.0156 (13)	0.1906 (13)	0.9315 (8)	0.082 (6)*	C63	0.1194 (3)	0.13506 (12)	0.4144 (3)	0.0388 (11)
C14¶	0.0173 (15)	0.2165 (13)	0.8868 (8)	0.048 (6)*	C64	0.2523 (3)	0.08098 (9)	0.2369 (2)	0.0257 (9)
					C65	0.1703 (3)	0.06165 (9)	0.1932 (2)	0.0249 (9)
					C66	0.1440 (3)	0.07143 (9)	0.1027 (2)	0.0249 (9)
					C67	0.0565 (3)	0.04913 (11)	0.0550 (3)	0.0319 (10)
					C68	0.2027 (3)	0.10098 (10)	0.0554 (2)	0.0275 (10)
					C69	0.2867 (3)	0.12071 (9)	0.0970 (2)	0.0265 (9)
					C70	0.3097 (3)	0.11100 (10)	0.1879 (2)	0.0282 (9)
					O71	0.3950 (2)	0.12803 (9)	0.22909 (18)	0.0375 (8)
					C72	0.3898 (4)	0.17743 (13)	0.2602 (3)	0.0500 (14)
					O73†	0.0816 (6)	0.4142 (3)	0.7032 (5)	0.073 (3)*
					C74‡	0.0762 (10)	0.4516 (4)	0.7594 (8)	0.067 (3)*
					C75‡	0.0319 (11)	0.4940 (4)	0.7122 (9)	0.064 (3)*
					O76‡	0.1464 (10)	0.4746 (4)	0.7621 (8)	0.089 (4)*
					C77‡	0.0780 (16)	0.5076 (6)	0.7307 (13)	0.074 (5)*
					C78‡	-0.0036 (16)	0.4861 (6)	0.6691 (14)	0.063 (4)*
					O79§	0.0519 (13)	0.4349 (6)	0.8093 (11)	0.070 (4)*
					C80§	0.0592 (15)	0.3864 (6)	0.8139 (13)	0.053 (4)*
					C81§	0.121 (2)	0.3477 (11)	0.781 (2)	0.114 (9)*

* U_{iso} .

† Occupancy 0.72.

‡ Occupancy 0.54.

§ Occupancy 0.10.

¶ Occupancy 0.08.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (Ib)

	x	y	z	U_{eq}
C1	0.3511 (3)	0.14875 (11)	0.0403 (2)	0.0253 (9)
C2	0.4195 (3)	0.12470 (11)	-0.0058 (3)	0.0326 (10)
C3	0.4775 (3)	0.14870 (11)	-0.0636 (3)	0.0341 (10)
C4	0.5483 (4)	0.12244 (14)	-0.1173 (4)	0.0592 (14)
C5	0.4679 (3)	0.19912 (11)	-0.0719 (2)	0.0285 (10)
C6	0.4016 (3)	0.22419 (11)	-0.0252 (2)	0.0263 (9)
C7	0.3413 (3)	0.19863 (11)	0.0281 (2)	0.0262 (9)
O8	0.2708 (2)	0.22273 (8)	0.07000 (16)	0.0302 (7)
C9	0.1889 (3)	0.23218 (12)	0.0089 (3)	0.0374 (11)
C10	0.3938 (3)	0.27770 (10)	-0.0322 (2)	0.0281 (9)
C11	0.3652 (4)	0.29926 (11)	-0.1140 (3)	0.0385 (12)
C12	0.3533 (4)	0.34946 (12)	-0.1212 (3)	0.0482 (15)
C13	0.3197 (6)	0.37216 (15)	-0.2101 (3)	0.089 (3)
C14	0.3689 (4)	0.37658 (11)	-0.0435 (3)	0.0410 (13)
C15	0.4011 (3)	0.35633 (10)	0.0401 (2)	0.0309 (10)
C16	0.4150 (3)	0.30619 (10)	0.0443 (2)	0.0272 (9)
O17	0.4510 (2)	0.28493 (7)	0.12405 (16)	0.0294 (7)
C18	0.5511 (4)	0.2806 (2)	0.1283 (3)	0.0543 (15)
C19	0.4237 (3)	0.38828 (10)	0.1195 (2)	0.0302 (10)
C20	0.4820 (3)	0.42841 (10)	0.1089 (2)	0.0313 (10)
C21	0.5073 (3)	0.45999 (10)	0.1804 (3)	0.0312 (10)
C22	0.5689 (4)	0.50380 (11)	0.1666 (3)	0.0420 (12)
C23	0.4738 (3)	0.45032 (10)	0.2642 (2)	0.0279 (9)
C24	0.4142 (3)	0.41088 (9)	0.2779 (2)	0.0251 (9)
C25	0.3880 (3)	0.38049 (10)	0.2041 (2)	0.0274 (9)
O26	0.3275 (2)	0.34258 (7)	0.21846 (17)	0.0302 (7)
C27	0.2326 (4)	0.34989 (16)	0.1832 (4)	0.0524 (14)
C28	0.3747 (3)	0.40322 (10)	0.3673 (2)	0.0249 (9)
C29	0.3081 (3)	0.43543 (10)	0.3970 (3)	0.0301 (10)
C30	0.2700 (3)	0.43020 (11)	0.4807 (3)	0.0335 (10)
C31	0.2007 (4)	0.46709 (13)	0.5134 (3)	0.0497 (13)
C32	0.2984 (3)	0.39053 (11)	0.5339 (2)	0.0310 (10)
C33	0.3670 (3)	0.35814 (10)	0.5071 (2)	0.0266 (9)
C34	0.4063 (3)	0.36522 (9)	0.4239 (2)	0.0247 (9)
O35	0.4835 (2)	0.33878 (7)	0.39990 (17)	0.0310 (7)
C36	0.4657 (3)	0.28969 (11)	0.3717 (3)	0.0341 (10)
C37	0.4012 (3)	0.31857 (10)	0.5690 (2)	0.0261 (10)
C38	0.4911 (3)	0.32200 (10)	0.6162 (2)	0.0287 (10)
C39	0.5261 (3)	0.28638 (10)	0.6749 (2)	0.0261 (9)
C40	0.6226 (3)	0.29120 (12)	0.7267 (3)	0.0332 (11)
C41	0.4713 (3)	0.24494 (10)	0.6841 (2)	0.0262 (10)
C42	0.3820 (3)	0.23992 (10)	0.6366 (2)	0.0270 (10)
C43	0.3461 (3)	0.27763 (10)	0.5823 (2)	0.0261 (10)
O44	0.2521 (2)	0.27450 (8)	0.54621 (17)	0.0327 (8)
C45	0.2368 (3)	0.26478 (12)	0.4524 (3)	0.0348 (11)
C46	0.3309 (3)	0.19293 (10)	0.6414 (2)	0.0250 (9)
C47	0.2856 (3)	0.17910 (11)	0.7179 (3)	0.0303 (10)
C48	0.2434 (3)	0.13386 (12)	0.7232 (3)	0.0337 (11)
C49	0.1957 (4)	0.11892 (15)	0.8073 (3)	0.0502 (14)
C50	0.2458 (3)	0.10274 (11)	0.6488 (2)	0.0332 (10)
C51	0.2898 (3)	0.11564 (10)	0.5710 (2)	0.0270 (9)
C52	0.3341 (3)	0.16096 (10)	0.5688 (2)	0.0257 (9)
O53	0.38366 (19)	0.17444 (7)	0.49589 (16)	0.0270 (6)
C54	0.4790 (3)	0.15644 (12)	0.4999 (3)	0.0382 (11)
C55	0.2959 (3)	0.08218 (10)	0.4938 (2)	0.0269 (9)
C56	0.3360 (3)	0.03616 (11)	0.5081 (3)	0.0323 (10)
C57	0.3482 (3)	0.00527 (11)	0.4359 (3)	0.0325 (10)
C58	0.3916 (4)	-0.04421 (12)	0.4535 (3)	0.0465 (14)

* U_{iso} .

† Occupancy 0.40.

‡ Occupancy 0.35.

§ Occupancy 0.25.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (Ic)

	x	y	z	U_{eq}
Cs46	0.3701 (1)	0.2489 (1)	3/4	0.0223 (3)
Cl47	0.1212 (3)	0.1567 (2)	3/4	0.022 (1)
O48	0.1160 (5)	0.1151 (4)	0.6921 (4)	0.031 (3)
O49	0.1946 (7)	0.1921 (7)	3/4	0.040 (5)
O50	0.0577 (7)	0.2055 (6)	3/4	0.029 (4)
Cl'†	0.3119 (3)	0.4257 (2)	0.1785 (2)	0.043 (2)
C1	0.4457 (7)	0.0240 (5)	0.8095 (6)	0.020 (3)*
C2	0.4170 (7)	-0.0433 (6)	0.6913 (6)	0.026 (3)*
C3	0.4021 (10)	-0.0766 (8)	3/4	0.026 (5)*
C4	0.3740 (12)	-0.1480 (9)	3/4	0.039 (5)*
O7	0.4594 (10)	0.0553 (9)	3/4	0.023 (5)*
O8	0.4877 (6)	0.1226 (5)	3/4	0.023 (3)*
C9	0.5718 (10)	0.1245 (8)	3/4	0.022 (4)*
C10	0.4671 (6)	0.0580 (6)	0.6274 (5)	0.015 (3)*
C11	0.5337 (6)	0.0359 (5)	0.5934 (5)	0.017 (3)*
C12	0.5558 (7)	0.0659 (6)	0.5332 (6)	0.023 (3)*
C13	0.6302 (7)	0.0430 (5)	0.4995 (5)	0.026 (3)*
C14	0.5083 (7)	0.1161 (6)	0.5089 (6)	0.023 (3)*
C15	0.4410 (6)	0.1391 (5)	0.5406 (6)	0.018 (3)*
C16	0.4215 (7)	0.1108 (6)	0.6006 (6)	0.020 (3)*
O17	0.3569 (4)	0.1334 (4)	0.6356 (4)	0.023 (2)*
C18	0.2858 (7)	0.1013 (6)	0.6153 (6)	0.024 (3)*
C19	0.3898 (7)	0.1933 (6)	0.5109 (6)	0.022 (3)*
C20	0.3505 (6)	0.1806 (6)	0.4525 (6)	0.022 (3)*
C21	0.3024 (7)	0.2301 (5)	0.4239 (6)	0.022 (3)*
C22	0.2567 (8)	0.2156 (7)	0.3618 (7)	0.046 (4)*
C23	0.2987 (7)	0.2945 (6)	0.4537 (6)	0.025 (3)*
C24	0.3380 (7)	0.3070 (6)	0.5130 (6)	0.018 (3)*
C25	0.3835 (6)	0.2577 (7)	0.5405 (4)	0.018 (2)*
O26	0.4243 (4)	0.2704 (3)	0.5984 (4)	0.021 (2)*
C27	0.5013 (8)	0.2952 (6)	0.5863 (6)	0.036 (4)*
C28	0.3360 (7)	0.3794 (6)	0.5394 (6)	0.020 (3)*
C29	0.3632 (7)	0.4320 (6)	0.5010 (5)	0.023 (3)*
C30	0.3626 (7)	0.4980 (5)	0.5246 (5)	0.022 (3)*
C31	0.3957 (7)	0.5553 (6)	0.4823 (6)	0.037 (4)*
C32	0.3319 (7)	0.5104 (6)	0.5855 (6)	0.022 (3)*
C33	0.3031 (7)	0.4584 (6)	0.6254 (6)	0.020 (3)*
C34	0.3061 (7)	0.3914 (6)	0.6021 (6)	0.024 (3)*
O35	0.2750 (4)	0.3395 (4)	0.6416 (4)	0.022 (2)*
C36	0.2017 (7)	0.3134 (6)	0.6199 (6)	0.026 (3)*
C37	0.2684 (6)	0.4773 (5)	0.6905 (5)	0.015 (3)*
C38	0.2071 (7)	0.5245 (6)	0.6910 (6)	0.022 (3)*
C39	0.1746 (9)	0.5485 (8)	3/4	0.012 (4)*

C40	0.1088 (10)	0.5996 (8)	3/4	0.027 (5)*	C60	0.2894 (8)	0.3280 (6)	0.9799 (2)	0.072 (2)
C43	0.2981 (10)	0.4526 (9)	3/4	0.021 (5)*	C61	0.3981 (7)	0.3030 (5)	0.9369 (2)	0.056 (2)
O44	0.3615 (7)	0.4092 (5)	3/4	0.023 (3)*	C62	0.3895 (7)	0.1919 (5)	0.9233 (2)	0.055 (2)
C45	0.4362 (13)	0.4433 (11)	3/4	0.055 (7)*	O63	0.4918 (5)	0.1640 (3)	0.8798 (1)	0.061 (2)
C'†	0.2965 (14)	0.4709 (12)	1/4	0.020 (6)*	C64	0.6591 (8)	0.1269 (6)	0.8900 (3)	0.086 (3)
C1''‡	0.9044 (13)	0.8598 (11)	3/4	0.100 (8)*	O 23B‡	0.4052 (10)	0.3553 (11)	0.6397 (4)	0.056 (5)*
C1'''§	0.996 (2)	0.8086 (18)	0.6374 (15)	0.137 (14)*	C 24B‡	0.2545 (12)	0.422 (2)	0.6248 (10)	0.124 (12)*

* U_{iso} .

† Occupancy 0.70.

‡ Occupancy 0.35.

§ Occupancy 0.17.

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq}
C1	0.5194 (8)	0.3912 (5)	0.9049 (2)	0.058 (2)
C2	0.6543 (8)	0.4299 (5)	0.9268 (2)	0.068 (2)
C3	0.7730 (8)	0.5071 (5)	0.8955 (2)	0.071 (3)
C4	0.7597 (8)	0.5440 (5)	0.8415 (2)	0.067 (2)
C5	0.6235 (7)	0.5089 (5)	0.8184 (2)	0.053 (2)
C6	0.5021 (7)	0.4338 (5)	0.8504 (2)	0.053 (2)
O7	0.3683 (5)	0.3983 (3)	0.8278 (1)	0.061 (2)
C8	0.2179 (8)	0.4705 (6)	0.8314 (3)	0.092 (3)
C9	0.5992 (7)	0.5527 (5)	0.7605 (2)	0.050 (2)
C10	0.5163 (7)	0.6585 (5)	0.7453 (2)	0.057 (2)
C11	0.4840 (8)	0.7003 (5)	0.6926 (2)	0.065 (2)
C12	0.5363 (8)	0.6312 (5)	0.6548 (2)	0.065 (2)
C13	0.6197 (7)	0.5233 (5)	0.6682 (2)	0.053 (2)
C14	0.6546 (7)	0.4855 (5)	0.7212 (2)	0.055 (2)
O15	0.7492 (6)	0.3821 (4)	0.7350 (2)	0.081 (2)
C16	0.6561 (10)	0.2747 (6)	0.7460 (3)	0.101 (3)
C17	0.6713 (8)	0.4516 (5)	0.6254 (2)	0.056 (2)
C18	0.8378 (8)	0.4499 (5)	0.6025 (2)	0.065 (2)
C19	0.8806 (9)	0.3908 (6)	0.5600 (2)	0.078 (3)
C20	0.7576 (10)	0.3300 (5)	0.5422 (2)	0.076 (3)
C21	0.5944 (8)	0.3275 (5)	0.5649 (2)	0.057 (2)
C22	0.5493 (7)	0.3903 (5)	0.6059 (2)	0.065 (2)
O23A†	0.3760 (8)	0.4185 (6)	0.6173 (2)	0.079 (3)
C24A†	0.3027 (11)	0.3605 (10)	0.6686 (3)	0.114 (5)
C25	0.4628 (8)	0.2625 (5)	0.5455 (2)	0.064 (2)
C26	0.3856 (9)	0.3117 (6)	0.4994 (2)	0.075 (3)
C27	0.2607 (8)	0.2517 (6)	0.4832 (2)	0.072 (2)
C28	0.2029 (8)	0.1436 (5)	0.5128 (2)	0.066 (2)
C29	0.2769 (8)	0.0927 (5)	0.5594 (2)	0.058 (2)
C30	0.4099 (8)	0.1514 (5)	0.5739 (2)	0.060 (2)
O31	0.4894 (6)	0.1004 (4)	0.6181 (1)	0.071 (2)
C32	0.6119 (9)	0.0124 (6)	0.6073 (3)	0.090 (3)
C33	0.2066 (8)	-0.0209 (5)	0.5926 (2)	0.062 (2)
C34	0.2033 (8)	-0.1231 (5)	0.5719 (2)	0.074 (3)
C35	0.1321 (9)	-0.2249 (5)	0.6020 (2)	0.083 (3)
C36	0.0661 (8)	-0.2268 (5)	0.6545 (2)	0.074 (3)
C37	0.0720 (7)	-0.1261 (5)	0.6768 (2)	0.058 (2)
C38	0.1366 (7)	-0.0222 (5)	0.6453 (2)	0.058 (2)
O39	0.1342 (5)	0.0802 (3)	0.6662 (1)	0.062 (2)
C40	-0.0183 (10)	0.1446 (7)	0.6647 (3)	0.106 (3)
C41	0.0033 (8)	-0.1285 (4)	0.7341 (2)	0.054 (2)
C42	-0.1673 (9)	-0.1438 (5)	0.7498 (2)	0.072 (3)
C43	-0.2355 (8)	-0.1426 (5)	0.8024 (2)	0.073 (2)
C44	-0.1263 (8)	-0.1299 (5)	0.8396 (2)	0.061 (2)
C45	0.0462 (8)	-0.1188 (4)	0.8259 (2)	0.054 (2)
C46	0.1073 (7)	-0.1156 (5)	0.7726 (2)	0.049 (2)
O47	0.2800 (5)	-0.1092 (4)	0.7567 (1)	0.067 (2)
C48	0.3627 (8)	0.0000 (6)	0.7579 (2)	0.077 (3)
C49	0.1600 (7)	-0.1131 (5)	0.8680 (2)	0.051 (2)
C50	0.2721 (8)	-0.2076 (5)	0.8831 (2)	0.065 (2)
C51	0.3789 (8)	-0.2027 (5)	0.9225 (2)	0.075 (2)
C52	0.3743 (8)	-0.1031 (6)	0.9460 (2)	0.072 (3)
C53	0.2682 (7)	-0.0080 (5)	0.9311 (2)	0.052 (2)
C54	0.1576 (7)	-0.0149 (5)	0.8926 (2)	0.049 (2)
O55	0.0402 (5)	0.0740 (4)	0.8806 (2)	0.065 (2)
C56	0.0864 (9)	0.1699 (6)	0.8394 (3)	0.097 (3)
C57	0.2746 (7)	0.1063 (5)	0.9507 (2)	0.056 (2)
C58	0.1664 (7)	0.1351 (6)	0.9939 (2)	0.070 (2)
C59	0.1759 (9)	0.2449 (6)	1.0081 (2)	0.082 (3)

Table 5. Close intermolecular approaches (\AA , °)

It is an arbitrary coincidence of the numbering that it is C40 that 'contacts' other rings in both (Ia) and (Ib). The symmetry operations and the nature of the contacts are quite different, as is evident by comparing Figs. 3 and 5. In (Ia), C40ⁱ 'contacts' four symmetrically disposed O atoms; in (Ib), C40ⁱⁱⁱ 'contacts' only two O atoms, coming no closer than 4.45 Å to any other O atom. In (Ia), the entire CH₃ group at C40ⁱ is closer to the best plane through the eight O atoms of the neighboring macrocycle (C at 2.03 Å, H's at 1.6–1.8 Å) than any of the four methoxy C atoms directed downward (2.27–2.56 Å). In (Ib), H40Bⁱⁱⁱ is 2.3 Å from the best plane through the eight O atoms of the host, closer to that plane than two of the methoxy C atoms on the same side of the plane, but further away than the other two. H40Aⁱⁱⁱ and H40Cⁱⁱⁱ are further away than any methoxy C atom, as is C40ⁱⁱⁱ.

Distances involving H atoms are given only to the nearest 0.1 Å, because the H atoms were refined as parts of rigid groups, with the C—H distance fixed at 1.08 Å. The H positions are not precise. In (Ib), O73 is in the disordered ethanol molecule with highest occupancy (0.40); O79, C80 and C81 are in that with the lowest (0.25). The postulated position of C80 is clearly suspect, as is that of C81.

	Atom 1	Atom 2	Atom 3	2—3	1—3	1—2—3
(Ia)	C40 ⁱ	H40B ⁱ	O53	2.3	3.35	169
	C40 ⁱ	H40A ⁱ	O35	2.6	3.40	130
	C40 ⁱ	H40C ⁱ	O71	2.4	3.43	158
	C40 ⁱ	H40C ⁱ	O17	3.0	3.46	109
	C14	H73A ⁱⁱ			2.6	
	C12	H73A ⁱⁱ			2.8	
(Ib)	C40 ⁱⁱⁱ	H40B ⁱⁱⁱ	O8	2.3	3.27	142
	C40 ⁱⁱⁱ	H40A ⁱⁱⁱ	O62	2.8	3.32	110
	C40 ⁱⁱⁱ	H40C ⁱⁱⁱ	O62	3.0	3.32	100
	O71		O73 ^{iv}		2.94	
	O71		O79 ^{iv}		3.00	
	O71		C80 ^{iv}		2.59	
	C13		C81 ^v		2.89	
(II)	C64	H64A	O55 ^{vi}	2.6	3.05	102
	C10	H10	O47 ^{vii}	2.5	3.22	122
	C11	H11	O47 ^{vii}	2.6	3.24	119

Symmetry codes: (i) $5/2 - x, y - 1/2, 1/2 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x - 1/2, 1/2 - y, z - 1/2$; (iv) $1/2 + x, 1/2 - y, z - 1/2$; (v) $x, y, z - 1$; (vi) $1 + x, y, z$; (vii) $x, 1 + y, z$.

Table 6. Cs⁺—O contacts in (Ic) (\AA)

O49 and O50ⁱⁱ are in different ClO₄⁻; O49 is 3.27 Å below the best plane through the eight O atoms of the host, and O50ⁱⁱ is 3.25 Å above that plane. Each of these O atoms lies nearly on the normal to this plane passing through the Cs⁺.

There are no uncommonly short intermolecular or interionic distances in this structure.

Cs46	O44	3.16 (1)	Cs46	O17	3.26 (1)
	O8	3.20 (1)		O17 ⁱ	3.26 (1)
	O49	3.20 (1)		O35	3.27 (1)
	O26	3.26 (1)		O35 ⁱ	3.27 (1)
	O26 ⁱ	3.26 (1)		O50 ⁱⁱ	3.33 (1)

Symmetry codes: (i) $x, y, 3/2 - z$; (ii) $1/2 + x, 1/2 - y, 3/2 - z$.

Table 7. Comparison of geometrical features

The capitalized name given in the second line of the table is the CSD REFCODE (Allen *et al.*, 1991). Distances are in Å, angles in °. Corrections for molecular motion have been applied only to O—CH₃ (second line).

	(Ia) FUDSIG	(Ib) FUDSOM	(Ic) FUDSUS	(II) FUDSEC	Average for (Ia), (Ib), (Ic) and (II)	Average for (III) and its complexes ^a	Average for (IV), bridged spherands ^b
Average aromatic ring-fold angle, about C···C—O line	1	3	1	2	2	5	10
Average absolute deviation of ring C from aromatic plane	0.007	0.012	0.008	0.010	0.009	0.024	0.043
Average absolute deviation of O from attached aromatic plane	0.08	0.12	0.04	0.07	0.07	0.13	0.33
Average absolute deviation of attached aryl C from aromatic ring plane	0.06	0.10	0.07	0.07	0.08	0.16	0.36
Average interplanar angle between adjacent aromatic rings	78	73	65	82	75	56	48
Average inter-ring C—C bond distance	1.494	1.494	1.494	1.508	1.497	1.497	1.492, 1.519 ^d
Average aromatic C—C bond distance	1.391	1.399	1.395	1.387	1.393	1.393	1.396, 1.408 ^e
Average O—CH ₃ bond distance corrected for motion	1.428 1.436	1.432 1.440	1.432	1.419 1.435	1.437	1.453	1.446
Average C _{arom} —O bond distance	1.382	1.388	1.396	1.380	1.383 ^f (1.396)	1.378 ^f (1.392)	1.376 ^f (1.394)
Average C _{arom} —CH ₃ bond distance	1.510	1.516	1.511		1.512	1.513	1.512
Shortest O···O distance	2.94	2.82	2.99	2.94		2.79	2.51
Ellipticity ^c	1.32	1.28	1.06	1.25			

Notes: (a) Trueblood, Maverick & Knobler (1991). (b) Knobler, Maverick & Trueblood (1992). (c) Ellipticity is defined here as the ratio of the average of the two largest intramolecular next-nearest O···O distances to the average of the two smallest such distances in each macrocycle. A circle would have 'ellipticity' = 1.00. (d) The two values given for the bridged spherands correspond to the average C—C distances between rings on the same side of a bridge (four values) and between bridges (two values), respectively. It is not surprising that the latter distance is significantly larger. (e) The two values given for the bridged spherands correspond to the average aromatic C—C distance not involving a bridgehead atom (28 values) and that involving bridgehead atoms (eight values), respectively. The difference is on the margin of significance. (f) The average C_{arom}—O distances are significantly larger in cationic complexes. The first value given is the average for uncomplexed hosts; the value below it, in parentheses, is the average for the cationic complexes. A similar but smaller effect is observed for O—CH₃ distances; because of the uncertainty of motional corrections, its significance is more questionable.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, and information from analysis of atomic and molecular motion have been deposited with the IUCr (Reference: FG1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Syn and Anti Isomers of [2.2]Paracyclonaphthane

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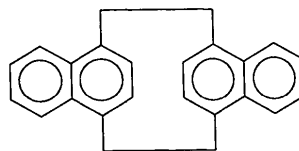
Abstract

The structures of the *anti* (1) and *syn* (2) isomers of [2.2]paracyclonaphthane, C₂₄H₂₀, can be understood in terms of molecules composed of four segments, two naphthalene rings and two ethylene groups bridging the naphthalene rings. Distortions from ideal geometries are described and attributed primarily to intramolecular effects. Several observations have been made: the bridged portion of the naphthalene ring is deformed into a boat shape in both (1) and (2); much of the π - π repulsion is taken up by bending angles α and β ; the naphthalene rings are parallel to each other in (1), but are non-parallel in (2); one naphthalene ring in (2) is twisted relative to the other, indicating a mode of strain reduction which is unique to this molecule, and the C—C distances and valency angles in the ethylene bridges are larger than normal values.

Comment

The structural features of the paracyclophanes, a class of molecules which can accommodate strain through intramolecular distortions, have been summarized by Mak (1992) and Keehn (1983). In the area of new synthetic procedures, Loy & Assink (1992) recently reported the use of paracyclophanes in copolymerization reactions with C₆₀. This work, which involves the X-

ray structure determination of the *anti* (1) and *syn* (2) isomers of [2.2]paracyclonaphthane, extends the study of the effects of transannular π - π interactions on molecular conformations to bridged naphthalenoid systems.



[2.2] Paracyclonaphthane

In the *anti* isomer, (1), the packing is determined by C···H and H···H interactions [2.87 (2) and 2.26 (3) Å, respectively]. The shortest C···C distance is 3.693 (3) Å. Since the intermolecular distances fall within the normal van der Waals range, distortions in the molecular geometry are attributed primarily to intramolecular interactions.

The asymmetric unit comprises two half molecules, designated A and B, each of which sits on a center of inversion. The averaging of bond distances in the molecule (Fig. 1) was carried out by superimposing the two halves, reasoning that one half was identical to the other. The average aromatic bond distance is 1.396 Å, which is equivalent to that found in benzene, 1.397 Å. The length of the bridging bond is 1.574 (3) Å in molecule A and 1.568 (4) Å in molecule B. This lengthening of the ethylene bridge is consistent with observations found in other [2.2]paracyclophanes (Mak, 1992).

A striking structural feature is the deformation of the bridged ring of the naphthalenoid system into a boat shape. C1A and C4A are 0.156 (2) and 0.158 (2) Å,

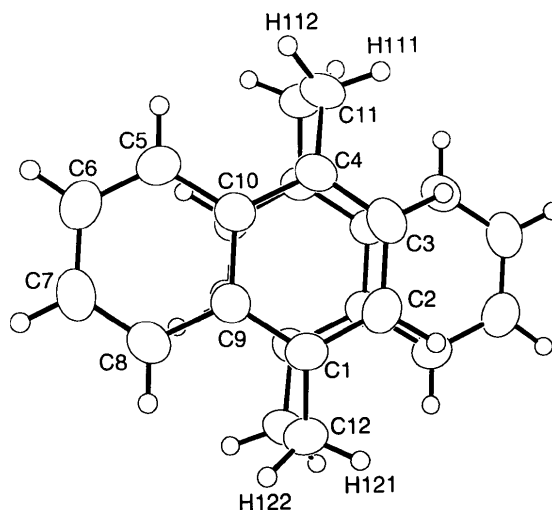


Fig. 1. ORTEP (Johnson, 1976) view of (1) with displacement ellipsoids at the 50% probability level. H atoms are numbered according to the attached C atom, except where indicated. A unit-cell diagram has been deposited with the supplementary material.