

A Hemispherand Containing Cyclic Urea and Anisyl Units and its 1:1 $(\text{CH}_3)_3\text{CNH}_3^+$ Complex

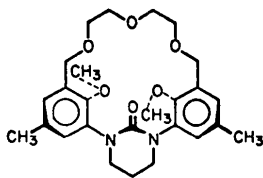
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(Received 25 April 1985; accepted 3 October 1985)

Abstract. 26,27-Dimethoxy-4,18-dimethyl-8,11,14-trioxo-1,21-diazatetracyclo[19.3.1.1^{2,6}.1^{16,20}]heptacos-2,4,6(26),16,18,20(27)-hexaen-25-one, $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_6$, (1), $M_r = 470.57$, orthorhombic, $P2_12_12_1$, $a = 10.124$ (4), $b = 11.964$ (4), $c = 21.317$ (5) Å, $V = 2582$ (2) Å³, $Z = 4$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.80$ cm⁻¹, $F(000) = 1008.4$, $T = 295$ K, $R = 0.106$ for 1956 observed reflections. The complex of (1) with $(\text{CH}_3)_3\text{CNH}_3^+\text{ClO}_4^-$, $\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_6 \cdot \text{C}_4\text{H}_{12}\text{N}^+\text{ClO}_4^-$, (2), $M_r = 644.16$, orthorhombic, $Fdd2$, $a = 46.037$ (9), $b = 25.930$ (4), $c = 10.900$ (2) Å, $V = 13012$ (2) Å³, $Z = 16$, $D_x = 1.32$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 14.4$ cm⁻¹, $F(000) = 5526.6$, $T = 115$ K, $R = 0.060$ for 2277 observed reflections. In the free host (1), the three O atoms of the $\text{O}(\text{CH}_2\text{CH}_2\text{O})_2$ bridge are turned outward, with some $-\text{CH}_2-$ groups turned inward. The host in (2) has been reorganized by the perching interaction of the *tert*-butylammonium ion; all the O atoms of the bridge now turn inward, two of them being hydrogen-bonded to the cation, which is also hydrogen-bonded to the urea O atom of the host.

Introduction. Hemispherands are hosts for which at least half of the cavity is organized for complexation during synthesis rather than during binding (Cram & Trueblood, 1981). This hemispherand, containing one urea unit and two anisyl units (shown below) is a much better binder of *tert*-butylammonium ion but a somewhat poorer binder for alkali metal ions and NH_4^+ than is the similar hemispherand that contains three anisyl units (Cram, Dicker, Lein, Knobler & Trueblood, 1982).



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Experimental. Host (1) and its complex with $(\text{CH}_3)_3\text{CNH}_3^+\text{ClO}_4^-$ (2) were prepared as described (Cram *et al.*, 1982) and recrystallized from ethanol and ethyl acetate respectively. For (1), Weissenberg photographs show systematic absences $h = 2n + 1$ for $h00$ reflections, $k = 2n + 1$ for $0k0$ reflections, and $l = 2n + 1$ for $00l$ reflections. Systematic absences for (2) were (hkl) $h + k = 2n + 1$, $k + l = 2n + 1$, $(0kl)$ $k + l \neq 4n$, $(h0l)$ $l + h \neq 4n$. A colorless platelet of (1), $0.4 \times 0.5 \times 0.1$ mm, on a Syntex $P\bar{1}$ diffractometer, graphite monochromator, at 295 K; orientation matrix and unit-cell dimensions by least-squares refinement of 15 reflections ($11 \leq 2\theta \leq 21^\circ$), θ - 2θ scan, $3.0^\circ \text{ min}^{-1}$ in 2θ , from 1.25° below $K\alpha_1$ to 1.25° above $K\alpha_2$; intensities measured for $2\theta < 50^\circ$ for the range $h = 0$ to 12, $k = 0$ to 14, $l = 0$ to 25; intensities of three standard reflections monitored every 97 reflections with 3% maximum intensity variation from average and no significant change during data collection; total of 2603 independent reflections, 1956 with $I > \sigma(I)$ used in structure solution and refinement; absorption corrections were not made ($\mu = 0.80 \text{ cm}^{-1}$); no correction for extinction; 22 atoms found by direct methods, remaining atoms (including most H atoms) located on Fourier and difference Fourier maps.

A colorless crystal of (2), $0.2 \times 0.2 \times 0.3$ mm, data collected in space group Cc , and later transformed to $Fdd2$, on a Syntex $P\bar{1}$ diffractometer, graphite monochromator, at 115 K (Strouse, 1976); orientation matrix and unit-cell dimensions by least-squares refinement of 15 reflections ($60 \leq 2\theta \leq 85^\circ$), θ - 2θ scan and, for $2\theta > 98.5^\circ$, parallel mode, $4.0^\circ \text{ min}^{-1}$ in 2θ , from 1° below $K\alpha_1$ to 1° above $K\alpha_2$; intensities measured for $2\theta < 150^\circ$ for the range $h = 0$ to 10, $k = 0$ to 32, $l = -29$ to 28; intensities of three standard reflections monitored every 97 reflections with 3% maximum intensity variation from average and no significant change during data collection; total of 5195 reflections measured, after transformation 2317 unique reflections with $I > 0$ (for merged reflections, $R_{\text{int}} = 0.08$, $R_{\text{int}} = \{\sum(N\sum\{w[F(\text{mean}) - F]^2\}) / \sum[(N-1)\sum(wF^2)]\}^{1/2}$, where inner summations are over the N equivalent reflections ($\pm hkl$) averaged to give $F(\text{mean})$, and the outer

summations are over all unique reflections), 2277 with $I > \sigma(I)$ used in structure solution and refinement; absorption corrections were not made ($\mu = 14.4 \text{ cm}^{-1}$); no correction for extinction; six atoms found by direct methods, remaining atoms (including most H atoms) located on Fourier and difference Fourier maps.

Except for those on N(39), all H atoms were kept in geometrically reasonable positions with C–H = 1.08 Å (and for the methyl groups, H–C–H = 109.5°, CH₃ group as rigid group) and with fixed displacement* parameters. Positions of H(39A), (B) and (C), the H atoms of the –NH₃⁺ group involved in host–guest complexation, were allowed to vary. In order to keep the ratio of F data to parameters above about eight, fewer than half of the non-H atoms in each structure were refined anisotropically; among the atoms refined were those in the conformationally flexible portion of the polyether chain.† For (1) the anisotropic atoms were the N and O atoms of the urea fragment, the C and O atoms of the three methoxy groups and the atoms of the –OCCOCCO– chain. For (2) the atoms refined anisotropically were N(39), the nine atoms of the –(COC)₃– chain and the five atoms of the ClO₄[–] ion. For the H atoms, displacement parameters were fixed at values based on those for the attached C or N. Refined by least squares on F ; for (1), refinement of 217 parameters converged to $R = 0.106$, $wR = 0.104$, $w = 1/\sigma^2(F_o)$, $S = 2.36$; ratio in final cycle of maximum least-squares shift to e.s.d. was 0.14 in a displacement parameter and 0.13 in a position parameter; maximum and minimum heights of 0.3 and $-0.5 \text{ e } \text{Å}^{-3}$ in the final difference Fourier synthesis. Although the final difference map is relatively featureless, there is probably disorder in the polyether chain, especially in the region of C(29) (note distances, angles, and displacement parameters involving this atom and its neighbors).

For (2), refinement of 260 parameters converged to $R = 0.060$, $wR = 0.071$, $w = 1/\sigma^2(F_o)$, $S = 2.96$; ratio in final cycle of maximum least-squares shift to e.s.d. was 0.24 for an H parameter, 0.10 for a displacement parameter, and 0.05 for a non-H position; maximum and minimum heights of 0.4 and $-0.3 \text{ e } \text{Å}^{-3}$ in the final difference Fourier synthesis.‡ Displacement parameters of the polyether fragment are somewhat higher than those of the remaining atoms of the host, although distinctly lower than those for the corresponding atoms in (1). Even in the complexed host, the polyether fragment is the least rigid part of the molecule.

* Commonly called 'vibration parameters' or 'temperature-factor parameters'.

† When all non-H atoms were allowed to refine anisotropically no problems arose; for 1956 reflections and 319 parameters, $R = 0.098$, $wR = 0.095$.

‡ When all non-H atoms, with the exception of 12 C of the two phenyl rings, were refined anisotropically no problems arose; for 2277 reflections and 359 parameters, $R = 0.052$, $wR = 0.060$, $S = 2.58$.

Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All 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*, *ORFLS*, *ORFFE*, *ABSORB*, *ORTEP* and *SHELX*, and local molecular-geometry and thermal-motion programs, *MG84* and *THMV9*) and *PLUTO78* (Motherwell & Clegg, 1978).

Discussion. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1; representative bond lengths and angles and torsion angles are given in Table 2.* Hemispherands have binding powers superior to those of corresponding crown ether hosts, apparently because in the hemispherands at least three adjacent binding sites are already organized for complexation. In both the host (Fig. 1) and its complex (Fig. 2), the two anisyl O atoms lie on the side of the macroring opposite to that of the urea O, which is also the side opposite to the guest in (2). In the free host, the other three O atoms are turned away from the cavity and H atoms of some methylene groups turn inward. In the complex, these O atoms are turned toward the cavity and none of the H atoms of methylene groups turn inward. The O–CH₂–CH₂–O dihedral angles for (1) are 173 (1) and 168.1 (9)°. Comparable angles for (2) are 68.6 (8) and 65.0 (9)°. Some geometrical features are compared in Table 2.

In complex (2), three of the six O atoms are involved in hydrogen bonding to the *tert*-butylammonium guest. The shortest N···O host–guest distance is from the N of the cation to the O atom of the urea group, N(39)···O(16) = 2.657 (7) Å. The distance from O(16) to H(39B) is 1.69 (7) Å, considerably shorter than the mean O···H distance of an NH···O=C bond for an RNH₃⁺···amide interaction [1.89 (3) Å (Taylor & Kennard, 1984)]. Distances from N(39) to the other O atoms involved in hydrogen bonding, two of the O atoms of the polyether chain, are 3.041 (8) and 3.002 (9) Å. Although the central O atom of this chain is closer to N(39) [O(30)···N(39) = 2.90 Å], it is not well situated for hydrogen bonding, nor are the methoxy O atoms O(8) and O(24), with distances to N(39) of 3.458 (8) and 3.014 (7) Å respectively. Presumably, however, these contacts contribute to the binding energy of the complex, involving a nonbonding electron pair on the ether O atom through direct

* Lists of anisotropic displacement parameters, bond distances, bond angles and torsion angles, H-atom parameters, observed and calculated structure factors and least-squares-planes parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42556 (33 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

	x	y	z	$\langle u^2 \rangle (\text{Å}^2)$
(a) Uncomplexed host (1)				
C(4)	0.2785 (11)	0.4162 (9)	0.2217 (4)	0.088
O(8)	0.2571 (8)	-0.0223 (6)	0.1199 (3)	0.082
C(9)	0.3769 (12)	-0.0813 (10)	0.1054 (5)	0.095
N(10)	0.4231 (6)	0.1462 (6)	0.0604 (3)	0.051
N(4)	0.4246 (7)	0.1208 (6)	-0.0486 (3)	0.049
O(16)	0.2327 (5)	0.1144 (5)	0.0064 (2)	0.056
C(20)	0.2191 (12)	0.2666 (9)	-0.2433 (5)	0.095
O(24)	0.3117 (7)	-0.0894 (5)	-0.0729 (3)	0.073
C(25)	0.4377 (14)	-0.1411 (9)	-0.0822 (5)	0.099
O(27)	-0.0110 (7)	-0.1108 (6)	-0.1369 (3)	0.087
C(28)	-0.0004 (12)	-0.1221 (12)	-0.0691 (5)	0.106
C(29)	-0.1026 (21)	-0.0752 (16)	-0.0389 (5)	0.205
O(30)	-0.1134 (9)	-0.0903 (8)	0.0253 (3)	0.113
C(31)	-0.0548 (12)	-0.0071 (10)	0.0634 (5)	0.088
C(32)	-0.0764 (13)	-0.0410 (10)	0.1291 (5)	0.102
O(33)	-0.0466 (6)	0.0448 (6)	0.1734 (3)	0.076
C(1)	0.1723 (9)	0.1181 (8)	0.1884 (4)	0.057 (2)*
C(2)	0.1788 (9)	0.2244 (8)	0.2126 (4)	0.064 (3)*
C(3)	0.2704 (8)	0.3017 (7)	0.1937 (4)	0.053 (2)*
C(5)	0.3518 (8)	0.2718 (7)	0.1440 (4)	0.052 (2)*
C(6)	0.3466 (8)	0.1690 (7)	0.1160 (3)	0.045 (2)*
C(7)	0.2623 (9)	0.0881 (8)	0.1410 (4)	0.055 (2)*
C(11)	0.5651 (9)	0.1792 (8)	0.0610 (4)	0.063 (3)*
C(12)	0.6329 (9)	0.1254 (8)	0.0054 (4)	0.062 (2)*
C(13)	0.5631 (9)	0.1537 (8)	-0.0540 (4)	0.061 (3)*
C(15)	0.3519 (8)	0.1268 (7)	0.0064 (4)	0.043 (2)*
C(17)	0.3467 (8)	0.1017 (7)	-0.1040 (4)	0.052 (2)*
C(18)	0.3256 (8)	0.1877 (7)	-0.1476 (4)	0.052 (2)*
C(19)	0.2418 (8)	0.1733 (8)	-0.1977 (4)	0.057 (2)*
C(21)	0.1723 (9)	0.0743 (8)	-0.2017 (4)	0.064 (3)*
C(22)	0.1946 (9)	-0.0144 (8)	-0.1607 (4)	0.058 (2)*
C(23)	0.2856 (8)	-0.0025 (8)	-0.1132 (4)	0.054 (2)*
C(26)	0.1121 (10)	-0.1218 (9)	-0.1677 (4)	0.074 (3)*
C(34)	0.0702 (10)	0.0353 (9)	0.2090 (4)	0.074 (3)*
(b) Complex (2)				
C(26)	0.0478 (1)	0.1073 (2)	-0.8353 (7)	0.041
O(27)	0.0706 (1)	0.0753 (1)	-0.7860 (5)	0.047
C(28)	0.0666 (2)	0.0220 (2)	-0.8171 (8)	0.064
C(29)	0.0521 (2)	-0.0069 (3)	-0.7211 (8)	0.062
O(30)	0.0698 (1)	-0.0125 (2)	-0.6146 (5)	0.056
C(31)	0.0586 (2)	-0.0427 (3)	-0.5193 (8)	0.065
C(32)	0.0789 (2)	-0.0511 (3)	-0.4200 (9)	0.076
O(33)	0.0867 (1)	-0.0048 (2)	-0.3547 (6)	0.066
C(34)	0.0736 (2)	0.0004 (2)	-0.2359 (8)	0.055
N(39)	0.0976 (1)	0.0822 (2)	-0.5360 (7)	0.038
Cl(81)	0.52986 (4)	0.39541 (5)	0.	0.050
O(82)	0.5230 (1)	0.4487 (2)	0.0016 (6)	0.076
O(83)	0.5513 (1)	0.3865 (2)	-0.0885 (7)	0.093
O(84)	0.5400 (1)	0.3788 (2)	0.1207 (6)	0.077
O(85)	0.5047 (1)	0.3661 (2)	-0.0295 (6)	0.064
C(1)	0.0785 (1)	0.0544 (3)	-0.1927 (7)	0.046 (2)*
C(2)	0.0991 (1)	0.0658 (3)	-0.1030 (7)	0.048 (2)*
C(3)	0.1054 (1)	0.1154 (3)	-0.0672 (7)	0.046 (2)*
C(4)	0.1259 (2)	0.1277 (3)	0.0376 (9)	0.064 (2)*
C(5)	0.0903 (1)	0.1560 (2)	-0.1248 (7)	0.040 (2)*
C(6)	0.0694 (1)	0.1463 (2)	-0.2120 (6)	0.037 (1)*
C(7)	0.0622 (1)	0.0951 (2)	-0.2400 (7)	0.039 (1)*
O(8)	0.0411 (1)	0.0852 (2)	-0.3274 (5)	0.051 (1)*
C(9)	0.0142 (2)	0.0699 (3)	-0.2721 (8)	0.060 (2)*
N(10)	0.0544 (1)	0.1873 (2)	-0.2731 (5)	0.035 (1)*
C(11)	0.0289 (1)	0.2113 (2)	-0.2175 (7)	0.040 (1)*
C(12)	0.0214 (1)	0.2601 (2)	-0.2878 (8)	0.036 (1)*
C(13)	0.0172 (1)	0.2476 (2)	-0.4217 (7)	0.039 (2)*
N(14)	0.0434 (1)	0.2205 (2)	-0.4679 (5)	0.031 (1)*
C(15)	0.0611 (1)	0.1922 (2)	-0.3943 (6)	0.028 (1)*
O(16)	0.0839 (1)	0.1723 (1)	-0.4357 (4)	0.029 (1)*
C(17)	0.0474 (1)	0.2161 (2)	-0.5999 (6)	0.033 (1)*
C(18)	0.0538 (1)	0.2580 (2)	-0.6696 (6)	0.033 (1)*
C(19)	0.0576 (1)	0.2530 (2)	-0.7970 (6)	0.036 (1)*
C(20)	0.0639 (2)	0.2994 (3)	-0.8753 (7)	0.049 (2)*
C(21)	0.0562 (1)	0.2036 (2)	-0.8473 (7)	0.035 (1)*
C(22)	0.0500 (1)	0.1606 (2)	-0.7789 (6)	0.034 (1)*
C(23)	0.0448 (1)	0.1672 (2)	-0.6519 (6)	0.032 (1)*
O(24)	0.0377 (1)	0.1246 (2)	-0.5830 (4)	0.038 (1)*
C(25)	0.0070 (2)	0.1143 (3)	-0.5753 (8)	0.052 (2)*
C(35)	0.1298 (1)	0.0899 (2)	-0.5561 (7)	0.040 (2)*
C(36)	0.1438 (2)	0.0877 (3)	-0.4287 (8)	0.060 (2)*
C(37)	0.1339 (2)	0.1423 (3)	-0.6158 (7)	0.050 (2)*
C(38)	0.1408 (2)	0.0466 (3)	-0.6383 (8)	0.056 (2)*

Units of each e.s.d., in parentheses are those of the least-significant digit of the corresponding parameter.

* Atom refined isotropically. Other isotropic values are $1/8\pi^2 \times$ 'equivalent B value' defined by Hamilton (1959).

pole-dipole interactions with the positive charge of the guest ion (Timko, Moore, Walba, Hiberty & Cram, 1977; Goldberg, 1980).

Table 2. Some features of the molecular geometry

A complete list of bond distances, bond angles and torsion angles has been deposited.

	Average value	Range of values	Typical e.s.d. of an individual value
(a) Bond distances			
C—O (urea)	(1) 1.22 (1) Å		
	(2) 1.253 (7)		
C _{arom} —O	(1) 1.38	1.37–1.39 Å	0.01 Å
	(2) 1.380	1.374–1.385	0.008
O—CH ₃	(1) 1.43	1.43–1.44	0.01
	(2) 1.437	1.433–1.441	0.009
C _{arom} —C _{arom}	(1) 1.38	1.37–1.41	0.01
	(2) 1.394	1.372–1.415	0.009
C _{arom} —N	(1) 1.44	1.43–1.44	0.01
	(2) 1.444	1.433–1.455	0.009
C _{arom} —C _{CH₃}	(1) 1.52	1.50–1.54	0.01
	(2) 1.505	1.495–1.515	0.009
N—C _{CH₃}	(1) 1.48	1.46–1.49	0.01
	(2) 1.472	1.460–1.483	0.008
N—C _{C=O}	(1) 1.38	1.37–1.38	0.01
	(2) 1.360	1.357–1.362	0.008
C _{CH₃} —C _{CH₃} (urea)	(1) 1.50	1.49–1.51	0.01
	(2) 1.514	1.508–1.520	0.007
C _{CH₃} —C _{CH₃} (ether)	(1) 1.40	1.34–1.47	0.02
	(2) 1.45	1.45–1.45	0.01
C _{CH₃} —O	(1) 1.41	1.38–1.45	0.01
	(2) 1.430	1.399–1.441	0.009
N(39)—H	(2) 0.98	0.89–1.06	0.07
H(39B)···O(16)	(2) 1.69 (7)		
H(39A)···O(27)	(2) 2.12 (8)		
H(39C)···O(33)	(2) 2.08 (7)		
N···O(84)	(2) 5.41	closest ClO ₄ ⁻ O to N(39)	
(b) Bond angles			
C—O—C _{CH₃}	(1) 117.3°	114.5–120.1°	0.8°
	(2) 113.0	111.7–114.4	0.5
CH ₂ —CH ₂ —O	(1) 113	107–119	1
	(2) 113.1	112.1–113.9	0.7
CH ₂ —O—CH ₂	(1) 115.6	112.6–118.3	0.8
	(2) 114.5	111.9–116.8	0.6
CH ₂ —CH ₂ —CH ₂	(1) 110.5 (7)		
	(2) 109.8 (5)		
CH ₂ —CH ₂ —N	(1) 108.9	108.6–109.2	0.7
	(2) 109.1	109.1–109.1	0.5
C _{arom} —N—CH ₂	(1) 119.0	117.5–120.4	0.6
	(2) 119.6	118.4–120.7	0.5
C _{arom} —N—C	(1) 114.9	114.0–115.7	0.6
	(2) 116.0	114.2–117.7	0.5
N—C—N	(1) 115.7 (7)		
	(2) 119.2 (5)		
N—C=O	(1) 122.2	121.5–122.8	0.7
	(2) 120.4	120.0–120.8	0.5
C—C—CH ₃	(1) 121.2	120.2–122.6	0.8
	(2) 121.0	119.0–122.8	0.7
CH ₃ —C—N (guest)	(2) 107.3	106.1–108.3	0.5
O(16)···H(39B)—N(39)	150 (6)	C(29)—O(30)···N(39)	114.0 (4)
O(27)···H(39A)—N(39)	171 (7)	C(31)—O(30)···N(39)	114.7 (4)
O(33)···H(39C)—N(39)	161 (6)		
(c) Torsion angles and dihedral angles			
	(1)	(2)	
O(27)—C(28)—C(29)—O(30)	173 (1)°	-68.6 (8)°	
O(30)—C(31)—C(32)—O(33)	-168.1 (9)	65.0 (9)	
Angles between normals to least-squares planes*			
	(1)	(2)	(1)
A—B	103°	123°	61°
A—C	49	44	110
B—C	110	102	13
			125

* Plane A is that of the atoms of one aromatic ring: C(1),C(2),C(3),C(5),C(6),C(7). Plane B involves the other aromatic ring of the hemispherand and includes C(17),C(18),C(19),C(21),C(22),C(23). Plane C is the least-squares plane defined by the six O atoms. Plane D is defined by N₂C=O of the urea cycle.

In (1) the C(15)—O(16) distance is 1.216 (10) Å and the N(10)—C(15) and N(14)—C(15) distances are 1.37 (1) and 1.38 (1) Å. In (2), the comparable distances are 1.253 (7), 1.362 (9) and 1.357 (8) Å. The longer C—O and shorter N—C distances in the complex could result from a greater contribution of the resonance form $>N^+=C-O^-$ (at the expense of $>N-C=O$) than in the uncomplexed host, although the differences here are scarcely significant. Angles around C(15) in the complex are nearly equal, N—C—O 120.0 (5) and 120.8 (5), N—C—N 119.2 (5)°. Much greater differences are found in the free host, N—C—O 122.8 (8) and 121.5 (7), N—C—N 115.7 (7)°. There is a small difference in the conformation of the urea cycle, which has the form of an 'envelope' in the complex, with atoms C(11), N(10), C(15), N(14) and C(13) coplanar [the greatest deviation from the least-squares plane through these atoms is 0.010 (6) Å]. O(16) lies only 0.066 (4) Å from this plane, while C(12), the urea-cycle atom most distant from O(16), is displaced 0.67 Å from the plane in a direction away from the center of the macrocycle. The conformation of the urea cycle in the uncomplexed host is similar at the C(12) end although the fold is in the opposite sense relative to the remainder of the macrocycle (*cf.* Figs. 1 and 2); furthermore, the ring has a small amount of 'chair' character, with C(15) being displaced 0.12 Å to one side and C(12) 0.66 Å to the opposite side of the plane through the other four ring atoms. We can compare angles between normals to planes through C(11), C(12), C(13) (*A*); N(10), C(11), C(13), N(14) (*B*); and

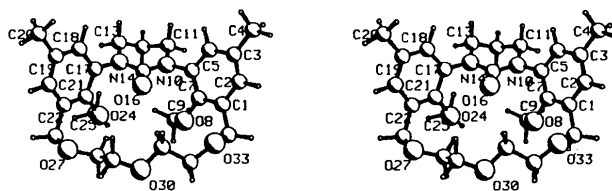


Fig. 1. Stereoview of the uncomplexed host (1), showing the numbering scheme.

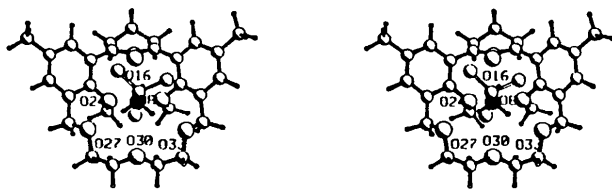


Fig. 2. Stereoview of the complex (2). The host is numbered as in Fig. 1; the bonds in the host are solid, those in the guest not. A few atom numbers are shown for reference. The N atom of the *tert*-butylammonium cation has been darkened; methyl H atoms have been omitted. The perchlorate ion is not included.

N(10), C(15), N(14) (*C*). For *A*—*B* these are 50.9 and 50.7° and for *B*—*C* these are 9.3 and 0.8° for (1) and (2), respectively. This conformational difference is apparent when Figs. 1 and 2 are compared.

The dihedral angles between the planes of the C—O—CH₃ groups and their attached aromatic rings average 85° in the complexed host and only 57° in the uncomplexed host. This kind of difference between hosts and their complexes has been noted before (Cram & Trueblood, 1981); in model uncrowded acyclic compounds, these angles are close to 0° (Trueblood & Maverick, 1986).

The 'perching' nature of the interaction of the guest with the host in (2) can be seen in Fig. 2. The C—NH₃⁺ line in the guest is nearly normal to the best plane through the O atoms of the host, making an angle of only 8° with the normal to that plane, an arrangement characteristic of such perching interactions (Cram & Trueblood, 1981). The strength of host—guest interaction in this complex, manifested particularly by the short N...O interaction involving the highly electronegative urea O atom, is consistent with the fact that the present hemispherand host binds perching guests more strongly than does its tris(anisyl) analog.

Because only a fraction of the atoms were refined anisotropically, it was not possible to carry out thermal-motion analysis on the host or on the guest cation. However, the ClO₄⁻ ion was refined anisotropically, and the displacement parameters of the O atoms were unusually high for such atoms at 115 K, as is evident by inspection of the equivalent isotropic values in Table 1(*b*). Although the bond angles for this ion were quite normal, ranging from 107.8 (6) to 110.4 (6)°, the distances were clearly foreshortened, averaging only 1.425 Å as compared to an expected value of about 1.45 Å. After correction for apparent rigid-body motion (the maximum apparent r.m.s. amplitude of libration was 11.4°), the distances averaged 1.458 Å.

There are no unusual intermolecular distances; the shortest intermolecular distance not involving H is 3.28 Å, from C(12) to O(16)($\frac{1}{2} + x, \frac{1}{2} - y, -z$) for (1), and 3.24 Å, from C(9) to O(85) (a perchlorate O at $\frac{1}{2} - x, \frac{1}{2} - y, z$) for (2). The shortest distance between N⁺ and an O atom of the ClO₄⁻ anion is 5.41 Å, to O(84).

This work was supported in part by a grant from the National Science Foundation (CHE82-05803).

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9,10-Anthracenedicarbaldehyde Bis[(4,5-dihydro-1H-imidazol-2-yl)hydrazone] Acetic Acid Hydrochloric Acid Trihydrate Salt (Bisantrene)

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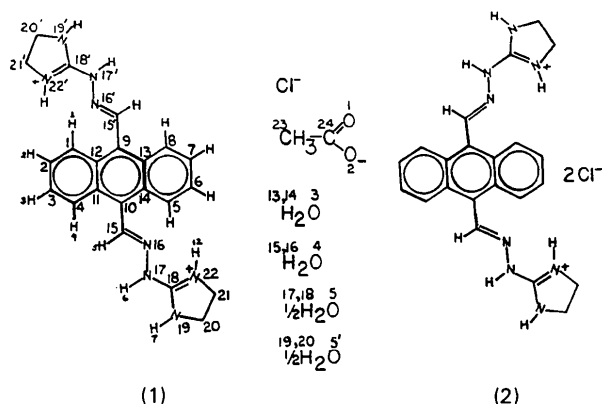
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(Received 28 June 1985; accepted 4 September 1985)

Abstract. C₂₂H₂₄N₈²⁺·C₂H₃O₂⁻·Cl⁻·3H₂O, *M_r* = 549.0, triclinic, *P*1̄, *a* = 8.022 (2), *b* = 14.175 (5), *c* = 14.307 (5) Å, α = 109.70 (3), β = 103.70 (2), γ = 106.25 (2)°, *U* = 1368.1 Å³, *Z* = 2, *D_m* = 1.33, *D_x* = 1.33 g cm⁻³, Mo *K*α, λ = 0.7173 Å, μ = 1.84 cm⁻¹, *F*(000) = 580, *T* = 293 K, final *R* = 0.060 for 2245 observed reflections. The unit cell of the antitumor agent bisantrene contains two independent molecules, each with a center of symmetry and *trans*-arranged side chains. In one molecule all non-H atoms are approximately coplanar (one π system for the dication) whereas in the other there is a significant bend (43°) about the first single bond in the side chains, which effectively separates three π systems. All of the rings are involved in stacking of the π systems along the *a* axis.

Introduction. Although the antitumor agent bisantrene [also called 'orange crush', (1) (Murdock *et al.*, 1982; Feigon, Denny, Leupin & Kearns, 1984) is now used commercially, its mechanism of action is not known. Surprisingly, no X-ray structure has been reported as yet for it, probably because the dihydrochloride (the usual form of the drug) does not form suitably large crystals. It has been proposed that it intercalates into DNA, preferring AT base pairs (Feigon *et al.*, 1984). When excellent orange crystals were found to grow from a solution of bisantrene dihydrochloride buffered with calcium acetate, we decided to carry out an X-ray study on them.

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Experimental. Orange crystals grown by slow evaporation from pH 5–6 calcium acetate buffer. *D_m* by flotation. Crystal dimensions 0.20 × 0.25 × 0.25 mm. Syntex *P*2₁ diffractometer. Cell constants from 20 reflections with 3 ≤ 2θ ≤ 24°. No absorption correction. 2θ_{max} = 45°. Range of *hkl*: 0–8, –15–14, –14–10. No decay correction, two check reflections every 98 data points showed only 1.3% change during data collection. 2245 of 3544 reflections with *I* > 3σ(*I*) used in *F*² refinement, *R*_{int} = 0.014. Structure solved by *MULTAN*80 (Main *et al.*, 1980) using 361 highest *E* values; 36 non-H atoms found in first *E* map, remaining three in difference map. Refinement of non-H atoms with isotropic temperature factors gave *R* = 0.10; final refinement (342 parameters) of non-H atoms with anisotropic temperature factors [except O(5) and O(5'),