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Structure and Binding in Molecular Complexes of Cyclic Polyethers. III.* Host–Guest Interaction Involving Two Assemblies of Binding Sites†

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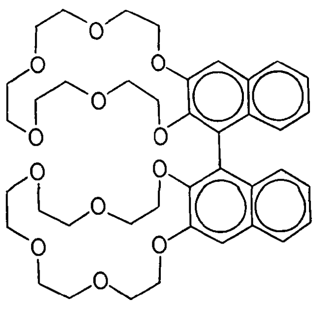
The crystal structure of the one-to-one complex between a synthetic ligand (I) ($C_{40}H_{50}O_{12}$) containing two 18-crown-6 macrocyclic moieties and a bis(hexafluorophosphate) salt of tetramethylenediamine has been determined by X-ray diffraction methods at low temperature (−160°C). Crystals are orthorhombic, space group *Pbcn*, with $a = 18{\cdot}971$ (3), $b = 19{\cdot}137$ (3), $c = 13{\cdot}932$ (2) Å, and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares methods to $R = 0{\cdot}059$ for 2371 independent reflexions measured by counter diffractometry. In the solid, the molecules are located on crystallographic twofold axes. The macro-ring assemblies of binding sites in the host are held in a convergent relationship through hydrogen bonding to functional groups of the guest species. The ammonium ions centre into the inside faces of the macrocycles, the tetramethylene chain being strung between the two rings. All the N to O distances range from 2·9 to 3·1 Å, suggesting that direct $N^+\cdots{:}\ddot{O}$ interactions are involved in stabilizing the host–guest complex. Molecular conformation and dimensions, and the geometry of the intermolecular binding are described in detail.

Introduction

The crystal structure of a complex of the semi-rigid system (I) containing two convergent polyether rings with the bis(hexafluorophosphate) salt of tetramethylenediamine has been investigated as part of a programme of studies on structural host–guest relationships among organic compounds. Such studies should throw light on the nature of binding interactions which stabilize complexes of polydentate ligands with smaller guest species, and provide evidence for the interplay of binding and repelling forces that control structural recognition between hosts and guests.



(I)

We have previously described the structures of two model complexes involving ligands with a single macro-ring assembly of binding sites (Goldberg, 1975*a*,*b*).

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* Part II: *Acta Cryst.* (1975). B**31**, 2592–2600.

† This work is also a contribution from the Department of Chemistry, University of California at Los Angeles, where a major part of it was carried out.

Compound (I) is chiral. It contains two 18-crown-6 macrocycles connected by a substituted 1,1′-binaphthyl unit, and provides a host for a variety of guest compounds (some biologically important) with two banks of binding sites. Recently, the synthesis and the complexing properties of (I) have been described (Tarnowski & Cram, 1976). The studies in the liquid phase demonstrated that polyfunctional guests such as dihydroxyphenylalanine, phenylenediamine and lysine salts given in aqueous solutions are readily complexed and lipophilized by (I), and driven into a non-polar medium. A similar adduct of the host with tetramethylenediamine salt crystallized as a one-to-one complex. The present analysis of this system was undertaken to characterize the conformations of the involved species and the complementary arrangement of binding sites between the host and the guest. The solid-state structure could render assistance in design of hosts of potential use in stereoselective reactions resembling behaviour of natural systems.

Experimental and structure determination

The solid compound was prepared and supplied as fragile plates by Professor D. J. Cram and Mr T. Tarnowski of the University of California at Los Angeles. Difficulties were experienced with choosing specimens suitable for the crystallographic study, as many of the crystals appeared to be twinned. A well formed crystal of approximate dimensions 0·40 × 0·20 × 0·10 mm was mounted on a glass fibre with epoxy cement, the longest dimension being nearly parallel to the fibre axis. During the low-temperature experiment, the crystal was kept in a sealed Lindemann glass capillary with 0·01 mm wall thickness in order to minimize any possible influence of the cold nitrogen stream on its equilibrium position. Preliminary Weissenberg and precession photographs taken with Mo $K\alpha$ radiation indicated *mmm* Laue symmetry with systematic absences $0kl$ with k odd, $h0l$ with l odd and $hk0$ with $h+k$ odd, uniquely determining the space group to be *Pbcn* (No. 60, D_{2h}^{14}).

Unit-cell parameters at approximately −160 °C and the orientation matrix were determined on a Syntex $P\bar{1}$ diffractometer equipped with a low-temperature device and a graphite monochromator (Bragg 2θ angle 23·96°), using Cu $K\alpha$ radiation. Fifteen reflexions were centred on the diffractometer, and used in least-squares refinement of the lattice parameters.

Crystal data

$C_{40}H_{50}O_{12}.C_4H_{14}N_2.(PF_6)_2$, M_r = 1102·9, orthorhombic, a = 18·971 (3), b = 19·137 (3), c = 13·932 (2) Å, V = 5058·0 Å^3, Z = 4, D_c = 1·448 g cm^{-3}, $F(000)$ = 2304. Cu $K\alpha$ radiation, λ = 1·5418 Å, μ(Cu $K\alpha$) = 17·3 cm^{-1}. Space group *Pbcn*. Working temperature −160 ± 5 °C.

One octant of diffraction data out to $2\theta = 126°$ ($\sin\theta/\lambda$ = 0·58 Å^{-1}) was collected with θ–2θ scans. The scan rate was 2° min^{-1} over the peak width, with a 2θ range below $K\alpha_1$ and above $K\alpha_2$ of 1·0°. Stationary-background counts were measured at the beginning and end of each scan with a total background-to-scan time ratio of 0·8. 3031 distinct reflexions were recorded. Three standard reflexions (302, 141, 330) monitored regularly showed significant variation in intensity throughout data collection. On average, a decrease of 4% in the intensities of these reflexions within 100 h of crystal exposure to radiation was observed.

The data processing was carried out in the usual manner. In addition to corrections for background and the Lorentz–polarization factor, the intensities were modified by $(1·0 - 0·0004T)^{-1}$, where T is the total exposure time (h) elapsed, to account for the slow deterioration of the crystal. An absorption correction was not applied.

The standard deviation of each intensity (I) was calculated as $\sigma(I) = [\sigma_s^2 + (pI)^2]^{1/2}$, where σ_s is the standard deviation due to counting statistics. The parameter p, introduced to avoid overweighting the strong reflexions, was set to 0·04. Of the available data, 2376 observations with $|F_o|^2 > 3\sigma(|F_o|^2)$ were used in the final refinement. The three strongest reflexions 020, 002 and 213, the intensities of which were not accurately measured, were omitted.

A Wilson plot was determined to obtain an approximate absolute scale factor and overall temperature factor, and the normalized structure factors were derived from the intensities. The structure was solved by direct phase-determining methods with *MULTAN* (Germain, Main & Woolfson, 1971) with 365$E(hkl)$ > 1·5. All the non-hydrogen atoms could be clearly located in the E map computed with the best set of phases; this set was characterized by the highest figure of merit and the lowest residual.

Initial refinement of the parameters was by block-diagonal least-squares methods which gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0·12$, when $\Sigma\, w(\Delta F)^2$ was minimized and isotropic thermal parameters were assumed. Further full-matrix calculations employing all non-hydrogen atoms with anisotropic temperature factors (325 adjustable parameters) converged to R 0·079 with 2376 reflexions weighted according to $w = 1/\sigma^2(F_o)$. Aromatic and methylene H atom positions were calculated by the program *HPOSN* with a C—H bond distance of 1·06 Å. Isotropic temperature factors for the H atoms were set at 0·031 Å^2 (B = 2·5). A subsequent electron-density difference map allowed location of the ammonium H atoms.

In the final refinement with the Oak Ridge *ORXFLS* routine the H positions were kept fixed because the data-to-parameters ratio was already low. The final discrepancy index is $R = 0{\cdot}061$ for all the data, and $R = 0{\cdot}059$ when five strong reflexions (200, 302, 310, 400, 411) which appear to suffer from secondary extinction are omitted. The weighted R given by $[\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$ was 0·063. The value of $[\Sigma\, w(\Delta F)^2/(n - m)]^{1/2}$ is 2·0 for $n = 2371$ and $m = 325$. In the final cycle the largest shift per standard

Table 1. *Atomic fractional coordinates* ($\times 10^4$) *and thermal parameters*

The e.s.d.'s are given in parentheses in units of the last decimal place. The anisotropic temperature factor for the heavy atoms is in the form $\exp[-2\pi^2(h_ia^i)(h_ja^j)U^{ij} \times 10^4]$, where h_i and a^i are reflexion indices and reciprocal unit-cell edges respectively.

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C(1)	6563 (3)	5545 (2)	5826 (5)	344 (31)	238 (24)	610 (50)	−66 (22)	−26 (32)	85 (31)
C(2)	6258 (2)	5057 (2)	5240 (4)	264 (27)	224 (20)	366 (41)	−7 (20)	39 (27)	62 (26)
C(3)	5761 (2)	4567 (2)	5626 (4)	234 (27)	142 (20)	419 (46)	14 (18)	−95 (27)	31 (26)
C(4)	5460 (2)	4057 (2)	5013 (4)	218 (26)	215 (20)	363 (39)	39 (18)	104 (25)	62 (26)
C(5)	4988 (2)	3585 (2)	5393 (4)	201 (26)	159 (20)	302 (41)	30 (18)	−14 (25)	−23 (24)
O(6)	4640 (2)	3074 (1)	4895 (2)	314 (18)	252 (15)	146 (24)	−26 (13)	43 (16)	−26 (16)
C(7)	4723 (3)	3072 (3)	3868 (4)	265 (29)	404 (28)	392 (44)	−24 (22)	0 (28)	−18 (30)
C(8)	4145 (3)	2630 (3)	3448 (4)	346 (31)	436 (30)	251 (39)	−45 (24)	−34 (28)	71 (28)
O(9)	4284 (2)	1909 (2)	3648 (3)	373 (20)	402 (19)	262 (26)	−13 (15)	−5 (17)	−132 (19)
C(10)	3820 (3)	1461 (3)	3125 (4)	658 (40)	531 (33)	162 (38)	−126 (29)	−109 (32)	−152 (30)
C(11)	4073 (3)	723 (3)	3294 (5)	639 (42)	423 (32)	554 (56)	−59 (28)	123 (37)	−341 (38)
O(12)	4015 (2)	515 (2)	4279 (3)	403 (22)	385 (19)	390 (30)	0 (17)	88 (20)	−138 (20)
C(13)	3334 (3)	238 (3)	4493 (5)	359 (33)	381 (28)	421 (48)	−8 (24)	0 (29)	−269 (31)
C(14)	3333 (3)	35 (2)	5534 (5)	404 (33)	259 (22)	483 (49)	−41 (22)	3 (31)	−246 (30)
O(15)	3373 (2)	620 (1)	6174 (3)	296 (20)	252 (17)	429 (27)	−17 (15)	19 (17)	−229 (18)
C(16)	2722 (2)	984 (4)	6254 (4)	214 (27)	310 (24)	580 (45)	−25 (22)	33 (28)	−220 (28)
C(17)	2802 (2)	1542 (2)	7005 (4)	215 (27)	254 (22)	419 (40)	−114 (20)	97 (27)	−106 (26)
O(18)	3288 (2)	2055 (1)	6653 (2)	244 (18)	223 (15)	354 (26)	−55 (13)	71 (16)	−167 (16)
C(19)	3263 (2)	2686 (2)	7208 (4)	230 (27)	248 (22)	235 (36)	−39 (18)	89 (24)	−176 (23)
C(20)	3659 (2)	3244 (2)	6704 (4)	173 (27)	208 (20)	266 (36)	−14 (17)	62 (23)	−39 (23)
O(21)	4399 (1)	3073 (1)	6739 (2)	166 (16)	165 (13)	237 (23)	−35 (11)	43 (15)	2 (15)
C(22)	4830 (2)	3594 (2)	6382 (4)	197 (26)	173 (20)	105 (35)	26 (17)	17 (23)	44 (23)
C(23)	5100 (2)	4091 (2)	6992 (3)	214 (26)	122 (19)	306 (35)	22 (18)	−51 (25)	24 (22)
C(24)	5586 (2)	4592 (2)	6607 (4)	275 (27)	180 (20)	205 (38)	12 (18)	−160 (27)	40 (24)
C(25)	5911 (3)	5105 (2)	7192 (4)	429 (31)	224 (22)	373 (43)	−93 (22)	−97 (29)	41 (26)
C(26)	6391 (3)	5568 (2)	6806 (5)	473 (36)	207 (24)	579 (51)	−129 (22)	−114 (33)	72 (30)
C(27)	5285 (3)	1220 (2)	7129 (4)	280 (29)	342 (26)	451 (44)	−9 (20)	15 (27)	−87 (28)
C(28)	5023 (2)	1057 (2)	6117 (4)	232 (26)	269 (22)	453 (39)	43 (20)	−25 (25)	−57 (26)
N(29)	4574 (2)	1626 (2)	5707 (3)	266 (22)	253 (19)	191 (28)	36 (15)	20 (20)	−79 (20)
P(30)	6602 (1)	2064 (1)	4844 (1)	177 (7)	343 (7)	389 (12)	16 (6)	29 (7)	−134 (7)
F(31)	5977 (1)	1623 (1)	4358 (2)	311 (16)	503 (17)	381 (22)	−62 (13)	−14 (15)	−157 (16)
F(32)	7155 (1)	1679 (2)	4159 (2)	344 (16)	691 (20)	496 (25)	67 (15)	194 (16)	−205 (19)
F(33)	6497 (2)	2667 (1)	4058 (2)	451 (18)	500 (19)	562 (26)	−46 (15)	21 (17)	82 (18)
F(34)	6696 (1)	1454 (1)	5626 (2)	336 (16)	400 (15)	389 (22)	95 (13)	−4 (15)	−37 (15)
F(35)	6028 (1)	2429 (1)	5523 (2)	350 (16)	358 (15)	468 (23)	88 (13)	74 (15)	−142 (16)
F(36)	7214 (1)	2499 (2)	5339 (2)	321 (18)	576 (19)	649 (27)	−156 (15)	−77 (16)	−137 (19)

	x	y	z		x	y	z
H(1)	6916	5898	5580	H(16*b*)	2595	1202	5593
H(2)	6395	5050	4512	H(17*a*)	2990	1328	7651
H(4)	5589	4027	4290	H(17*b*)	2313	1780	7133
H(7*a*)	5213	2860	3698	H(19*a*)	3497	2593	7897
H(7*b*)	4685	3581	3613	H(19*b*)	2737	2831	7325
H(8*a*)	4130	2710	2700	H(20*a*)	3568	3731	7019
H(8*b*)	3656	2772	3740	H(20*b*)	3492	3266	5977
H(10*a*)	3824	1559	2401	H(25)	5781	5114	7926
H(10*b*)	3296	1514	3394	H(26)	6623	5951	7276
H(11*a*)	4604	685	3125	H(27*a*)	5539	1702	7154
H(11*b*)	3776	368	2914	H(27*b*)	5658	826	7335
H(13*a*)	3234	−208	4088	H(28*a*)	4720	604	6143
H(13*b*)	2945	608	4394	H(28*b*)	5459	988	5677
H(14*a*)	3762	−304	5675	H(29*a*)	4459	1664	5015
H(14*b*)	2863	−248	5690	H(29*b*)	4137	1758	6067
H(16*a*)	2329	628	6461	H(29*c*)	4804	2094	5771

deviation was 0·3. A final difference map showed no peaks whose absolute heights exceeded 0·2 e Å^{-3}, confirming the correctness of the structure.*

Scattering factors for the non-hydrogen atoms were taken from Hanson, Herman, Lea & Skillman (1964) and for H atoms from Stewart, Davidson & Simpson (1965). The final parameters are listed in Table 1. The standard deviations of the parameters were estimated from the corresponding diagonal elements of the inverse matrix of the normal equations.

It should be pointed out that, in fact, two independent data sets from *two* different crystals were measured during the experiment. The first set of data was used to solve the structure. Surprisingly, within this set a number of reflexions required to be absent by the space-group symmetry showed measured intensities significantly above background; they were below the visual threshold on the photographs. Least-squares refinement of the trial structure converged to R 0·074 with 1777 observations, most of the largest discrepancies between the observed and model-determined structure factors occurring for weak reflexions with large value of l. The results showed quite a reasonable geometry for the molecular species and no unusually short intermolecular distances in the crystal. However, the amplitudes of the assumed atomic thermal motion along the c axis were systematically two to three times larger than vibration amplitudes along **a** and **b** (further calculations based on data corrected for absorption led to similar observations). It is possible that the anomalies described above were caused by crystal twinning or disorder of an unrecognized nature, or by the crystal containing a small amount of impurity that altered the space group without affecting significantly the adjusted positional parameters.

The results reported in this paper are based on the second data set which appeared to be much more consistent with the proposed space group and structural model. Nevertheless, the values of the estimated standard deviations $\sigma(z)$ and $\sigma(U^{33})$ are still relatively large (Table 1).

Discussion

Perhaps the most interesting feature in the present structure is the pairing configuration between the host and the guest, both of which contain multiple assemblies of binding sites. In the solid the molecules are situated on crystallographic twofold axes, with respect to which the geometry of the formed adduct is symmetric. An illustration of the observed ligand–substrate binding mode is given in Fig. 1. The organic host simultaneously complexed the hydrogen-bonding parts of the guest, the ammonium ions being nearly centred and tightly fitted within the macrocyclic cavities. The tetramethylene chain is strung between the two macro-rings. In the resulting structure the hydrophilic ammonium groups are hidden within the hydrophilic cavities and covered by a lipophilic skin of C—H bonds.

Hydrogen bonding and direct $N^{+}\cdots:\ddot{O}$ interactions appear to contribute the most to the intermolecular attraction. The hydrogen-bonding scheme is described in Fig. 1 and in Table 2. The ammonium H atoms H(29*a*) and H(29*b*) interact with the ether O atoms O(9) and O(18). The parameters in these bonds (averaged distances N···O 2·93 and H···O 1·95 Å, and angle N—H···O 173°) are characteristic of a strong binding (Hamilton & Ibers, 1968). The third H

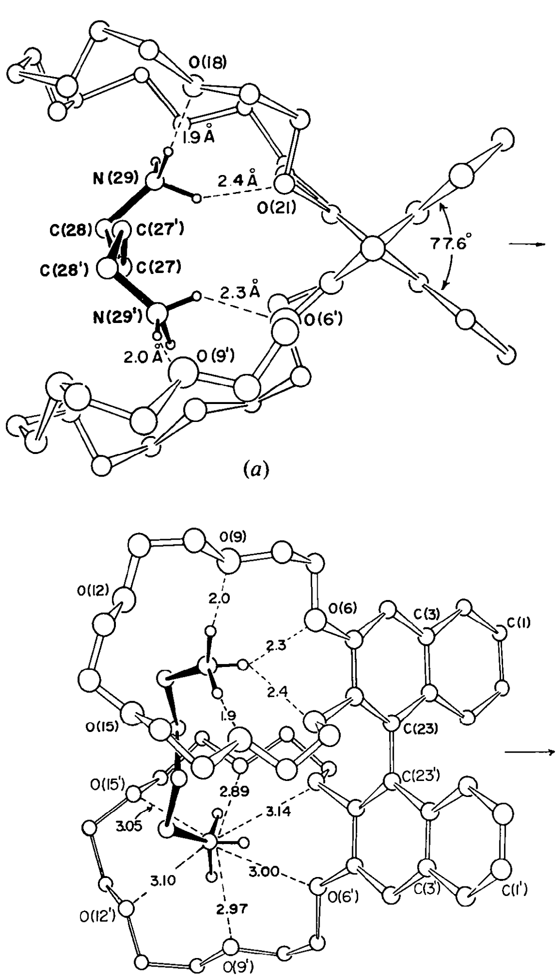

Fig. 1. Two perspective views of the host–guest complex. The primed atoms are related to unprimed atoms by a twofold axis parallel to **b**. All N···O and H···O nonbonding distances which describe the binding interaction are shown.

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* The structure factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32063 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Details of the hydrogen bonds*

	N–H···O–R	N–H	N···O	H···O	N–H···O	H···O–R
(1)	N(29)–H(29*a*)···O(9)–C(8)	0·99 Å	2·97 Å	1·99 Å	170°	116°
	–C(10)					117
(2)	N(29)–H(29*b*)···O(18)–C(17)	1·00	2·89	1·89	175	119
	–C(19)					121
(3)	N(29)–H(29*c*)···O(6)–C(5)	1·00	3·00	2·26	129	105
	–C(7)					121
	N(29)–H(29*c*)···O(21)–C(20)	1·00	3·14	2·43	127	118
	–C(22)					100

atom, H(29*c*), is directed toward the region between the aryl O atoms, the corresponding H(29*c*)···O(6) and H(29*c*)···O(21) distances at 2·3 and 2·4 Å being also shorter than the ideal van der Waals distance of 2·6 Å. Presumably H(29*c*) is engaged in a bifurcated hydrogen bond to O(6) and O(21); the geometrical details indicate a somewhat stronger linkage of the H atom to O(6). Furthermore, all O atoms of the ring system seem to be involved in stabilization of the complex through direct pole–dipole interactions with the positive charge of the guest ions. All the O atoms are turned toward the centre of the macro-ring, the N to O distances ranging from 2·89 to 3·14 Å. Comparative studies of the complexing ability of some heterocrown ligands with *tert*-butylammonium thiocyanate in chloroform indicated indeed that considerable binding is associated with the Ö:···N interaction (Cram *et al.*, 1975).

The 18-crown-6 framework in the present structure is markedly distorted from the nearly ideal 'crown' conformation observed in several complexes of the unsubstituted hexaether host (Dunitz, Dobler, Seiler & Phizackerley, 1974). This is mainly due to geometric constraints imposed on the polyether ring by the particular mode of the host–guest interaction, as well as by the presence of the aromatic substituent. Thus, in correlation with the pattern of hydrogen bonding, the hexagon defined by the six ether O atoms is expanded along two diagonals and contracted along the third. The distance O(9)···O(18) between atoms which are hydrogen bonded to the centred ammonium group is 4·60 Å; the corresponding distances along the other diagonals O(6)···O(15) and O(12)···O(21) are 5·57 and 6·02 Å respectively.

The conformation of the macro-ring is best described in terms of the torsion angles about the ring bonds (Table 3). We observe that the conformation about all the alkyl C–C bonds is characteristically *gauche*, and about the C–O bonds it is most commonly

Table 3. *Torsion angles*

1	2	3	4	Dihedral angle 1–2–3–4 (°)	Distance 1–4 (Å)
C(22)	C(5)	O(6)	C(7)	174·4	
C(5)	O(6)	C(7)	C(8)	–163·1	
O(6)	C(7)	C(8)	O(9)	–72·3	2·906
C(7)	C(8)	O(9)	C(10)	–169·9	
C(8)	O(9)	C(10)	C(11)	173·1	
O(9)	C(10)	C(11)	O(12)	64·2	2·855
C(10)	C(11)	O(12)	C(13)	86·6	
C(11)	O(12)	C(13)	C(14)	179·7	
O(12)	C(13)	C(14)	O(15)	68·1	2·914
C(13)	C(14)	O(15)	C(16)	76·0	
C(14)	O(15)	C(16)	C(17)	174·8	
O(15)	C(16)	C(17)	O(18)	67·3	2·831
C(16)	C(17)	O(18)	C(19)	165·4	
C(17)	O(18)	C(19)	C(20)	–168·5	
O(18)	C(19)	C(20)	O(21)	–69·8	2·873
C(19)	C(20)	O(21)	C(22)	–173·3	
C(20)	O(21)	C(22)	C(5)	–89·2	
O(21)	C(22)	C(5)	O(6)	4·6	2·609
C(27′)	C(27)	C(28)	N(29)	68·8	
C(28′)	C(27′)	C(27)	C(28)	154·2	

Table 4. *Least-squares planes*

In the equation of the plane, *x*, *y*, *z* are fractional coordinates of a point in the plane, and the right-hand side is the distance of the plane from unit-cell origin. Deviations (Å) of relevant atoms from these planes are given in square brackets.

Plane (*a*): the naphthalene ring

$$14{\cdot}286x - 11{\cdot}997y + 2{\cdot}783z = 4{\cdot}331$$

[C(1) 0·01; C(2) 0·00; C(3) –0·01; C(4) 0·00; C(5) –0·01; C(22) 0·03; C(23) –0·01; C(24) –0·02; C(25) –0·01; C(26) 0·01; O(6) –0·03; O(21) 0·14; F(33) 2·88; F(35) 2·90]

Plane (*b*): the 18-membered ring

$$16{\cdot}031x - 7{\cdot}513y + 5{\cdot}058z = 7{\cdot}448$$

[O(6) 0·16; O(9) –0·17; O(12) 0·77; O(15) 0·62; O(18) –0·36; O(21) 0·70; N(29) 1·55]

Plane (*c*): O(6), O(9), O(18), O(21)

$$13{\cdot}616x - 11{\cdot}972y + 4{\cdot}260z = 4{\cdot}964$$

[O(6) –0·24; O(9) 0·14; O(18) –0·11; O(21) 0·22; O(12) 1·71; O(15) 1·52; N(29) 1·75]

Plane (*d*): the six ether O atoms

$$16{\cdot}525x - 6{\cdot}574y + 4{\cdot}890z = 8{\cdot}017$$

[O(6) 0·02; O(9) –0·41; O(12) 0·37; O(15) 0·17; O(18) –0·68; O(21) 0·53; N(29) 1·26; F(31) 2·92; F(33) 2·95; F(35) 3·05] antiplanar. However, in the peripheral region of the 18-crown-6 unit not involved in hydrogen bonding, the torsion angles about the C(11)—O(12) and C(14)—O(15) bonds are 86 and 76° respectively. This deformation of the ring system introduces 1–4 steric repulsion between the $>\mathrm{CH_2}(13)$ and the $>\mathrm{CH_2}(10)$ and $>\mathrm{CH_2}(16)$ methylene groups, causing the valency angles at C(11) and C(14) to assume values significantly greater than tetrahedral. In addition, the twisting of the 18-crown-6 cavity to optimize the N—H··· O hydrogen bonding is reflected to some extent in the intermediate value of the torsion angle about the O(21)—C(22) bond. Similar characteristics of low-energy molecular deformations in macrocyclic polyether species, which indicate that most of the deformation strain is usually accommodated in torsion angles about the C—O bonds, have been described previously (*e.g.* Dunitz *et al.*, 1974; Goldberg, 1976).

The overall shape of the complexed host and the geometry of its interaction with a potential guest are strongly influenced by the dimensions of the particular guest. In the resulting conformation of the present complex, the dihedral angle between the planes of the naphthalene rings attached to one another is 77·6°, and the O(21)··· O(21′) distance is 3·11 Å; in the uncomplexed and isolated molecule of the host the dihedral angle can vary between extremes of about 60 to 120°. It is also interesting to note that the C(28)—N(29) bond is significantly tilted relative to the mean plane defined by the ether O atoms, the angle between the normal to this plane and the C—N bond being 28°. The shortness of the methylene bridge [consisting of two internal methylene groups in an *anti* relationship and the $\mathrm{CH_2}(27)$ and $\mathrm{CH_2}(28)$ groups in a *gauche* conformation] may be responsible for such a non-ideal arrangement and the consequent departures from an ideal hexagonal symmetry in the hexaether cavity.

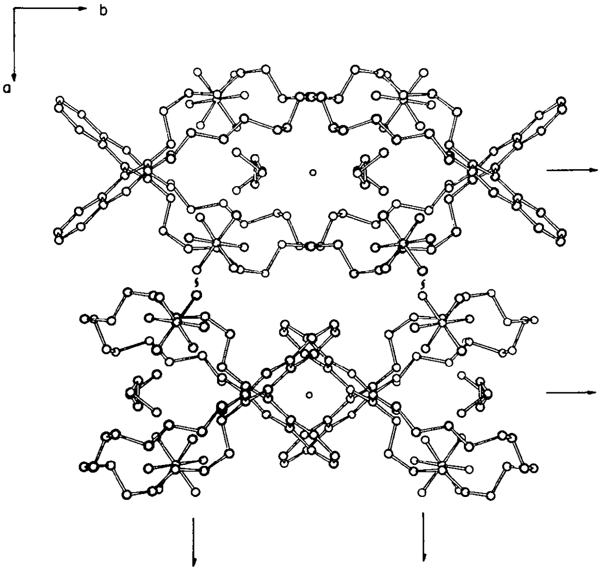

Fig. 2. Projection of the structure down the *c* axis. Symbols for some of the symmetry elements are marked. The thickness of the circles represents the relative height of the corresponding atom from a reference plane of the projection.

Least-squares planes through various groups of atoms in the structure are presented in Table 4.

The packing arrangement viewed down the *c* axis is shown in Fig. 2. The unit cell of the crystals contains two of each of the enantiomers of the complex. An interesting feature of the crystal structure is the ion-pairing configuration between the alkylammonium species and the $\mathrm{PF_6^-}$ counter ions. The following details describe interactions among the ion pairs. (*a*) A relatively short contact is formed between the ammonium ion and the negatively charged hexafluorophosphate group; relevant distances include N(29)···F(35) 3·17 and N(29)···F(31) 3·26 Å. (*b*) The approach between the $>\mathrm{CH_2}(28)$ group and the F(31) atom is slightly shorter than the corresponding van der Waals contact. Keeping in mind that the acidity of H atoms on C(28) is probably increased due to the nearest electrophilic $-\mathrm{NH_3^+}$ group, the distances C(28)···F(31) and H(28*b*)···F(31) at 3·23 and 2·4 Å may reflect a weak attractive interaction. These and some other short intermolecular contacts involving the $\mathrm{PF_6}$ group are listed in Table 5. The high density of the substance, 1·448 g cm^{-3}, along with the data of Table 5 indicate that the egg-shaped structural units, each comprising the host–guest complex and two $\mathrm{PF_6^-}$ counter ions, form an efficiently packed structure.

It should be pointed out, however, that the attraction of the ionic guest to the polyether host seems to be very little affected by the competitive interaction between the $\mathrm{R{-}NH_3^+}$ and $\mathrm{PF_6^-}$ species carrying opposite charges. In fact, it has been observed in the crystal structure of another complex involving similar moieties and a similar type of host–guest interaction that the separation between the F atoms and the N atom exceeded 5·4 Å (Goldberg, 1977).

Table 5. *Some intermolecular contact distances* (Å)

Within the asymmetric unit

F(31)···C(28)	3·23	F(35)···O(6)	3·04
F(31)···N(29)	3·26	F(35)···N(29)	3·17
F(34)···C(28)	3·33	F(35)···C(28)	3·35
F(34)···C(29)	3·43	F(35)···C(4)	3·37
F(35)···C(5)	2·97	F(35)···C(22)	3·40

F(32)···C(19$^{\mathrm{I}}$)	3·09	F(31)···C(14$^{\mathrm{III}}$)	3·44
F(32)···C(20$^{\mathrm{I}}$)	3·10	F(34)···C(13$^{\mathrm{III}}$)	3·24
F(33)···C(17$^{\mathrm{I}}$)	3·26	F(34)···C(14$^{\mathrm{III}}$)	3·28
C(7)···C(28$^{\mathrm{II}}$)	3·48		

Equivalent positions relative to the reference asymmetric unit at x,y,z: (I) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (II) $1-x$, $1-y$, $1-z$; (III) $1-x$, $-y$, $1-z$.

The bond lengths (not corrected for thermal vibrations) and valency angles in the structure are given in Tables 6 and 7, and are illustrated in Fig. 3. The somewhat poor quality of the diffraction data (see above) and the non-rigidity of the molecules with respect to thermal vibrations affected the precision of molecular structure determination. The average standard deviations in the bond distances and angles are 0·007 Å and 0·4° in the complex, and 0·003 Å and 0·2° in the PF_6 group. The dimensions of the naphthalene substituents are close to those reported for naphthalene in other structures, and are consistent with the known picture of incomplete delocalization in this molecule (Cruickshank, 1957; Shaanan, Shmueli & Rabinovich, 1976). The PF_6 group forms an almost perfect octahedron. The molecular dimensions of the macro-ring exhibit characteristic features usually observed in structures of polyether compounds (*e.g.* Truter, 1973; Dunitz *et al.*, 1974). Presumably the shortening of the C(sp^3)–C(sp^3) bonds in these compounds is a real effect, as it has been observed also in seven different structures analysed on the basis of low-temperature diffraction data (Goldberg, 1975*a*,*b*, 1976, 1977). In the present complex, the C–C bond lengths within the macrocycle average 1·50 Å. The various aspects of molecular geometry found in structures of the heterocrown species will be reviewed in detail elsewhere.

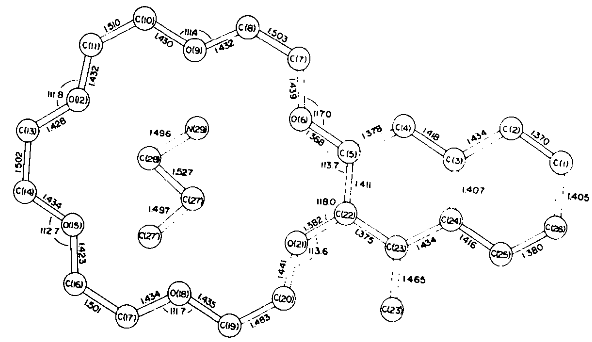

Fig. 3. Molecular geometry of the host and the guest species. The bond distances (Å) are not corrected for the effects of thermal motion.

Table 6. *Bond distances* (Å)

C(1)–C(2)	1·370 (7)	C(20)–O(21)	1·441 (5)
C(2)–C(3)	1·434 (6)	O(21)–C(22)	1·382 (5)
C(3)–C(4)	1·418 (7)	C(22)–C(23)	1·375 (6)
C(4)–C(5)	1·378 (6)	C(23)–C(24)	1·434 (6)
C(5)–O(6)	1·368 (5)	C(24)–C(25)	1·416 (7)
O(6)–C(7)	1·439 (7)	C(25)–C(26)	1·380 (7)
C(7)–C(8)	1·503 (7)	C(26)–C(1)	1·405 (9)
C(8)–O(9)	1·432 (6)	C(24)–C(3)	1·407 (8)
O(9)–C(10)	1·430 (7)	C(22)–C(5)	1·411 (7)
C(10)–C(11)	1·510 (8)	C(23)–C(23′)	1·465 (7)
C(11)–O(12)	1·432 (8)	C(27)–C(27′)	1·497 (7)
O(12)–C(13)	1·428 (6)	C(27)–C(28)	1·527 (8)
C(13)–C(14)	1·502 (9)	C(28)–N(29)	1·496 (6)
C(14)–O(15)	1·434 (6)	P(30)–F(31)	1·605 (3)
O(15)–C(16)	1·423 (5)	P(30)–F(32)	1·599 (3)
C(16)–C(17)	1·501 (7)	P(30)–F(33)	1·604 (3)
C(17)–O(18)	1·434 (5)	P(30)–F(34)	1·606 (3)
O(18)–C(19)	1·435 (5)	P(30)–F(35)	1·602 (3)
C(19)–C(20)	1·483 (6)	P(30)–F(36)	1·586 (3)

Table 7. *Bond angles* (°)

C(26)–C(1)–C(2)	120·2 (5)	C(23)–C(22)–C(5)	122·2 (4)
C(1)–C(2)–C(3)	120·0 (5)	C(22)–C(23)–C(24)	118·1 (4)
C(2)–C(3)–C(4)	119·3 (5)	C(22)–C(23)–C(23′)	120·0 (4)
C(2)–C(3)–C(24)	119·8 (4)	C(24)–C(23)–C(23′)	121·9 (4)
C(4)–C(3)–C(24)	120·9 (4)	C(23)–C(24)–C(25)	121·8 (5)
C(3)–C(4)–C(5)	118·8 (5)	C(23)–C(24)–C(3)	119·5 (4)
C(4)–C(5)–O(6)	125·9 (5)	C(25)–C(24)–C(3)	118·7 (4)
C(4)–C(5)–C(22)	120·4 (4)	C(24)–C(25)–C(26)	120·6 (5)
O(6)–C(5)–C(22)	113·7 (4)	C(25)–C(26)–C(1)	120·7 (5)
C(5)–O(6)–C(7)	117·0 (4)	C(28)–C(27)–C(27′)	113·8 (4)
O(6)–C(7)–C(8)	108·0 (4)	C(27)–C(28)–N(29)	112·9 (4)
C(7)–C(8)–O(9)	109·3 (4)	F(31)–P(30)–F(32)	89·5 (2)
C(8)–O(9)–C(10)	111·4 (4)	F(31)–P(30)–F(33)	89·9 (2)
O(9)–C(10)–C(11)	*106·7 (5)*	*F(31)–P(30)–F(34)*	*89·3 (2)*
C(10)–C(11)–O(12)	112·7 (5)	F(31)–P(30)–F(35)	88·6 (2)
C(11)–O(12)–C(13)	111·8 (4)	F(31)–P(30)–F(36)	179·2 (2)
O(12)–C(13)–C(14)	107·4 (4)	F(32)–P(30)–F(33)	90·3 (2)
C(13)–C(14)–O(15)	113·5 (4)	F(32)–P(30)–F(34)	89·9 (2)
C(14)–O(15)–C(16)	112·7 (4)	F(32)–P(30)–F(35)	178·1 (2)
O(15)–C(16)–C(17)	108·3 (4)	F(32)–P(30)–F(36)	91·2 (2)
C(16)–C(17)–O(18)	108·3 (4)	F(33)–P(30)–F(34)	179·1 (2)
C(17)–O(18)–C(19)	111·7 (3)	F(33)–P(30)–F(35)	90·2 (2)
O(18)–C(19)–C(20)	109·4 (4)	F(33)–P(30)–F(36)	90·5 (2)
C(19)–C(20)–O(21)	108·3 (3)	F(34)–P(30)–F(35)	89·6 (2)
C(20)–O(21)–C(22)	113·6 (3)	F(34)–P(30)–F(36)	90·3 (2)
O(21)–C(22)–C(5)	118·0 (4)	F(35)–P(30)–F(36)	90·7 (2)
O(21)–C(22)–C(23)	119·8 (4)	[H–C–H] average	109 ± 2

The structure determined in the present work provides an excellent example of the useful role that interactions of hydrogen bonding play in structuring complexes of organic hosts with organic guests.

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The Crystal Structures of the Two Isomers of Isopropyl *N*-(Methylfuroxan)carbamate, $C_7H_{11}N_3O_4$

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The structures of the positional isomers of the title furoxan derivative were solved by direct methods, and refined by block-diagonal least squares, from diffractometer intensities (Cu $K\alpha$). Isopropyl 3-methyl-4-furoxan carbamate (m.p. 110–112°) is monoclinic, space group $P2_1/c$, with $a = 8{\cdot}915\,(2)$, $b = 12{\cdot}873\,(2)$, $c = 17{\cdot}591\,(3)$ Å, $\beta = 100{\cdot}79\,(1)°$; $Z = 8$ ($R = 4{\cdot}7\%$). Isopropyl 4-methyl-3-furoxancarbamate (m.p. 105–107°) is monoclinic, space group $P2_1/c$, with $a = 4{\cdot}844\,(1)$, $b = 22{\cdot}559\,(4)$, $c = 8{\cdot}962\,(1)$ Å, $\beta = 97{\cdot}98\,(1)°$; $Z = 4$ ($R = 5{\cdot}6\%$). All H atoms, located on difference syntheses, were refined isotropically. The furoxan group is rigorously planar in both the independent molecules, whose bonds and angles are very similar, of the higher-melting isomer, whilst it deviates from strict planarity in the lower-melting isomer. In all three molecules the furoxan and carbamate groups are rotated, to different extents, and no conjugation between the two groups is revealed.

Introduction

After investigating a few disubstituted furoxans and furazans with electron-withdrawing substituents, we carried out an X-ray analysis of the pair of isomers with the electron-releasing isopropyl carbamate function. The title positional isomers were prepared by Gasco, Mortarini, Ruà & Menziani (1972) who assigned structures on the basis of NMR spectroscopy. Their assignment was confirmed by the present analysis: the higher-melting isomer is isopropyl 3-methyl-4-furoxancarbamate and the lower-melting isomer is isopropyl 4-methyl-3-furoxancarbamate. They will be distinguished as isomer *A* and isomer *B* respectively, following Gasco & Boulton (1973).

Structure determination

Experimental results

The compounds, recrystallized from acetone–water or ethanol, yielded prismatic transparent crystals suitable for the X-ray analysis. The space groups were determined from Weissenberg photographs; the cell parameters and intensities were measured, at room tem-