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Evidence for cation-π interactions in calixcrown•KPic complexes from X-ray crystal structure analysis and energy calculations

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The crystal and molecular structures of the 1,3-diisopropoxy-p-tertbutyl calix[4]arene crown-5 fixed in the partial cone conformation and that of its potassium picrate salt have been determined by single crystal X-ray diffraction studies. Energy calculations have been performed to gain more insight on the stabilizing cation...ligand interactions. The calculation of the total potential energy indicates that the contribution which comes from the electrostatic polarization induced by the electric field of the cation on the rotated nucleus gives a net stabilizing contribution of almost 6 kcal/mol. A comparison between the molecular geometry of some partial cone 1,3-disubstituted-p-tertbutylcalix[4]arene derivatives is reported and discussed in view of the *preorganization* principle.

INTRODUCTION

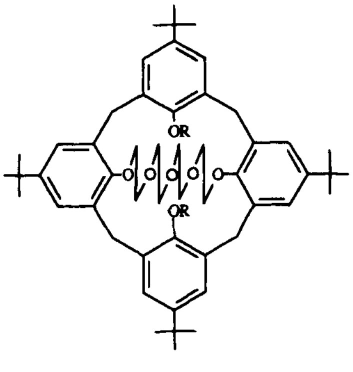
Previously we have reported the synthesis and complexing properties of a new class of powerful potassium-selective ionophores, the p-tertbutylcalix[4]arene crown ethers, which are either conformationally mobile (e.g. **1**) or fixed in the partial cone (**2a**), cone (**2b**) or 1,3 alternate (**2c**) conformations[1]. These ligands have been also used in ion selective sensors (CHEMFETs)[2]. Previous studies performed with these ligands have shown that partial cone isomers of ligands **2**–**4** are the most efficient and the most selective in the complexation of the potassium cation. As a further contribution to these studies we report in this paper the X-ray crystal and molecular structures of the conformationally rigid 1,3-diisopropoxy-p-tertbutylcalix[4]arene crown-5 **3** and its potassium picrate salt **3•KPic**.

The analysis of these molecular structures and the potential energy calculations supports a participation of the rotated aryl nucleus in the complexation of the potassium cation in complexes having a partial cone structure.

RESULTS AND DISCUSSION

Molecular structures

The molecular structures of the free ligand **3** and that of its potassium picrate complex **3•KPic**, determined by single crystal X-ray diffraction methods, are shown in Fig. 1 and 2 respectively. The atomic coordinates of **3** and **3•KPic** are reported in Tables 1 and 2, respectively. The most relevant bond distances and non-bonding contacts, compared with those observed in the complex



1: R = CH_3
2a,b,c: R = C_2H_5
3: R = $CH(CH_3)_2$
4: R = $C_6H_5CH_2$

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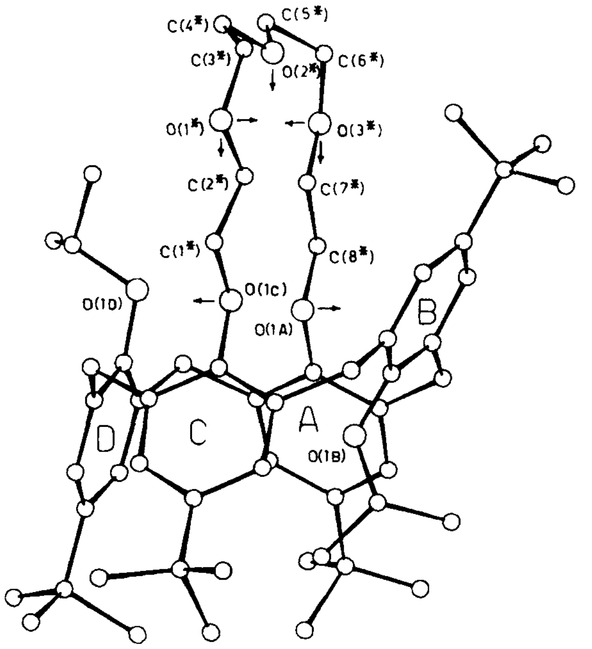

Figure 1 Molecular structure of the free ligand **3**. H-atoms are omitted.

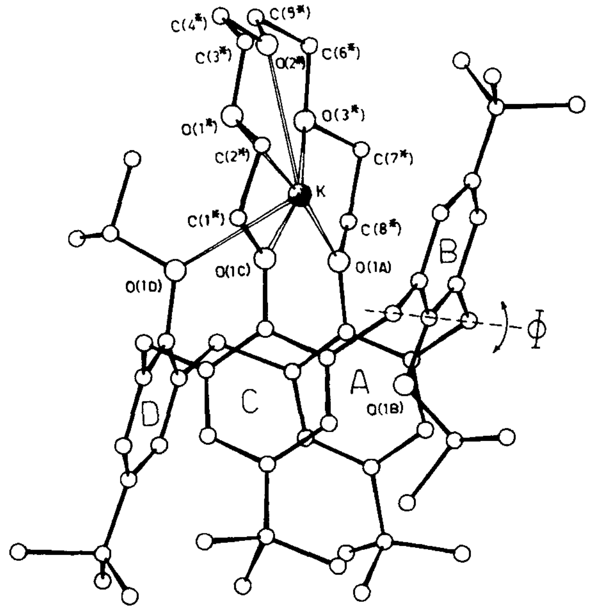

Figure 2 Molecular structure of the complex **3•KPic**. H-atoms are omitted.

2b•KPic, are summarized in Table 3; the conformational parameters[3,4] of the calixarene moieties are reported in Table 4.

In the complex **3•KPic** the K-O bond distances are all in the range 2.748(8)–3.01(1) Å and these are significantly longer than those observed in the complex of **2b** in which the receptor is fixed in the cone conformation and where the coordination sphere is closer to the K^+ ion[1] (Fig. 3).

On the other hand, Fig. 2 shows that the rotated aromatic nucleus B is in an almost ideal orientation to interact with the potassium ion in an η^6 coordination fashion, the angle between the vector $K^+...B_2$ (B_2-barycentre of the phenyl ring B) and the perpendicular to B being only 1.4(3)°. The K^+...aromatic distances, which range from 3.45(1) to 3.55(1) Å, indicate a contribution of a cation-π interaction. Although, these distances are longer than the value of 3.02 Å found for the shortest potassium-benzene (solvent) distance observed so far[5], they are not very different from those observed in other system. Atwood[6] has found K^+...aromatic distances between 3.27 and 3.58 Å in several X-ray crystal structures of $K[Al_2Me_6X]$ aromatic complexes, whereas recently, Jacoby et al.[7] have found 3.10(1)–3.25(1) Å for K^+...aromatic interactions when a potassium cation coordinates in an η^6 fashion a toluene solvent molecule.

Energy calculations

In order to obtain more insight in the role of the K^+...aromatic interactions, we have performed energy calculations on the K^+ complex of the ligand **3**, taking into account the electrostatic polarization induced by the electric field of the cation on the rotated ring B.

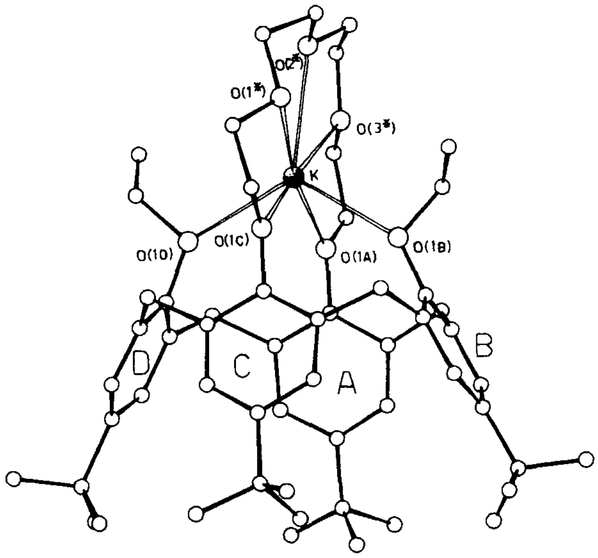

Figure 3 Molecular structure of the complex **2b•KPic**[1]. H-atoms are omitted.

Starting from the atomic coordinates obtained from the crystallographic study, and using parallel computational tools, the total potential energy was calculated as a function of any rigid rotation of Φ degrees of the phenolic ring B around the dashed line shown in Fig. 2, whereas the remaining host moiety was maintained as it was. For any Φ value the equilibrium molecular conformation

Table 1 Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 × 10^4) for the non-hydrogen atoms of the free ligand 3

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
O(1A)	2409(2)	3841(3)	2553(2)	467(24)
C(1A)	2900(3)	3696(4)	2754(4)	456(36)
C(2A)	3122(3)	4055(4)	2428(4)	492(38)
C(3A)	3613(3)	3909(5)	2649(4)	600(46)
C(4A)	3893(3)	3417(5)	3163(4)	586(43)
C(5A)	3660(3)	3073(5)	3485(4)	545(42)
C(6A)	3170(3)	3206(4)	3293(4)	459(37)
C(7A)	4448(3)	3252(7)	3409(5)	837(56)
C(8A)	4604(8)	3515(16)	2929(12)	766(78)
C(9A)	4777(8)	3697(16)	4139(12)	805(91)
C(10A)	4580(14)	2442(21)	3585(24)	1434(143)
C(20A)	2830(3)	4552(5)	1812(4)	644(48)
O(1B)	2971(2)	5442(3)	2979(3)	572(27)
C(1B)	2523(3)	5522(4)	2360(4)	481(38)
C(2B)	2159(3)	6000(4)	2291(4)	478(38)
C(3B)	1702(3)	6008(5)	1660(4)	508(39)
C(4B)	1613(3)	5562(4)	1097(4)	508(37)
C(5B)	1988(3)	5085(5)	1177(4)	523(40)
C(6B)	2443(3)	5070(4)	1801(4)	512(41)
C(7B)	1104(3)	5604(5)	392(4)	637(43)
C(8B)	677(5)	5501(9)	511(7)	767(45)
C(9B)	1090(5)	6379(8)	69(7)	750(45)
C(10B)	1090(5)	5025(7)	-140(7)	776(47)
C(11B)	3341(4)	6009(7)	3205(5)	955(59)
C(12B)	3765(4)	5728(10)	3912(6)	1386(85)
C(13B)	3511(5)	6118(9)	2697(7)	1400(96)
C(20B)	2222(3)	6560(4)	2832(4)	556(40)
O(1C)	1934(2)	5305(3)	3316(2)	447(24)
C(1C)	2305(3)	5745(4)	3817(4)	404(35)
C(2C)	2521(3)	5559(4)	4535(4)	398(34)
C(3C)	2869(3)	6042(4)	5015(4)	436(37)
C(4C)	3016(3)	6668(4)	4826(4)	464(37)
C(5C)	2811(3)	6789(4)	4106(4)	483(41)
C(6C)	2455(3)	6338(4)	3605(4)	433(35)
C(7C)	3399(3)	7192(5)	5372(4)	579(41)
C(8C)	3915(8)	7056(14)	5417(14)	861(89)
C(9C)	3248(8)	7994(11)	5133(10)	677(65)
C(10C)	3411(11)	7151(16)	6090(14)	946(85)
C(20C)	2420(3)	4855(4)	4765(4)	437(38)
O(1D)	2187(2)	3646(3)	3814(2)	412(22)
C(1D)	2677(3)	3765(4)	4313(4)	406(35)
C(2D)	3054(3)	3370(4)	4313(4)	426(36)
C(3D)	3546(3)	3454(5)	4861(4)	510(40)
C(4D)	3670(3)	3942(4)	5401(4)	497(38)
C(5D)	3290(3)	4368(5)	5358(4)	496(41)
C(6D)	2797(3)	4300(4)	4823(4)	419(37)
C(7D)	4220(3)	4035(6)	6000(5)	714(48)
C(8D)	4284(7)	4646(12)	6534(10)	883(75)
C(9D)	4418(8)	3291(13)	6359(12)	1042(81)
C(10D)	4537(9)	4320(15)	5658(13)	1125(91)
C(11D)	1920(3)	3200(5)	4067(4)	523(40)
C(12D)	1368(4)	3398(7)	3563(6)	879(60)
C(13D)	2058(5)	2422(6)	4093(7)	825(72)
C(20D)	2943(3)	2881(5)	3694(4)	500(42)
C(1*)	1448(3)	5504(6)	3188(5)	656(46)
C(2*)	1087(3)	5092(6)	2534(4)	726(47)
O(1*)	607(5)	5307(17)	2479(7)	585(56)
C(3*)	200(3)	4913(8)	1867(5)	918(59)
C(4*)	202(4)	4113(9)	1815(6)	1071(72)
O(2*)	494(2)	3901(5)	1502(4)	898(40)
C(5*)	453(4)	3160(8)	1302(7)	1072(79)
C(6*)	750(4)	3032(7)	950(6)	1127(71)
O(3*)	1269(5)	2960(8)	1329(16)	677(73)
C(7*)	1548(3)	3565(5)	1823(5)	743(51)
C(8*)	2074(3)	3338(6)	2037(5)	726(49)

[a]Equivalent Isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2 Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters (Å^2 × 10^4) for the non-hydrogen atoms of the complex **3•KPic**

Atom	*x/a*	*y/b*	*z/c*	$U_{eq}{}^a$
K	5175(1)	1728(1)	8179(2)	174(7)
O(1A)	4077(4)	2218(3)	6716(6)	383(32)
C(1A)	4044(6)	2719(5)	6218(10)	342(31)
C(2A)	3828(7)	3162(5)	6705(10)	413(35)
C(3A)	3718(7)	3667(6)	6173(11)	418(36)
C(4A)	3777(7)	3708(5)	5153(10)	452(34)
C(5A)	4030(7)	3262(6)	4725(11)	481(36)
C(6A)	4179(7)	2764(5)	5250(10)	398(33)
C(7A)	3621(8)	4243(6)	4538(12)	599(42)
C(8A)	3264(26)	4128(14)	3397(28)	1082(126)
C(9A)	4250(21)	4549(19)	4571(39)	1322(151)
C(10A)	3161(22)	4616(13)	4979(25)	951(115)
C(20A)	3724(7)	3131(6)	7784(11)	449(60)
O(1B)	5210(5)	3459(4)	8333(7)	486(39)
C(1B)	5006(7)	3085(5)	8954(10)	362(34)
C(2B)	5527(7)	2858(5)	9825(10)	362(32)
C(3B)	5319(7)	2474(5)	10436(10)	422(33)
C(4B)	4633(7)	2300(6)	10247(11)	487(38)
C(5B)	4150(7)	2517(5)	9334(10)	456(35)
C(6B)	4322(6)	2896(5)	8688(10)	330(31)
C(7B)	4427(8)	1887(6)	10948(12)	571(43)
C(8B)	4072(21)	1381(16)	10270(31)	761(137)
C(9B)	3815(21)	2125(17)	11348(32)	891(148)
C(10B)	4999(22)	1723(19)	11880(34)	863(154)
C(11B)	5077(12)	4010(7)	8445(15)	809(94)
C(12B)	5367(13)	4281(9)	7649(22)	1382(141)
C(13B)	5210(18)	4227(9)	9454(27)	1682(207)
C(20B)	6268(7)	3057(6)	10169(10)	408(54)
O(1C)	6482(4)	2172(3)	8934(7)	395(34)
C(1C)	6739(6)	2675(5)	8750(9)	338(31)
C(2C)	7076(7)	2729(5)	7948(10)	385(33)
C(3C)	7411(7)	3224(5)	7915(10)	431(33)
C(4C)	7390(7)	3665(6)	8573(11)	448(37)
C(5C)	6985(6)	3589(5)	9299(10)	371(32)
C(6C)	6672(6)	3117(5)	9372(10)	349(32)
C(7C)	7755(7)	4193(6)	8462(11)	511(38)
C(8C)	7445(23)	4413(17)	7344(32)	929(138)
C(9C)	7527(16)	4663(11)	9026(23)	666(104)
C(10C)	8566(17)	4055(14)	8577(35)	888(117)
C(20C)	7040(7)	2303(5)	7144(10)	398(54)
O(1D)	5690(4)	1775(4)	6340(7)	450(35)
C(1D)	5835(7)	2235(5)	5823(10)	376(33)
C(2D)	5302(7)	2473(5)	4986(10)	424(34)
C(3D)	5476(8)	2853(6)	4394(12)	512(39)
C(4D)	6165(8)	3045(6)	4576(12)	545(41)
C(5D)	6633(8)	2849(6)	5443(11)	521(39)
C(6D)	6497(7)	2451(5)	6110(10)	403(33)
C(7D)	6352(10)	3463(7)	3852(15)	814(53)
C(8D)	6950(17)	3175(14)	3346(26)	977(129)
C(9D)	6713(19)	3922(15)	4480(27)	961(122)
C(10D)	5792(20)	3554(16)	2793(29)	913(124)
C(11D)	5861(17)	1278(8)	5898(16)	1079(128)
C(12D)	5661(26)	848(10)	6519(27)	3221(407)
C(13D)	5522(21)	1147(14)	4910(33)	2387(261)
C(20D)	4537(7)	2312(6)	4819(11)	450(59)
C(1*)	7035(8)	1837(7)	9615(13)	590(64)
C(2*)	6721(10)	1405(7)	10130(14)	698(74)
O(1*)	6323(5)	1040(4)	9376(8)	671(46)
C(3*)	6128(10)	584(7)	9864(14)	728(78)
C(4*)	5608(9)	248(7)	9043(14)	744(79)
O(2*)	4981(6)	556(4)	8655(8)	715(48)
C(5*)	4456(9)	278(6)	7931(14)	674(75)
C(6*)	3821(9)	597(7)	7619(15)	794(84)
O(3*)	3933(5)	1099(4)	7128(8)	609(44)
C(7*)	3378(8)	1474(7)	6986(13)	599(72)
C(8*)	3439(7)	1908(5)	6291(12)	455(59)
C(1P)	2981(9)	4567(7)	8751(14)	824(50)

Table 2 continued

Atom	*x/a*	*y/b*	*z/c*	U_{eq}^{a}
C(2P)	3442(10)	4456(7)	9711(14)	891(53)
C(3P)	3325(9)	3981(7)	10171(13)	805(47)
C(4P)	2824(10)	3622(8)	9692(15)	968(58)
C(5P)	2371(9)	3748(7)	8735(14)	875(52)
C(6P)	2432(10)	4235(8)	8233(15)	954(56)
N(1P)	3076(14)	5046(6)	8120(13)	2231(127)
O(1P)	3124(14)	5453(6)	8629(13)	1885(44)
O(2P)	2745(14)	5027(6)	7202(13)	1885(44)
N(2P)	3857(11)	3788(8)	11154(8)	1833(89)
O(3P)	3716(11)	3416(8)	11637(8)	1947(46)
O(4P)	4238(11)	4147(8)	11576(8)	1947(46)
N(3P)	1779(11)	3349(6)	8103(16)	1890(86)
O(5P)	1868(11)	3101(6)	7375(16)	2268(48)
O(6P)	1421(11)	3177(6)	8616(16)	2268(48)
O(7P)	1973(9)	4350(7)	7310(14)	1651(62)

[a] Equivalent Isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Interatomic bond distances and non-bonding contacts (Å) in the free ligand **3** and in the complexes **3•KPic** and **2b•KPic**

	3	*3•KPic*	*2b•KPic*
O(1A)...O(1C)	3.872(9)	4.86(1)	4.90(1)
O(1*)...O(3*)	5.93(4)	4.85(1)	4.66(1)
O(1A)...O(3*)	3.59(2)	2.85(1)	2.73(1)
O(1C)...O(1*)	3.58(2)	2.90(1)	2.81(1)
K—O(1A)		2.750(7)	2.76(1)
K...O(1B)		4.284(8)	2.64(1)
K—O(1C)		2.748(8)	2.78(1)
K—O(1D)		2.91(1)	2.67(1)
K—O(1*)		2.927(9)	2.87(1)
K—O(2*)		3.01(1)	2.83(1)
K—O(3*)		2.921(9)	2.80(1)
K...B_2		3.21(1)	

(B_2 is the barycentre of the phenolic ring B)

was searched by adjusting the orientation of the p-tert-butyl group of the ring B. A first set of calculations was carried out taking into account both van der Waals (E_1) and Coulombian (E_2) interactions respectively.

$$E_1 = \sum_{i,j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}}\right] \qquad [1]$$

$$E_2 = \sum_{i,j}\frac{q_i q_j}{r_{ij}} \qquad [2]$$

In Fig. 4(a) the global energy profile shows that the ring B lies in a broad local minimum so that a certain degree of static structural disorder should be expected to affect the ring B itself from the crystallographic study, but this was not the case. The role of the K^+ cation and of the phenyl ring B becomes more evident if the energy contribution coming from the energy that the electric dipoles induced by the K^+ electric field have in that field itself (E_3) is taken into account. Following Hopfinger[8] such a contribution, for a set of inducing charges q_j, is given by eq. [3].

$$E_3 = \sum_{i,j} q_j \frac{\mathbf{m}_i \bullet \mathbf{r}_{ij}}{r_{ij}^{3}} \text{ in which } \mathbf{m}_i = \alpha_i \sum_j \mathbf{e}_j \qquad [3]$$

Table 4 Conformational parameters in the free ligand **3** and in its potassium picrate complex **3•KPic**

Dihedral angles (°) of the phenolic units with respect to the molecular reference planes R in the calix[4]arene moieties according to ref. 3.

	3	***3KPic***
A-R	124.3(2)	109.2(4)
B-R	242.2(2)	245.8(5)
C-R	119.3(2)	109.8(3)
D-R	104.3(2)	112.0(3)

Conformational parameters (°) ϕ and χ according to ref. 4.

	3		***3KPic***	
	ϕ	χ	ϕ	χ
A-D	86(1)	-66(1)	71(2)	-74(2)
D-C	70(1)	-85(1)	75(2)	-76(2)
C-B	135.1(9)	136.2(8)	127(1)	136(1)
B-A	-133.7(9)	-143.5(9)	-133(1)	-127(1)

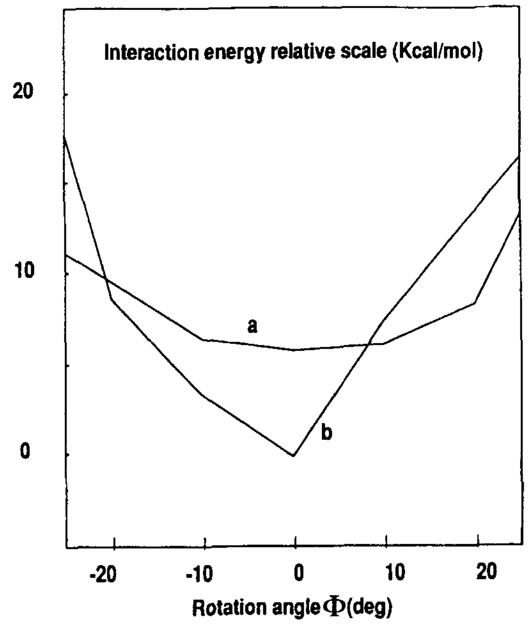

Figure 4 Potential energy of complex **3•KPic** as a function of the rigid rotations of Φ degrees of the phenolic ring B. Curve (a) $E_1 + E_2$. Curve (b) $E_1 + E_2 + E_3$.

In eq. [3] α_i are the coefficients of the atomic polarizability and $\mathbf{e}_j$ the electric field generated by q_j in $\mathbf{r}_i$. Fig. 4(b) shows the profile of the total potential energy $E_1 + E_2 + E_3$ and shows the energetical effects of the presence of the polarizable nucleus B at suitable distances from the cation. Considering the role of E_3, in our calculation this gives a net stabilizing contribution of almost 6 kcal/mol showing that the geomerical configuration observed in the solid state (Φ = 0°) take advantage from the K^+ induced-dipols interactions. It seems that the model here proposed to evaluate the K^+...aromatic interactions, compared with the "pseudoanion" model proposed by Dougherty[9], allows a better fitting of the decrease of the cation-π coupling with the distance.

The role of the preorganization of the partial cone stereoisomers

Since the molecular structures of the KPic complexes of **2a** and **4** are not available so far, we assume that in their complexes the polar cage around the cation has to be quite similar to that observed in **3•KPic** here reported. This is also supported by the observation that the K^+ cation in **3•KPic** is quite close to the barycentre B_1 of the four nearest neighbour oxygens O(1A), O(1C), O(1*), O(3*). The most significant structural deformations (δO...O, δB_1...O) required to achieve a molecular geometry of the polar cage of the free ligands **2a**, **3** and **4** that fit that of the complex **3•KPic** are indicated by the arrows in Fig. 1. Their values are summarized in Table 5.

Assuming the harmonic approxymation and a global force constant for the entire crown ether chain, for each ligand molecule the sum $\Sigma\delta^2$ roughly estimates the energy cost for the deformation of the host during the complexation. Assuming for the two independent molecules of **2a** a mean value of 2.117 for $\Sigma\delta^2$, the reported data (Tab. 5) show that the most preorganized[10] ligand is **2a** followed by **4** and **3**.

In agreement with this finding, the binding studies have shown that **2a** is indeed the most efficient and most potassium selective ligand in this series[1]. The dibenzyl derivative **4** was found to be the least efficient of all partial cone stereoisomers[1], thus indicating that steric effects of the *syn* oriented alkoxy groups decrease the stability of the complexes.

Another question is why the ligands in the partial cone and not those in the 1,3 alternate conformation prefer to bind the K^+ cation in this series of ligands derived from p-tertbutylcalix[4]arenes. The 1,3 alternate conformation, being less polar and less solvated, should maximize the cation-π interaction giving better ionophores as recently found in other calixarene ligands[11,12]. In this case two tert-butyl groups facing the crown moiety in the 1,3 alternate conformation probably decrease, for steric reasons, the stability of the complexes. For p-tertbutylcalix[4]arene derivatives, the partial cone structure seems to offer the best compromise between stabilizing cation-π interactions and destabilizing steric effects of the alkyl groups present in the *para* position, but the situation may change with p-H calix[4]arenes. We are currently investigating the effect of the alkyl substituents at the upper rim of the calix on the stability and structure of the calix[4]arene crown ethers potassium complexes.

EXPERIMENTAL SECTION

a) X-ray measurements

The crystal data and the most significant experimental details of the X-ray experiments are reported in Table 6. Although many efforts to obtain crystals suitable of accurate X-ray measurements, the crystals of compound **3** were of poor quality and showed a tendency to decompose.

Table 5 Most significant interatomic distances (Å) in the complex **3•KPic** and in the free ligands **3**, **2a** (two independent molecules I° and II°) and 4. (B_1 is the barycentre of the O(1A), O(1C), O(1*), O(3*) atoms.)

	3•KPic	*3*	*2a(I°)*	*2a(II°)*	*4*
O(1A)...O(1C)	4.86(1)	3.872(9)	3.97(2)	3.91(1)	3.82(1)
O(3*)...O(1*)	4.85(1)	5.93(4)	5.11(2)	5.50(2)	5.18(1)
O(1A)...O(3*)	2.85(1)	3.59(2)	3.50(2)	3.69(2)	3.54(1)
O(1C)...O(1*)	2.90(1)	3.58(2)	3.67(2)	3.47(2)	3.58(1)
B_1...O(1A)	2.82(1)	2.70(1)	2.78(2)	2.77(2)	2.82(1)
B_1...O(3*)	2.86(1)	3.34(3)	2.95(2)	3.19(2)	2.91(1)
B_1...O(1*)	2.83(1)	3.51(3)	3.26(2)	3.31(2)	3.33(1)
B_1...O(1C)	2.83(1)	2.47(2)	2.53(2)	2.46(2)	2.33(1)

Observed variations of the interatomic distances (Å) in the free ligand 3 and expected ones in the free ligands **2a** and **4** after complexation. In square brackets the sums of squares $\Sigma\delta^2$ (Å^2) are reported.

		3	*2a(I°)*	*2a(II°)*	*4*
δO(1A)...O(1C)		0.988	0.89	0.95	1.04
δ(O3*)...O(1*)		-1.08	-0.26	-0.65	-0.33
δO(1A)...O(3*)		-0.74	-0.65	-0.84	-0.69
δO(1C)...O(1*)		-0.68	-0.77	-0.57	-0.68
	$\Sigma\delta^2$	[3.153]	[1.879]	[2.355]	[2.129]
δB_1...O(1A)		0.12	0.04	0.05	0.00
δB_1...O(3*)		-0.48	-0.09	-0.033	-0.005
δB_1...O(1*)		-0.68	-0.43	-0.48	-0.50
δB_1...O(1C)		0.36	0.30	0.37	0.50

X-ray measurements were carried out at room temperature using Ni-filtered Cu-K_α radiation (λ = 1.54178 Å). During the data collection one standard reflection was monitored every hundred reflections. The maximum intensity variations were less than 15% for **3** and less than 5% for **3•KPic**. The intensities were determined by profile analysis according to Lehmann and Larsen[13] and corrected for Lorentz and polarization effect but not for absorption.

b) Structure analyses and refinements

The structure solutions were obtained by Direct Methods using SHELX86[14]. Both structures were refined by blocked full matrix least—squares methods using SHELX76[15] for a total of 272 + 397 parameters for **3** and 500 + 63 for **3•KPic**. In **3** and **3•KPic** all the tert-butyl groups were statistically distributed over two alternative orientations. Static disorder was also found in the crown chain of **3**, where both O(1*) and O(3*) were disordered in two different positions with occupancy factors of .54 and .46. In **3•KPic** the picrate anion was affected by severe disorder and was subjected to constrained least-squares refinement. Anisotropic displacement parameters for all non-hydrogen atoms, except the atoms affected by disorder, were refined for **3a**. For **3b** the lower number of observed reflections allowed to assign anisotropic displacement parameters only for the K^+ ion, the phenolic oxygens, the carbon atoms of the CH_2

Table 6 Experimental data for the X-ray diffraction studies

compound	***3***	***3-KPic***
crystal habit and colour	transparent prism	yellow prism
formula	$C_{58}H_{82}O_7$	$C_{64}H_{84}KN_3O_{14}$
cryst syst	monoclinic	monoclinic
space group	*C2/c*	*P2₁/n*
cell parameters at 295K[a]		
a,Å	31.196(3)	20.084(4)
b,Å	18.558(3)	24.723(4)
c,Å	22.208(2)	13.225(3)
α,deg	90	90
β,deg	120.47(2)	107.10(2)
γ,deg	90	90
V,Å^3	11081(3)	6276(2)
Z	8	4
D_{calcd},g cm^{-3}	1.068	1.226
mol wt	891.28	1158.48
cryst dimens, mm	0.3 × 0.2 × 0.5	0.5 × 0.2 × 0.3
linear abs coeff. cm^{-1}	5.043	12.54
diffractometer	Siemens AED	Siemens AED
diffraction geometry	equatorial	equatorial
scan type	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg/min	3÷12	3÷12
scan width, deg	see[b]	see[b]
radiation	Cu-Kα (1.54178 Å)	Cu-Kα (1.54178 Å)
2θ range, deg	6 ÷ 120	6 ÷ 120
reflcns measd	±h,±k,l	±h,k,l
total data measd	17082	10062
unique total data	8261	9331
criterion for obsn	$I \geq 2\sigma(I)$	$I \geq 2\sigma(I)$
obsd data measd	9470	4383
unique obsd data	4977	4158
agreement between equivalent obsd reflcns	0.03	0.09
No. of variables	669	563
max Δ/σ on last cycle	0.8	0.8
$R = \Sigma\vert\Delta F\vert/\Sigma\vert F_0\vert$	0.10	0.11
$R_w = \Sigma w^{1/2}\vert\Delta F\vert/\Sigma w^{1/2}\vert F_0\vert$	0.10	0.11
$GOF = [\Sigma w\vert\Delta F\vert^2/(NO\text{-}NV)]^{1/2}$	4.2	3

[a]Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections chosen from diverse regions of reciprocal space. [b]$(\theta - 0.6) - [\theta + (0.6 + \Delta\theta)]°$; $\Delta\theta = (\lambda\alpha_2 - \lambda\alpha_1)\lambda^{-1} \tan\theta$.

bridges and those of the isopropyl groups and for the atoms of the crown ether chain.

In both compounds the H atoms were taken in their calculated positions and refined "riding" on their carbon atoms.

The atomic scattering factors of the non-hydrogens were taken from Cromer and Waber[16], the values of Δf' and Δf" were those of Cromer[17]. The geometrical calculations were obtained by PARST[18].

Lists of atomic coordinates of hydrogen atoms, complete lists of bond distances and angles, displacement parameters and observed and calculated structure factors are available from F.U. upon request.

All the crystallography calculation were performed on the Gould 6040 powernode of Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. Parma, Italy.

Energy calculations were carried out on the Connection Machine at the Faculty of Engeneering of the University of Parma.

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