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Temperature Dependence of the Weak Host-guest Interactions in the *p*-tertbutylcalix[4]Arene 1:1 Toluene Complex

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The temperature dependence of the $CH_3 \ldots \pi$ host-guest interaction in the *p*-tertbutylcalix[4]arene 1:1 toluene complex has been investigated by comparison of its known molecular structure at room temperature (RT) with that at 220 K determined by single crystal X-ray diffraction. The diffraction pattern showed a phase transition when the temperature was decreased from 298 to 220 K.

The structure at 220 K could be solved assuming a twin by pseudo-merohedry with a fourfold twin axis [001] relating two monoclinic components with equal volumes of space group $P\ 112/a$ $a = b = 17.899(2)$, $c = 13.827(1)$ Å, $V = 4429.8(8)$ Å^3, $Z = 2$, mol. weight 741.06 a.m.u., $D_{calc} = 1.111$ g·cm^{-3}.

The structure refinement converged to $R1 = 0.103$ and $wR2 = 0.256$ for 1655 unique observed data.

The complex exists in two different conformations of the hosts which exhibit two different host-guest structural relationships both indicating that the most relevant differences induced by the low temperature are concerning the host-guest interaction mode.

Particularly unexpected is the different temperature dependence of the $CH_3 \ldots \pi$ interactions between the tert-butyl of the host and the aromatic moiety of the guest with respect to that of the van der Waals interactions. The $CH_3 \ldots \pi$ interactions, which stabilizes the complex at RT, strongly decrease as the temperature decreases.

Keywords: Crystal structure, calixarenes, host-guest interactions, $CH_3 \ldots \pi$ interactions

INTRODUCTION

One of the main goals of supramolecular chemistry is the use of noncovalent binding forces to obtain in selective way stable host-guest complexes. In the last few decades, several synthetic procedures have been developed with the aim of obtaining selective receptors able to bind, through specific host-guest interactions, ions and neutral molecules [1]. In particular, some classes of cyclic oligomers have proved to

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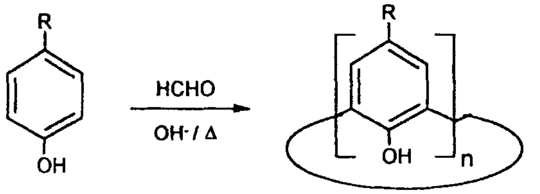
[*] Corresponding author.

act as good receptors for ions or neutral molecules. Among them, the calix[n]arenes 1 are widely used as molecular platforms on which functional groups with suitable binding sites can be introduced in the appropriate orientation for the selective binding of ions [2].



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On the other hand, the hydrophobic intramolecular cavity created by the *n*-phenolic units and by the *R* groups present at the *upper rim* of the calixarene, exhibits complexing properties towards neutral aromatic molecules as benzene, pyridine, toluene, xylene isomers and anisole. In fact, the solid state studies on calix[4]arene complexes at RT showed that they always exhibit high stability and that the aromatic guest molecule is held inside the intramolecular cavity of the calix[4]arene host [3, 4].

Guest selectivity properties, established by competitive crystallization experiments using *p*-tertbutylcalix[4]arene as host and equimolar mixtures of two competing aromatic guests, showed that benzene is always preferentially included and it is also remarkable that selective discrimination is observed between the xylene isomers being the *para*-xylene preferred over the the *meta* and *ortho* isomers [3]. Further solid state studies have also demonstrated that *p*-octylcalix[4]arene [5] shows no selectivity and is unable to distinguish between the xylene isomers due to the *exo-calix* complexation mode of the host. All these results indicate that the binding ability and the selectivity of the host calix[4]arene is a specific property of the intramolecular cavity created at the *upper rim*.

With the aim of exploring more deeply the origin of this property experienced by the intramolecular cavity, we undertook several INS (Inelasting Neutron Scattering) experiments on the *p*-tertbutylcalix[4]arene 1:1 toluene complex in the solid state. This allowed us to establish that the methyl group of toluene inside the intramolecular cavity of the host acts as a almost free quantum rotor from 2 to 60 K [6(a–d)]. The experiments allowed also the evaluation of the energy barrier exerted from the intramolecular cavity of the calix[4]arene host against the rotation of the methyl group of the toluene guest molecule. The pattern of the potential barrier could be described as a composition of a one-fold/two-fold symmetry in contrast with the expected four-fold symmetry showed by the calixarene host molecule in the solid state at RT.

It was also observed that the *p*-tertbutylcalix[4]arene 1:1 toluene complex undergoes a phase transition at $T = 248\,\mathrm{K}$. Here we report the crystal and molecular structure of this complex at $T = 220\,\mathrm{K}$ in order to understand the structural origin of the unexpected low symmetry of the host-guest potential energy barrier derived from the precise INS measurements.

RESULTS AND DISCUSSION

The complex exists in the two independent molecules both lying on a two-fold crystallographic axis which coincides with the C —CH_3 bonds of the toluene guest depicted in Figures 1a and 1b.

The final atomic coordinates are reported in Table I; bond lengths and angles are consistent with the different hybridization of the carbon atoms and it is not worth to mention them. The main attention should be focused on the conformational modifications induced by the phase transition with respect to the structure determined at RT [4].

AT 220 K the complex shows the loss of the perfect *cone* structure and decrease its symmetry passing from C_{4v} to C_{2v} according to the variable temperature ^{13}C NMR measurements [7]. Both the two independent molecules of the complex show a flattening of the aromatic pocket with

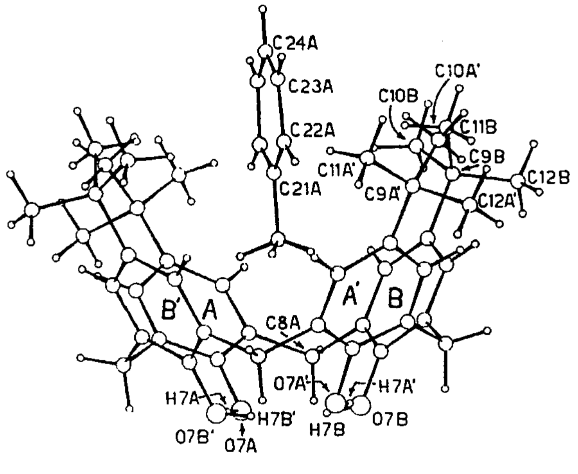

FIGURE 1a PLUTO view of the complex unit A-B-A'-B' at 220 K.

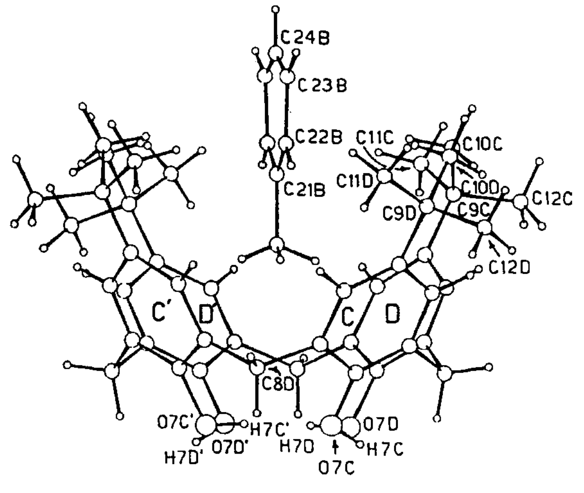

FIGURE 1b PLUTO view of the complex unit C-D-C'-D' at 220K.

two opposite phenolic unit A and A' pushed towards the exterior of the macroring whereas B and B' are pushed towards the interior. The dihedral angles between the phenolic rings and the reference molecular plane R, according to Ref. [8]., run from the unique value of 123.03(7)° at RT to 126.1(3)° (A-R) and 120.4(3)° (B-R) in one complex unit and to 119.4(3)° (C-R) and 124.3(3)° (D-R) thus justifying the presence of two independent molecules in the asymmetric unit.

The Conformational Parameters [9] reported in Table II give the unequivocal description of the molecular conformations of the two complex units. The *Symbolic Representation* of the molecular conformation of the two complex units according to the rules reported in Ref. [9] is C_2+ -,+ -.

However, it must be emphasized that the observed asymmetric distortion of the intramolecular cavity at low temperature is realized without significant perturbations of the intramolecular cyclic array of hydrogen bonds created by the four OH groups at the *lower rim* and whose geometrical parameters are reported in Table III. In particular, since the values of the interatomic O...O distances between adjacent oxygen atoms in both the two independent molecules of the complex are very close to the value of 2.67(1)Å observed at RT, it is expected that the conformational rearrangement at low temperature is mainly realized through a gain in the lattice energy rather than through a gain in the total potential energy of the complexes. This seems also confirmed by the calculated density that passes from 1.096 to 1.111 gcm^{-3} when the temperature is decreased. A perspective view of the molecular packing is shown in Figure 2.

We have already pointed out with experimental results [3, 10] and by calculations [11], that as driving force for the inclusion of aromatic molecules inside the intramolecular cavity of calix[4]arenes possessing *p*-tertbutyl groups, a specific attractive weak $CH_3 \ldots \pi$ interaction between the tert-butyl of the host and the aromatic moiety of the guest must be invoked and that host-guest interaction can be described by an effective potential derived from that proposed by Morse [11]. Thus, the present structural determination allows to understand how such host-guest interaction is temperature dependent.

First of all, the inclusion mode of the toluene is quite different in the two complex units at low temperature and significantly different from that observed at RT.

TABLE I Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^4$) with E.s.d.'s in parentheses for the non-hydrogen atoms of *p*-tertbutylcalix[4]arene 1:1 toluene complex at 220 K

	x/a	*y/b*	*z/c*	U_{eq}[a]
C1A	3928(6)	1153(6)	4115(9)	359(30)
C2A	3905(6)	467(6)	4510(9)	388(32)
C3A	4313(6)	−156(6)	4134(9)	388(31)
C4A	4742(6)	−3(6)	3333(9)	467(35)
C5A	4780(7)	705(7)	2894(9)	500(35)
C6A	4370(6)	1267(7)	3322(9)	448(34)
O7A	3487(5)	326(5)	5352(6)	481(23)
C8A	3434(7)	1768(6)	4547(9)	406(34)
C9A	5275(6)	818(6)	2027(9)	469(31)
C10A	5260(12)	215(11)	1312(16)	1090(60)
C11A	5145(11)	1533(10)	1540(16)	1216(62)
C12A	6113(8)	774(9)	2395(14)	939(47)
C1B	3636(6)	−1379(6)	4103(9)	383(31)
C2B	2907(6)	−1406(6)	4554(9)	389(32)
C3B	2357(6)	−1790(6)	4106(10)	433(32)
C4B	2487(7)	−2149(7)	3235(9)	463(32)
C5B	3178(7)	−2150(6)	2811(9)	443(32)
C6B	3747(6)	−1758(6)	3251(9)	365(31)
O7B	2830(5)	−1029(5)	5392(6)	505(24)
C8B	4282(7)	−945(7)	4514(10)	496(37)
C9B	3333(7)	−2540(7)	1815(11)	643(37)
C10B	2618(8)	−2771(8)	1325(13)	758(42)
C11B	3697(9)	−2004(9)	1087(13)	946(48)
C12B	3865(9)	−3171(9)	2006(13)	973(50)
C20A	2500(0)	0(0)	2693(13)	695(45)
C21A	2500(0)	0(0)	1643(10)	390(34)
C22A	1998(8)	−408(7)	1164(12)	768(41)
C23A	2023(10)	−417(9)	143(16)	1082(54)
C24A	2500(0)	0(0)	−320(20)	1051(67)
C1C	6114(6)	3837(6)	4231(9)	388(31)
C2C	6117(7)	4524(7)	4660(9)	472(34)
C3C	5742(6)	5161(6)	4228(10)	392(31)
C4C	5386(7)	5022(7)	3371(9)	470(33)
C5C	5377(7)	4328(7)	2895(10)	562(37)
C6C	5757(7)	3756(7)	3395(10)	562(38)
O7C	6482(5)	4664(5)	5545(6)	541(25)
C8C	6569(7)	3221(7)	4709(10)	433(34)
C9C	4974(6)	4191(7)	1971(9)	512(34)
C10C	5542(9)	3811(9)	1244(14)	970(50)
C11C	4658(10)	4886(10)	1495(15)	971(54)
C12C	4339(9)	3643(9)	2089(13)	939(49)
C1D	6367(7)	6412(7)	4260(10)	443(33)
C2D	7079(6)	6424(6)	4699(8)	363(31)
C3D	7632(6)	6824(6)	4286(10)	422(32)
C4D	7502(7)	7244(7)	3475(9)	462(33)
C5D	6806(6)	7249(6)	3039(8)	373(30)
C6D	6253(6)	6832(6)	3440(9)	395(32)
O7D	7174(5)	6007(5)	5514(6)	566(26)
C8D	5728(8)	5937(7)	4645(11)	541(38)
C9D	6665(7)	7757(7)	2156(11)	657(38)
C10D	7323(7)	7634(7)	1384(10)	575(35)
C11D	5943(9)	7639(9)	1687(14)	978(49)
C12D	6699(9)	8580(8)	2475(14)	998(50)
C20B	7500(0)	5000(0)	2755(15)	838(53)
C21B	7500(0)	5000(0)	1679(14)	704(47)
C22B	7971(10)	4536(9)	1202(15)	1025(52)
C23B	7930(13)	4537(13)	153(22)	1497(79)
C24B	7500(0)	5000(0)	−204(24)	1244(20)

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

TABLE II Conformational parameters ϕ and χ for the two independent complex units (°)

	ϕ	χ
Complex A-B-A'-B'		
B-A	89(1)	−93(1)
A-B'	89(1)	−82(1)
Complex C-D-C'-D'		
D-C	91(1)	−88(1)
C-D'	83(1)	−87(1)

In the two complexes at low temperature the distances from the toluene methyl carbon atom from the reference plane R are 2.54(2) Å for (complex A-B-A'-B') and 2.66(2)Å (complex C-D-C'-D') *vs.* 2.574(5) Å in the complex at RT. Thus, in the first complex the toluene penetrates more deeply in the intramolecular cavity, while in the other is more outside that in the complex at RT.

Quite different in the two complex units is also the orientation of the toluene ring with respect to the calixarene macroring. The dihedral angle between the toluene and a plane through the two fold axis and one CH_2 bridge (C21A-C24A-C8A; C21 B-C24B-C8D) is 22.3(4)° (complex A-B-A'-B') and 10.0(1)° (complex C-D-C'-D') *vs.* the value of 20.9(2)° at RT.

Such dramatic change in the reciprocal host-guest orientation is responsible of a relevant lengthening of the $C_{But}\cdots C_{toluene}$ host-guest interatomic contacts thus weakening the $CH_3\ldots\pi$ interactions at low temperature. In fact, such weak interaction that at RT was clearly indicated by short distance of 3.345(5) Å between one of the methyl group of the host and one C_{ph} of the toluene, increases up to a minimum of 3.75(2) Å in the C-D-C'-D' complex unit whereas in the other complex unit A-B-A'-B' the contacts are all greater than 4 Å (see Tab. IV) . Also the $C_{toluene}\cdots H_{tert\text{-}butyl}$ are significantly increased being all greater than 3.2 Å.

This indicates the different temperature dependence of the two driving forces for the intramolecular complexation of the toluene guest. As the temperature decreases the van der Waals forces, which depends on T^{-1}, increase whereas the $CH_3\ldots\pi$ interactions do not follow the same trend. Thus the calixarene host molecule is distorted mainly by the gain in the van der Waals lattice energy and the $CH_3\ldots\pi$ interactions decrease as the host-guest interatomic contacts increase, even if the toluene guest still remain included inside the intramolecular cavity of the host.

EXPERIMENTAL SECTION

(a) X-ray Measurements

The experiment was carried out at the Laue diffraction beamline [12] of the European Syn-

TABLE IV Shortest host-guest contacts (Å) in the two independent complex units

Complex A-B-A'-B'			
C10A...C22A	4.06(2)	C10B...C22A	4.38(2)
C10A...C23A	4.41(3)		
C11A...C22A	4.36(2)	C11B...C21A	4.25(2)
		C11B...C22A	4.17(2)
Complex C-D-C'-D'			
C10C...C21B	4.14(3)	C10D...C22B	3.75(2)
C10C...C22B	4.11(2)	C10D...C23B	4.10(3)
C10B...C23B	4.42(3)		
C11C...C22B	4.43(2)	C11D...C22B	4.25(2)

TABLE III Geometrical parameters for the cyclic intramolecular hydrogen bonds between OH groups

	Donor-H(Å)	Donor...Acceptor (Å)	Donor-H...Aceptor(°)
O7A-H7A...O7B	0.83(8)	2.69(1)	165.4(6)
O7B-H7B...O7A$^{(i)}$	0.83(8)	2.67(2)	154.9(6)
O7C-H7C...O7D	0.83(8)	2.70(1)	177.9(2)
O7D-H7D...O7C$^{(ii)}$	0.83(8)	2.69(1)	109.9(6)

Symmetry operations: (i) 1/2-*x*,−*y*,*z*; (ii) 1+1/2−*x*, 1−*y*,*z*.

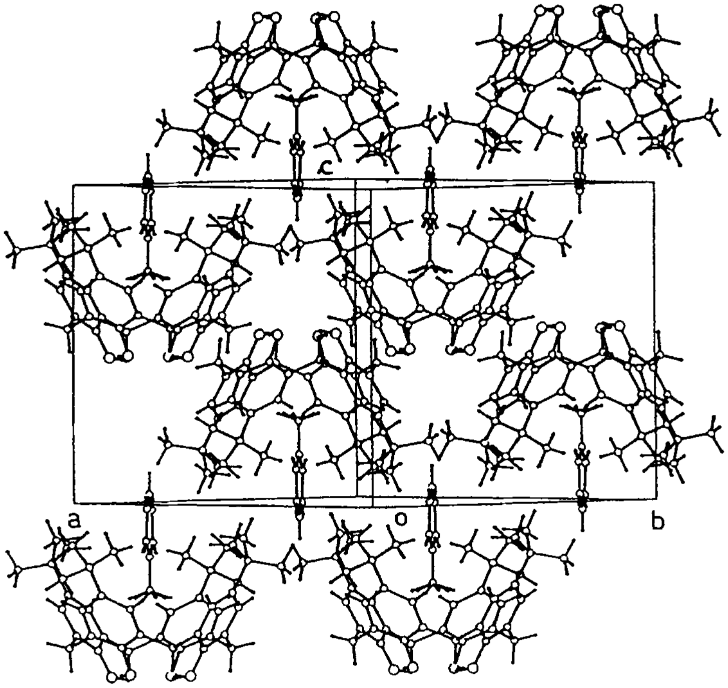

FIGURE 2 PLUTO view of the molecular packing of the complex at 220 K.

chrotron Radiation Facility (ESRF), Grenoble, France, using the rotating crystal method. The energy was kept fixed at 14.64 keV by using a Laue-Bragg silicon (111) monochromator, while the crystal was rotating around the vertical axis between 0 and 90 degrees, with an angular step of 5 degrees. Data were collected on a 30 cm MAR image plate mounted on the goniometer. The sample-to-detector distance amounted to 150 mm. Measurements were first performed at room temperature, and then at T=220 K where additional spots could be observed. The exposure time for each frame was 15 s. The temperature was regulated with a precision of 1 K *via* a nitrogen stream cryo-cooler.

(b) Structure Analysis and Refinement

The crystal data and the most significant experimental details and crystal structure refinement are reported in Table V. Data were reduced by the DENZO program [13]. The frames of the data collection at 220 K show a diffraction pattern with a 4/m tetragonal Laue symmetry. The spots were indexed assuming a primitive lattice with axes $a = 17.899(2)$ Å and $c = 13.827(1)$ Å. Attempts of solving the structure by direct methods based on several tetragonal 4/m space groups failed. The metric relations between the RT ($a = 12.756(2)$ Å, $c = 13.792(1)$ Å) and the 220 K lattices suggested the possibility of solving the structure at 220 K starting from the already solved RT structure [4]. In fact the two cells are strictly related: nearly the same c axis, and a ratio of about $\sqrt{2}$ times for the a axes. The RT structure was solved using the P4/n space group [4]. This structure revealed a fourfold symmetry axis running through the guest toluene molecule and the centre of the host p-tert-butylcalix[4]arene, so that 1/2 molecule of toluene and 1/4 of the p-tert-butylcalix[4]arene constitute the structurally independent unit. Furthermore, the independent tert-butyl group was found disordered in two positions. To obtain about the same cell in both cases, the primitive RT lattice has to be transformed into a centred C lattice taking as new *a* and *b* axes, the diagonals of the (001) face of the primitive cell. With this choice the conventional space group P4/*n* is transformed into the unconventional C4/*a* space group. However, at 220 K the diffraction pattern does not present the systematic absences of a C lattice, so that the space group should be P4/*a*. This space group cannot exist because of the incongruity between the symmetry operators (a four-fold axis perpendicular to an axial glide plane *a*). On the other hand, the four-fold axis does not permit the expected reorder of the guest toluene molecule with the phase transition. These two aspects suggested the presence of a transformation twin. In fact, the pseudo space group with P4/*a* symmetry can be simulated assuming a rotation twin with a four-fold twin axis [001] relating monoclinic components of space group P112/*a* (unique axis *c*). For equal volumes of the twin components, the diffraction pattern of this twin by pseudo-merohedry exhibits 4/m Laue symmetry. The electron density maps and the refinements of the structure showed two crystallographic independent host-guest complexes, intramolecularly related by a two-fold symmetry. Furthermore, the toluene molecules and the tert-butyl groups were both ordered. The structure was refined by the full-matrix least-squares method with isotropic thermal parameters for all non-H atoms and H atoms in calculated positions. Calculations were carried out by using the SHELX93 [14].

(c) Supplementary Material

Tables of the thermal parameters (Table SI), atomic coordinates of the hydrogen atoms (Table SII), complete list of bond lengths and angles (Table SIII) are available from F.U on request. They can also be obtained as standard. cif files by e-mail to the following address: ugoz@inpruniv.cce. unipr.it.

TABLE V Experimental data for the X-ray diffraction studies

Formula	$C_{51}H_{64}O_4$
cryst syst	monoclinic
space group	*P* 112/*a*
cell parameters at 220(1)K[a]	
a, Å	17.899(2)
b, Å	17.899(2)
c, Å	13.827(1)
α, deg	90
β, deg	90
γ, deg	90
V, $Å^3$	4429.8(8)
Z	4
Dcalcd, g cm^{-3}	1.111
F(000)	1608
mol wt	741.06
linear abs coeff, cm^{-1}	0.68
radiation (Sincrotron)	0.84700 Å)
2θ range, deg	3.84 to 45.14
Index ranges	$1\leq h\geq 16$
	$-10\leq k\geq 11$
	$0\leq l\geq 12$
Reflect. measd	1707
criterion for obsd	$1\geq 2\sigma(I)$
unique obsd data	1655
parameters, restraints	239,0
wR2 (all data)[b]	0.256
a, *b*[b]	0.2299, 5.7074
*R*1[I>4σ(I)][b] observed reflect.	0.1029
goodness-of-fit on F^2 (all data)[b]	1.418
maximum shift/σ	
peak, hole in final difference map, $eÅ^{-3}$	0.308, −0.219
extinction coefficient	
absolute structure parameter	

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30reflections found in a random search on the reciprocal space.

[b] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [\Sigma w(Fo^2\text{-}Fc^2)^2/\Sigma wFo^4]^{1/2}$. goodness-of-fit $= [\Sigma w(Fo^2\text{-}Fc^2)^2/(n\text{-}p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

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References

[1] Parker, D. (1996). (Ed.) *Macrocycle Synthesis, a practical Approach*, Oxford University Press, N.Y.

[2] (a) Vicens, J. and Böhmer, V. (1977). (Eds.) *Calixarenes. A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, The Netherlands 1991; (b) Gutsche, C. D, In: *Calixarenes*, Monograph in Supramo-

lecular Chemistry, **1**, Stoddart, J. F. (Ed.) The Royal Soc. of Chemistry, Cambridge 1989; (c) Ikeda, A. and Shinkai, S. (1997) *Chem. Rev.*, **97**, 1713.

[3] Ungaro, R., Arduini, A., Casnati, A., Ori, O., Pochini, A. and Ugozzoli, F. (1994). In: *Computational Approaches in Supramolecular Chemistry*, NATO ASI Series C, Mathematical and Physical Sciences, Vol. 426, 277, Georges Wipff Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands.

[4] Andreetti, G. D., Ungaro, R. and Pochini, A. (1979). *J. Chem. Soc. Chem. Comm.*, 1005.

[5] Andreetti, G.D, Pochini, A. and Ungaro, R. (1985). *J. Chem. Soc. Perkin Trans.*, **2**, 197.

[6] (a) Caciuffo, R., Francescangeli, O., Melone, S., Prager, M., Ugozzoli, F., Andreetti, G.D., Amoretti, G., Coddens, G. and Blank, H. (1992). *Physica B*, **180 and 181**, 691; (b) Caciuffo, R., Amoretti, G., Fillaux, F., Francescangeli, O., Melone, S., Prager, M. and Ugozzoli, F. (1993). *Chem. Phys. Lett.*, **201**, 427; (c) Prager, M., Caciuffo, R., Amoretti, G., Carlile, C. J., Coddens, G., Fillaux, F., Francescangeli, O. and Ugozzoli, F. (1994). *Mol. Phys.*, **81**, 609; (d) Caciuffo, R., Amoretti, G., Carlile, C. J., Fillaux, F., Francescangeli, O., Prager, M. and Ugozzoli, F. (1994). *Physica B*, **202**, 279.

[7] Facey, G. A., Dubois, R. H. and Zakrzewski, M. (1993). *Supr. Chem.*, **1**, 199.

[8] Perrin, M. and Oehler, D. (1992). In: *Calixarenes. A Versatile Class of Macrocyclic Compounds*, Vicens, J. and Böhmer, V. (Eds.), Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 65.

[9] Ugozzoli, F. and Andreetti, G. D. (1992). *J. Incl. Phen. and Mol Rec. in Chem.*, **13**, 337.

[10] Andreetti, G. D. and Ugozzoli, F. (1991). In: *Calixarenes. A Versatile Class of Macrocyclic Compunds*, Vicens, J. and Böhmer, V. (Eds.), Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 87.

[11] Andreetti, G.D., Ori, O., Ugozzoli, F., Alfieri, C., Pochini, A. and Ungaro, R. (1988). *J. Incl. Phenom.*, **6**, 523.

[12] Wulff, M., Ursby, T., Bourgeois, D., Schotte, F., Zontone, F. and Lorenzen, M. (1996). *J. Chem. Phys.*, **93**, 1915.

[13] Otwinowski, B. Oscillation Data Reduction Program, In: *Proceedings of the CCP4 Study Weekend: Data Collection and Processing*, 29–30 January 1993, Compiled by: Sawyer, L., Isaacs, N. and Bailey, S. SERC Daresbury Lab., England, p. 56.

[14] Sheldrick, G. M. (1993). SHELXL-93, *Program for Crystal Structure Refinement*, University of Göttingen, Germany.