Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 429 (2005) 111–117
thermochimica acta
www.elsevier.com/locate/tca

Thermo gravimetric analysis of supramolecular complexes of *p-tert*-butylcalix[6]arene and ammonium cations: crystal structure of diethylammonium complex

Márcio Lazzarotto[a,*], Francine Furtado Nachtigall[a], Egon Schnitzler[b],
Eduardo Ernesto Castellano[c]

[a] *Departamento de Química Orgânica, UFRGS, Av. Bento Gonçalves 9500, CEP 91501 970, C.P. 15003,*
Porto Alegre, Rio Grande do Sul, Brazil
[b] *Departamento de Química, Universidade Estadual de Ponta Grossa, Campus de Uvaranas, Av. General Carlos Cavalcanti 4748,*
CEP 84030 900 Ponta Grossa, Paraná, Brazil.
[c] *Departamento de Física, Universidade de São Paulo, São Carlos, Av. Trabalhador Sãocarlense 400, Centro, CEP 13566-590, São Carlos, SP, Brazil*

Received 22 March 2004; received in revised form 23 November 2004; accepted 23 November 2004
Available online 8 January 2005

Abstract

Thermo gravimetric analysis of ammonium-*p-tert*-butylcalix[6]arene salts were carried out to determine the stoichiometry of the inclusion compounds and the temperature of leaving of the ammonium cation, as amine, from the solid phase by a reverse proton transfer reaction to calixarene. The chain length of the amine molecules and their relative basicity order are the main factors which determine the decomplexation temperatures for the ammonium salts of piperidinium, diethylammonium, ethylenediammonium, morpholinium, *s*-butylammonium, butylammonium, hexylammonium and triethylammonium salts of *p-tert*-butylcalix[6]arene anion. The solid state structure of bis-diethylammonium-*p-tert*-butylcalix[6]arene dianion is reported. The calix moiety adopts a 1,2,3 alternate conformation, with one ammonium as *exo*-calix and other as *endo*-calix, with an intricate array of hydrogen bonds between phenol, phenolate and ammonium cations.

Keywords: Calixarenes; Supramolecular chemistry; Thermal analysis; Ammonium cations; Inclusion compounds

1. Introduction

Molecular inclusion has attracted an increased interest by the new properties of the included molecules and kinetic of decomplexation for controlled deliver of drugs [1]. Calixarenes and their derivatives [2] are synthetic receptors with a hydrophobic cavity which has the ability to interact by hydrogen bonding, C–H···π and N^+–H···π with a great variety of guests, [3] from apolar compounds as fullerenes [4] to charged molecules as metallic cations [5] and with organic [6] and inorganic anions [7]. These abilities make calixarenes suitable for the construction of selective sensors [8].

Complexes of ammonium cations with calixarenes are formed in solution, in *endo*- [9] or *exo*-calix position [10], with a complementary fit of the sizes of the calix cavity by the ammonium. Substitution of calixarene on *para*-position expands the size of the hydrophobic cavity and provides additional contact points for molecular interactions between host and guest. There are few examples of structures of salts of homooxacalixarene [11] or calixarene anions and ammonium cations determined by X-ray crystallography [12] and they show a variable position of the ammonium cation, which in some complexes bind the cavity by interactions with the π clouds and others only by hydrogen bonding to the phenolic oxygens.

Calix[6]arenes have been less studied than calix[4]arenes, due to the increase in conformational mobility, which de-

---

[*] Corresponding author. Tel.: +55 5133166284; fax: +55 5133167304.
E-mail address: marcio@iq.ufrgs.br (M. Lazzarotto).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.11.032

creases the pre-organization of the host and makes it more difficult to assign the structure of complexes and nature of the host–guest interactions in solution.

The aim of this work is to provide additional results on this kind of structure and molecular interactions and to use the thermo gravimetric analysis, not very often used in this context [13], to provide valuable insight on supramolecular interactions and particularly on the forces involved in complexation.

2. Experimental

The complexes of *p*-*tert*-butylcalix[6]arene and ammonium cations (Scheme 1) in solid phase were obtained by addition of the respective amine to a suspension of *p*-*tert*-butylcalix[6]arene in 95% ethanol (hexylamine, piperidine, butylamine, *s*-butylamine) or ethanol:acetonitrile (morpholine, diethylamine, dipropylamine, dibutylamine, triethylamine and ethylenediamine) mixtures, observing complete or partial solubilization. The amine added was in excess of 20:1 for all crystallization experiments, so that the overall ability of the proton transfer by the calixarene for each tested amine was reached. The solutions were filtered to remove unreacted calixarene and after slow evaporation of solvent, the colorless solid was filtered, washed out with hexane to remove the excess of amine, and stored in dry atmosphere by 1 week prior to the analysis.

The thermo gravimetric analysis were carried out using TGA TA2960SDT equipment. The average sample size was 5 mg and the nitrogen flow was maintained at 70 cm^3/min, with a constant heating ratio of 20 °C/min until 350 °C, when begins the decomposition of the *tert*-butyl-calix moiety. Amines were purchased from Sigma–Aldrich and *p*-*tert*-butylcalix[6]arene was synthesized as described in the literature.[14]

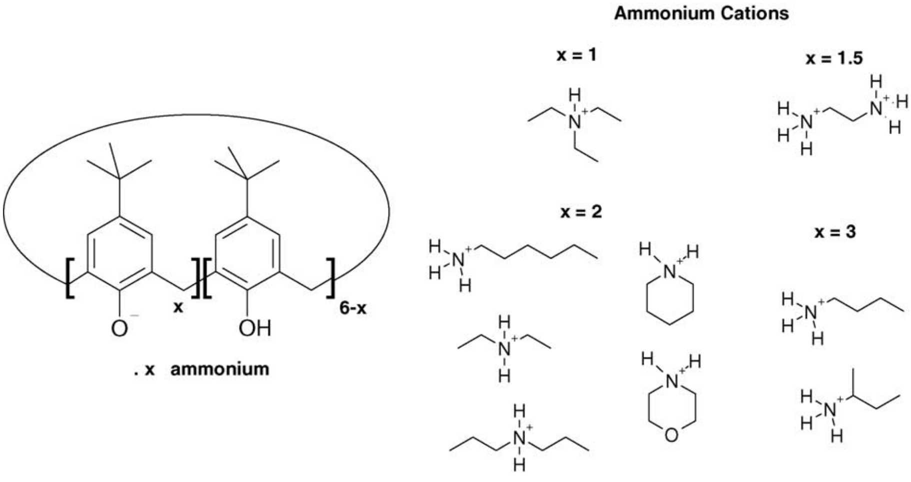
2.1. X-ray crystallographic study

Single crystals of the complex of bis-diethylammonium *p*-*tert*-butylcalix[6]arene diphenolate were obtained by slow evaporation of its acetonitrile/ethanolic solution. Data were collected on an Enraf–Nonius Kappa-CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), up to 50° in 2θ and final unit cell parameters were based on all reflections. The temperature was controlled using an Oxford Cryosystem low temperature device operating at 120 K. Data collection was carried out using the COLLECT program [15]. Integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [16,17], and numerical absorption corrections were performed. The structure was solved using direct methods with SHELXS-97 [18]. The model was refined by full-matrix least-squares on F^2 by with SHELXL-97. Hydrogen atoms were located on stereochemical grounds and refined with the riding model; for methyl and phenolic hydrogens, the rotating model was used. Hydrogen atoms were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the carbon to which each one is bonded; this percentage was set to 50% for the hydrogen atoms of methyl groups. One of the *t-butyl* groups was refined in two different positions of equal weight, rotated approximately 60 degrees from one another. Crystal structure has been deposited with the number 234165 on the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Thermal analysis behavior

The profile of the thermo gravimetric analysis of ammonium-calix[6]arene salts shows a weight loss between 140 and 210 °C, corresponding to the leave of the relative



Scheme 1. Ammonium *p*-*tert*-butylcalix[6]arene salts analyzed.

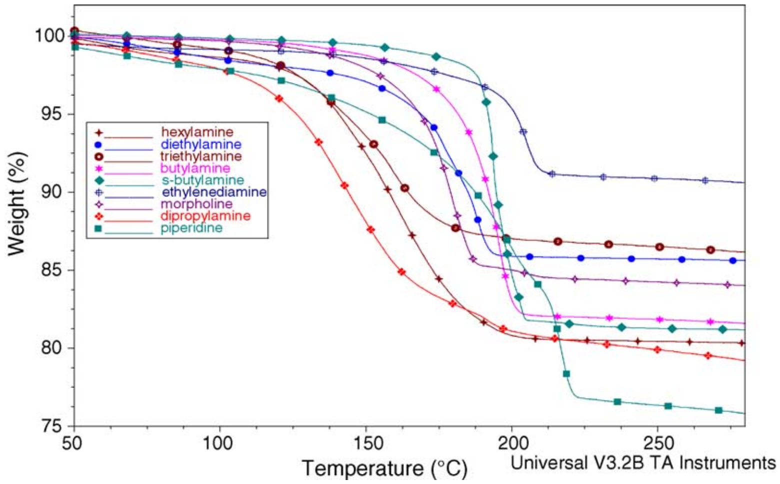


Fig. 1. Thermo gravimetric analysis profiles for ammonium calixarene complexes.

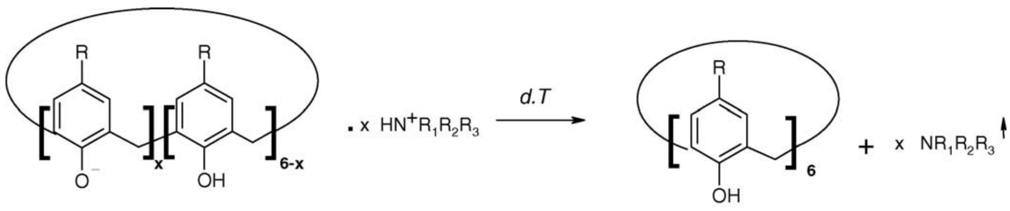
amine from the solid phase, as seen in Fig. 1. The data allow the determination of the stoichiometric ratio between calixarenes and ammonium cation in the solid phase, as well as the temperature of leaving of the amine or decomplexation temperature (*dT*) from the solid.

With raise of the temperature, there is a decomplexation of the ammonium cation, which leaves from the solid as amine, promoted by a reverse proton transfer from the ammonium cation for the calixarene moiety, as seen in Scheme 2. We can analyze the absolute values of *dT*, for comparison between the complexes, or the difference of the temperature from *dT*, and the boiling point of the amine ($\Delta t = dT - \text{bp}$), which reflects in a qualitative form, the molecular forces in solid phase between ammonium cation and calixarenes compared with the aggregation forces in the liquid phase. The values were assigned by differentiation of the TG curve and the maximum values are reported in Table 1.

Complexes of butylammonium cations have a high (3:1) stoichiometric relation with calixarenes, probably because the short chains of *n*-butyl and *s*-butylammonium are more able to accommodate in the free spaces of the crystal. The variable ratio of host:guest with the length of the chain is also described for complexes of calixarenes with alkanes [19]. Complexes of hexylammonium and secondary ammonium cations have a 2:1 stoichiometry for *p*-*tert*-butylcalix[6]arene and only triethylamine shows a 1:1 stoichiometric ratio, which is in apparent contrast with the 2:1 stoichiometry [20] of the calix[6]arene triethylammonium salt, of which structure was determined by X-ray crystallography. This difference should be related with the pK_a of both calixarenes, following the same trend of the pK_a order of *t*-butylphenol (pK_a = 10.9), which compared with phenol (pK_a = 9.9), is 10-fold less acid. So, the proton transfer for the amine is less effective for the *t*-butylcalix[6]arene than for calix[6]arene. This behavior do not be attributed for sterical effects, once than the salt of triethylammonium reported is *exo*-calix and is not proximal to the groups located at *para* position. The 1.5:1 stoichiometry of the ethylenediammonium complex should be related to a 3:2 structure, with one ethylenediammonium molecule interacting with more than one calix unit, but we were not able to obtain crystals suitable for X-ray analysis to confirm this hypothesis. Other inclusion compounds from

Table 1
values of decomplexation temperatures

Amine	Amine:calix	*dT* (°C)	bp (°C)	Δ*T* (°C)
Butylamine	3:1	196	78	118
s-Butylamine	3:1	194; 201	63	131; 138
Dibutylamine	2:1	136	159	−23
Diethyamine	2:1	176; 188	55	121; 133
Hexylamine	2:1	146; 178	132	12; 46
dipropylamine	2:1	142	110	32
Triethylamine	1:1	159	89	70
Piperidine	2:1	200; 217	106	92; 111
Morpholine	2:1	177	129	48
Ethylenediamine	3:2	200	118	82



Scheme 2. Decomplexation of ammonium cations by temperature.

calixarenes and diamines exhibits fractionary stoichiometry [21].

The relative order of *dT* for the different amines is dependent of several factors and it is often not possible to define which one is playing a major role. Piperidine and morpholine have similar structures and number of hydrogen atoms available to interact by hydrogen bonding, so the high *dT* value may be attributed to the relative basicity of the amines, which is higher for piperidine ($pK_{aH} = 11.22$) than for morpholine ($pK_{aH} = 8.36$) [22]. Piperidinium cation is more stable than morpholinium and remains as an ammonium cation in the solid until higher temperatures.

There is an unexpected decrease of *dT* for amines with longer chains, for which higher values were expected by their higher boiling temperatures of the corresponding amines. This effect may be exemplified for butylamine and hexylamine and for the series diethyl, dipropylamine and dibutylamine. This effect can not be related to pK_{aH} of the ammonium cations, which are very similar. This order may be related with the increase of repulsive van der Waals interactions of these ammonium cations in a crystal lattice, an effect which becomes more important for longest chains at higher temperatures in *endo*-calix, which imposes severe sterical restrictions to the complexed ammonium cationic species. The increase of atomic vibrations of the ammonium cations of longer chains will cause the collapse of the *endo*-complex, and the leave at lower temperature. This factor also operates for the low *dT* of triethylamine, whose branched structure is not expected to be well accommodated in the lattice.

The differences in the behavior of the longest chain amine complexes are more accentuated when ΔTs are analyzed, because in the liquid phase prevail attractive Van der Waals forces, which become more important with chain elongation.

Hexylamine, diethylamine, piperidine show two distinct values of *dT* for the corresponding ammonium cations in solid phase, indicating that the ammonium cations occupy non-equivalent places in the crystal cell of the solid phase. For the piperidinium salt, the DTA peaks were far enough to allow the integration of weight loss areas, which resulted identical for both values of *dT*, corresponding to the consecutive loss of amines at 198 and 217 °C, as seen in Fig. 2. For *s*-butylamine, the second weight loss appears only as a shoulder on the DTA profile.

This assertion is confirmed by the X-ray structure of the diethylammonium complex with *p*-*tert*-butylcalix[6]arene dianion reported below in this article, which reveals that the diethylammonium cations occupy different sites in the lattice. Above 350 °C, the profile of all analysis is identical for the *p*-*tert*-butylcalix[6]arene with loss of *t*-butyl, followed by decomposition of organic material.

Thermo gravimetric analysis of some ammonium-calixarene complexes shows weight losses prior to 100 °C: piperidine (2.5%), ethylenediamine (1%), dipropylamine (2%) and diethylamine (2.5%), attributed as solvent of crystallization, which correspond to less than one molecule per salt unit. The ethanol molecule is maintained in the crystal by hydrogen bonds with the calixarenes and the ammonium cation. The knowledge of the thermal stability of these complexes can provide a better understanding of the molecular forces and contribute to the development of specific sensors and sequestering agents for nitrogenated compounds. We are not able to compare the values of energy exchange by the variable stoichiometry of the complexes in the solid, but in all cases the leave of amine is endothermic by the loss of the ionic hydrogen bonds.

3.2. *X-ray structure of bis-diethylammonium-p-tert-butylcalix[6]arene dianion complex*

The X-ray diffractometric analysis shows that the *p*-*tert*-butylcalix[6]arene is in dianionic form with two diethylam-

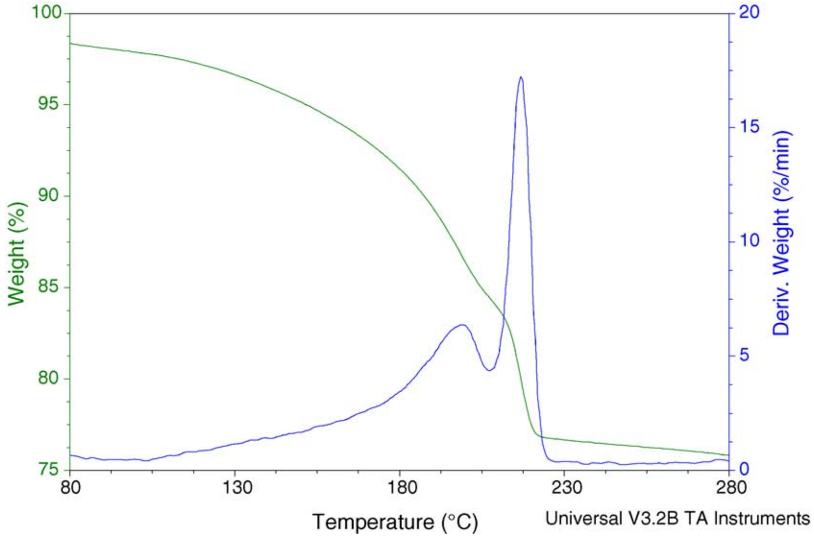


Fig. 2. Thermal analysis (TG, DTA and DSC) of bis-piperidinium-*p*-*tert*-butylcalix[6]arene dianion.

Table 2
Selected hydrogen bond lengths (Å) and angles (°) in the crystal structure of dihexylammonium–*p*-*tert*-butylcalix[6]arene diphenolate

Donor	Acceptor	D–A	D—H°···A
N7–H7B	O61	2.606(2)	176
N8–H8A	O21	2.743(3)	153
N8–H8B	O1	2.926(3)	168
O11–H11	O61	2.5920(19)	164
O21–H21	O31	2.455(2)	167
O41–H41	O31	2.577(2)	170
O51–H51	O61	2.590(2)	168

Table 3
Calixarene molecules generated by symmetry operations

Molecule/interaction	H···X	Distance H–X (Å)
Exo-diethylammonium		
N—H···π	H7A···C51[a]	2.5914
N—H···π	H7A···C52[a]	2.4544
C—H···π	H72A···C35	2.8932
C—H···π	H74A···C61[b]	2.6811
C—H···π	H74A···C66[b]	2.8628
Endo-diethylammonium		
C—H···O	H82A···O41	2.5941
C—H···π	H81A···C15	2.8421
C—H···π	H82B···C62	2.8793
C—H···π	H84B···C52	2.7787
C—H···π	H84B···C53	2.7368

[a] $x, (1/2)-y, -(1/2)+z$.
[b] $1-x, -(1/2)+y, (1/2)+z$.

monium cations, which supports the finding from the TGA analysis. The solvent molecules of ethanol and acetonitrile are very labile after removal of the crystals from the mother liquor, which required the use of protective oil in mounting the sample for X-ray data measurements.

Diethylammonium cations are located at different places in the unit cell, one of them out (*exo*-ammonium) of the calix cavity and the other included in the inner space (*endo*-ammonium) defined by the benzene rings of the calixarene. The calix[6]arene dianion adopts a 1,2,3 alternate conformation, forming two *semi-calixes* sub-structures with one of them occupied by one diethylammonium and the other is empty.

Phenolate oxygens are in distal positions, forming two OH···O$^-$···HO arrays of hydrogen bonds, with short distances between oxygen atoms, as reported in Table 2. The intricate hydrogen bond network is shown (top vision) in Fig. 3. The angle formed by the two *semi-calixes* was measured as the angle between planes defined by their methylene units (C12′, C23′, C34′, C45′, and C12′, C61′, C56′, C45′) and has the value of 230.43(5)°.

The *exo*-diethylammonium unit is located parallel to the aromatic ring of one phenolate of the calixarene molecule shown in asymmetric unit and has one C–H···π contact with this one (H72A···C35). Furthermore, it interacts with a second calixarene molecule through one hydrogen bond to the phenolate oxygen O61 and C–H···π interactions, and with a third calixarene molecule though N–H···π contacts (Tables 2 and 3).

Endo-ammonium interacts by hydrogen bonds with one of the phenolic units and with ethanol, that also interacts with other phenolic unit (Table 2). Furthermore, the diethylammonium molecule has C–H···O (H82A···O41) and C–H···π

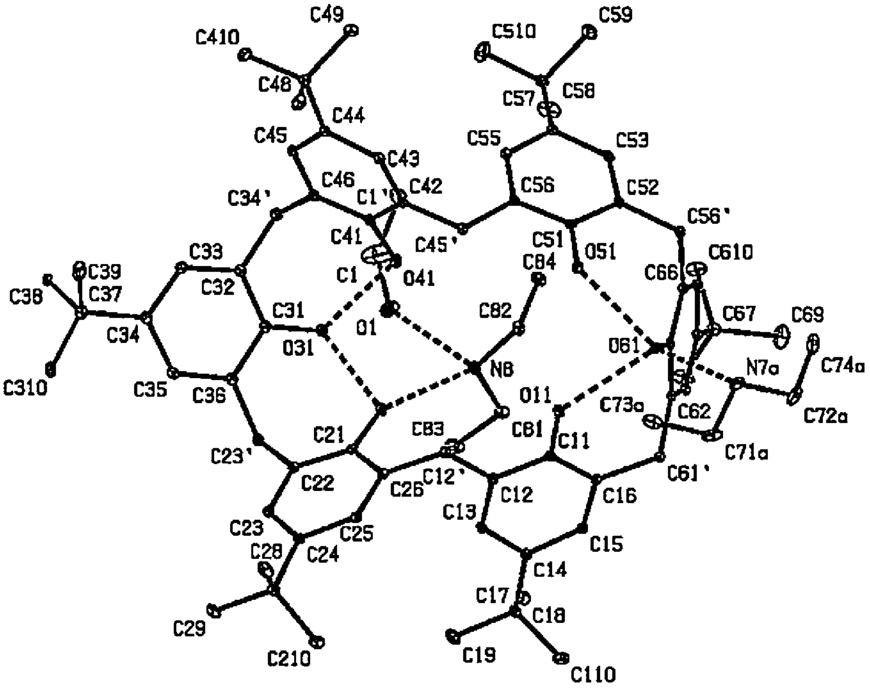


Fig. 3. Hydrogen bond network formed by calix unit, *endo*-diethylammonium, *exo*-diethylammonium (generated by symmetry: $1-x, (1/2)+y, (1/2)-z$) and ethanol, as described in Table 2. Acetonitrile molecule and hydrogen atoms omitted for clarity.

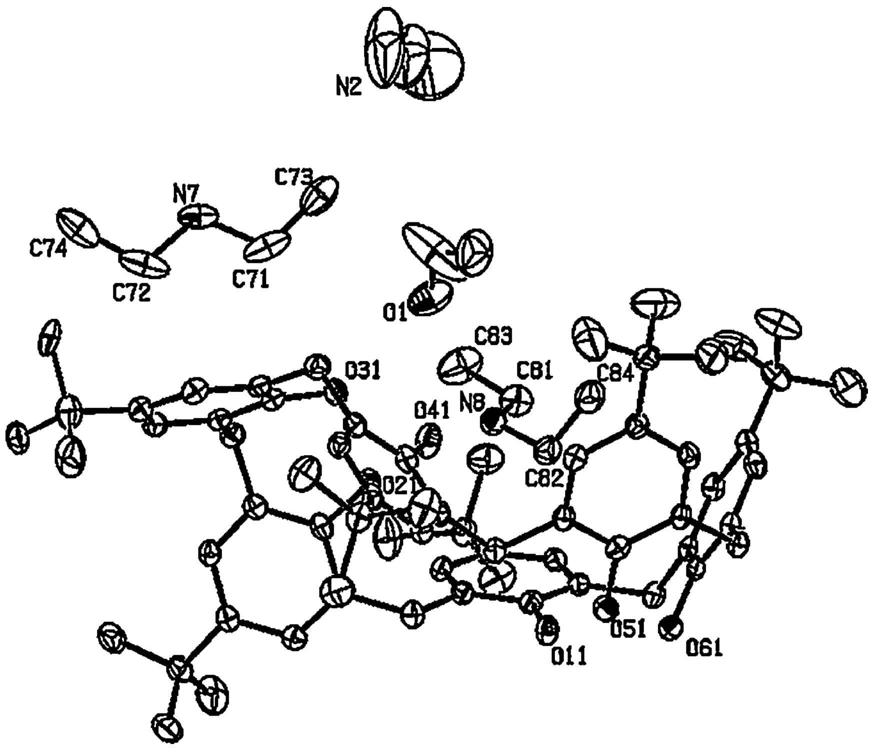


Fig. 4. ORTEP diagram of the *p-tert*-butylcalix[6]arene dianion bis(diethylammonium)acetonitrile. Ethanol structure.

contacts with benzene rings of the semi-calix in which it is included (Table 3). The molecule of *endo*-ammonium is bent with an approximately gauche conformation (torsion angle of 79.6(3)° for C81–N8–C82–C84) due to the sterical crowding by the calixarene benzene ring bound to O51, as shows the ORTEP diagram in Fig. 4.

Crystal data: $C_{66}H_{82}O_6$, $2(C_4H_{12}N)$, C_2H_6O, C_2H_3N; FW = 1205.72, crystal size: 0.12 mm × 0.20 mm × 0.20 mm, monoclinic, $P21/c$, $Z = 4$, $\mu_{\mathrm{Mo}} = 0.069\,\mathrm{mm}^{-1}$, $a = 12.5880(10)$ Å, $b = 22.6890(10)$ Å, $c = 25.9040(10)$ Å; $\beta = 102.400(10)°$, $V = 7225.8(7)$ Å^3, 12689 reflections measured, 8951 unique, $R(\mathrm{int}) = 0.0590$, final $R1 = 0.0941$.

4. Conclusions

Thermo gravimetric analysis is a valuable tool for the analysis of inclusion compounds of calixarenes, providing also a comprehensive method to analyze qualitatively the trends of molecular forces involved in the complexation. The ammonium-*p-tert*-butylcalix[6]arene complexes from aliphatic amines have a variable stoichiometry in solid state, and the amine:calix ratio is higher for amines of shorter chain. The increase of temperature promotes a reverse acid–base reaction, with the loss of the amine of the solid, and the temperature of leaving of the amine decreases for longest chain amines. The X-ray structure of diethylammonium salt shows one *endo*-ammonium, linked by hydrogen bonds and C–H···π interactions.

Acknowledgements

The authors gratefully acknowledge the financial support from CNPq-CTPetro and PROSET.

References

[1] F. Giordano, C. Novak, J.R. Moyano, Thermochim. Acta 380 (2001) 123.
[2] (a) R. Ungaro, L. Mandolini (Eds.), Calixarenes in Action, Imperial College Press, London, 2000;
(b) R. Ludwig, N.T.K. Dzung, Sensors 2 (2002) 397.
[3] F. Sansone, E. Chierici, A. Casnati, R. Ungaro, Org. Biomol. Chem. 1 (2003) 1802.
[4] (a) B.S. Sherigara, W. Kutner, F. D'Souza, Electroanalytical 15 (2003) 753;
(b) T. Haino, H. Araki, Y. Fujiwara, Y. Tanimoto, Y. Fukazawa, Chem. Commun. (2002) 2148.
[5] W. Abraham, J. Incl Phenom. Macromol. 43 (2002) 159.
[6] F. Sansone, L. Baldini, A. Casnati, M. Lazzarotto, F. Ugozzoli, R. Ungaro, Proc. Natl. Acad. Sci. USA 99 (2002) 4842.
[7] A. Casnati, L. Pirondini, N. Pelizzi, R. Ungaro, Supramol. Chem. 12 (2000) 53.
[8] (a) R. Pinalli, F.F. Nachtigall, F. Ugozzoli, E. Dalcanale, Angew. Chem. Int. Ed. 38 (1999) 2377;
(b) E.J. Kim, J.I. Choe, S.K. Chang, Tetrahedron Lett. 44 (2003) 5299;
(c) R.F. Ziessel, L.J. Charbonniere, M. Cesario, T. Prange, M. Guardigli, A. Roda, A. Van Dorsselaer, H. Nierengarten, Supramol. Chem. 15 (2003) 277.
[9] (a) G. De Salvo, G. Gattuso, A. Notti, M.F. Parisi, S. Pappalardo, J. Org. Chem. 67 (2002) 684;
(b) S. Pappalardo, M.F. Parisi, J. Org. Chem. 61 (1996) 8724.

[10] F.F. Nachtigall, M. Lazzarotto, F. Nome, J. Brazil. Chem. Soc. 12 (2001) 255.

[11] (a) B. Masci, M. Nierlich, P. Thuery, New J. Chem. 26 (2002) 766;
(b) B. Masci, M. Nierlich, P. Thuery, New. J. Chem. 26 (2002) 120.

[12] (a) F.F. Nachtigall, M. Lazzarotto, F. Nome, I. Vencato, Acta Crystallogr. C 54 (1998) 1007;
(b) P. Thuery, Z. Asfari, M. Nierlich, J. Vicens, Acta Crystallogr. C 58 (2002) O223–O225;
(c) J.M. Harrowfield, W.R. Richmond, A.N. Sobolev, J. Incl. Phenom. Macro. 19 (1994) 257.

[13] (a) J. Schatz, F. Schildbach, A. Lentz, S. Rastätter, J. Chem. Soc., Perkin Trans. 2 (1998) 75;
(b) F. Benevelli, A. Bond, M. Duer, J. Klinowski, Phys. Chem. Chem. Phys. 2 (2000) 3977.

[14] C.D. Gutsche, L. Lin, Tetrahedron 42 (1986) 1633.

[15] Enraf-Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 1997–2000.

[16] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276, Academic press, New York, pp. 307–326.

[17] P. Coppens, L. Leiserowitz, D. Rabinovich, Acta Crystallogr. 18 (1965) 1035.

[18] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.

[19] K.A. Udachin, G.D. Enright, E.B. Brouwer, J.A. Ripmeester, J. Supramol. Chem. 1 (2001) 97.

[20] P. Thuery, N. Keller, M. Lance, J.D. Vigner, M. Nierlich, J. Incl. Phenom. Macro. 20 (1994) 89.

[21] E.B. Brouwer, K.A. Udachin, G.D. Enright, J.A. Ripmeester, Chem. Commun. 19 (2000) 1905.

[22] H.K. Hall Jr., J. Am. Chem. Soc. 79 (1957) 5441.