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A thiourea calix[6]arene-based synthon that generates a supramolecular porous crystal structure

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The role of intra- and intermolecular interactions which lead to the self-assembly in a porous crystalline structure of a thiourea-based calix[6]arene synthon containing three thiourea groups, has been investigated by X-ray diffraction and quantum chemical calculations.

Keywords: calix[6]arenes; self-assembly; X-ray diffraction; quantum chemical calculations; thioureas

1. Introduction

Because of their extreme versatility, calix[n]arenes have been extensively employed as molecular platform to orient in space functional groups and binding sites yielding a large variety of receptors for ions and neutral molecules (1). More recently, they demonstrated their potential also for the construction of self-assembled supramolecular species (2). In this latter context, non-covalent intermolecular interactions have been exploited as driving force for the formation and for the design of dimeric (3) or tubular (4)supramolecular architectures. We have recently shown that heteroditopic calix[4]arene and calix[6]arene derivatives, when mixed with suitable ion pair-based guests, may give rise to highly ordered aggregates of self-assembled capsules (5) and oriented channels (6) in the solid state. Among the several non-covalent interactions responsible of the formation of these supramolecular architectures, the bifurcated H-bonding between the phenylurea moieties present on the wide rim of these macrocycles and the anion of the ion pairs plays a fundamental role. On the other side, the role that these urea-type additional binding units play on the conformational preferences of the macrocycles and on the tuning of their self-assembly properties has been far less studied. Based also on our previous studies on model ureatype compounds (7), herein we report on the structural and quantum mechanical studies of a thiourea-based calix[6] arene compound whose molecular conformation allows the self-organisation in one-dimensional polymeric chains via multiple intra- and intermolecular hydrogen bonds. The self-assembly of the polymeric chains in the crystal lattice generates a porous crystalline structure.

2. Results and discussion

The thiourea calix[6]arene **5** was prepared using the synthetic pathway illustrated in Scheme 1 and fully characterised through NMR and mass measurements.

Crystals suitable for X-ray diffraction measurements were obtained from slow evaporation of a solution of **5** in toluene. The single crystal X-ray structure is illustrated in Figure 1. The macrocycle is blocked in a '1,2,3-alternate' conformation by the two intramolecular hydrogen bonds involving the thiourea nitrogen atoms N2A and N2E (see Table 1).

The stronger N2E-H···O2C attraction [H···O1C 2.142(2) Å] involves the ether oxygen O2C blocking the phenolic rings E and C in the mutual transorientation. At the same time, the weaker intramolecular hydrogen bond N2A-H···O1B [H···O1B 2.470(2)Å] orients the phenolic ring B in trans with respect to ring A. In such a way, the role of the two intramolecular hydrogen bonds becomes pivotal for the pre-organisation of the macrocycle towards two different kinds of non-covalent intermolecular interactions between individual calix[6]arenes. This leads to very large spatial separations between the three thiourea groups. In particular, those at rings A and E are exposed at the molecular surface with their donor N1-H and acceptor S1 groups available for multiple cooperative hydrogen bonding. The third thiourea group at the phenolic ring C protrudes outside the macroring acting as a long 'tong' towards the neighbouring calix[6]arene via hydrogen bonds through their N2-H and S1 groups as illustrated in Figure 1.

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Scheme 1.

The complete and unequivocal description of the conformation of the macrocycle is accounted by both the dihedral angles δ between the weighted least-squares plane through the four methylene bridging groups which link the six aromatic rings and the weighted least-squares planes through the six benzene rings (8) and by the conformational parameters ϕ and χ (*1b*, 9) collected in Table 2. The sequence of signs of ϕ and χ indicates that the symbolic representation of the molecular conformation of the macrocycle is C_1++ , -+, --, +-, +-, --,



Figure 1. (Colour online) Stick view of the molecular conformation of **5**. Elements mapping: C, white circles; O, dark grey circles; N, white circles with grids; S, shaded large white circles. Only relevant hydrogen atoms are reported for clarity (small white circles). Intramolecular hydrogen bonds evidenced by dashed lines.

Table 1. Intra- and intermolecular hydrogen bonds in 5.

Bond	D···A (Å)	H···A (Å)	D−H···A (°)
$\begin{array}{c} \hline N2A - H \cdots O1B^{a} \\ N2E - H \cdots O2C^{a} \\ N2C - H \cdots S1C^{b} \\ N1A - H \cdots S1E^{c} \\ N1E - H \cdots S1A^{c} \end{array}$	3.185(3)	2.470(2)	138.8(2)
	2.946(3)	2.142(2)	151.6(2)
	3.271(3)	2.492(1)	147.8(2)
	3.297(3)	2.476(1)	155.6(2)
	3.357(3)	2.537(1)	155.5(2)

^a Intramolecular hydrogen bond.

^b Symmetry equivalent: -x - 1, -y, 1 - z.

^c Symmetry equivalent: -x, 1 - y, -z.

In the symmetry-expanded structure, infinite onedimensional polymeric chains are generated by two different sets of four and two hydrogen bonds, respectively, as illustrated in Figure 2. The four hydrogen bonds allow the formation of a centrosymmetric dimer due to one calix[6]arene which donates the two N1A—H and N1E—H hydrogen bonds to the acceptor sulphur atoms

Table 2. Dihedral angles δ (°) between the molecular reference plane R (the weighted least-squares plane through the four CH₂ groups which link the four aromatic rings) and the weighted leastsquares planes of the benzene rings; conformational parameters ϕ and χ (°) in the molecular structures of **5**.

	δ (°)		ϕ (°)	χ (°)
R^A	80.7(5)	A–B	93.6(3)	97.5(4)
R^B	291.5(8)	B-C	-10.9(4)	88.7(5)
R^C	216.4(6)	C–D	-94.3(4)	31.7(3)
R^D	282.1(6)	D-E	-105.1(5)	-93.8(4)
R^E	80.7(7)	E-F	28.7(3)	- 81.9(4)



Figure 2. (Colour online) Perspective view of the one-dimensional polymeric chain of **5** with intermolecular hydrogen bonds evidenced by dashed lines (crystallographic centres of symmetry evidenced by black spots).

S1E and S1A of the adjacent calix[6]arene at the equivalent position -x, 1 - y, -z. At the same time, it accepts with its S1E and S1A the hydrogen bonds donated by the N1A—H and N1E—H groups of the symmetry-related calix[6]arene at the equivalent position -x, 1 - y, -z.

As shown in Figure 2, the two thiourea groups which protrude from both sides of the dimer at the phenolic rings C become the structure-directing factor for the self-assembly of the dimers in infinite one-dimensional polymeric chains via two hydrogen bonds: the N2C-H group donates the hydrogen bond to the acceptor sulphur atom S1C of the nearest neighbouring dimer at the equivalent position -x - 1, -y, 1 - z; vice versa, the N2C—H group donates the hydrogen bond to the sulphur S1C atom of the previous dimer. It is noteworthy that the four and two sets of multiple hydrogen bonds lie on two non-equivalent crystallographic inversion centres as shown in Figure 2. However, the mechanistic hypothesis that the self-assembly in dimers occurs prior polymerisation, is based on the assumption that a greater driving force is expected for four hydrogen bonds rather than for two. To give a theoretical ground to our hypothesis, the binding processes for dimerisation and polymerisation were investigated separately by quantum chemical calculations. To this purpose, due to the enormous number of atoms which prevents the use of rich basis sets, the quantum mechanical calculations were carried out with a semiempirical method at PM6 level (10). After having minimised the molecular geometry of the monomer, two models have been selected: complex A for calculation of the binding energy under polymerisation and complex B for calculation of the binding energy involved in the dimerisation process. The two structures were then minimised and their final geometries are shown in Figure 3. The calculated binding energies are -29.78 kJ/mol in complex A and -90.24 kJ/mol in complex B, confirming that the highest attraction (the energy is more negative) occurs in the dimerisation of calix[6]arenes via four hydrogen bonds. However, such difference between the two energy values suggests that the greater attraction between the two calix[6]arenes in complex B is due to the contribution of other weak non-covalent interactions beside hydrogen bonds.

In order to highlight this aspect, we performed extensive quantum chemical calculations addressed to a characterisation of the electron density displacement $\Delta \rho(x, y, z)$ during the formation of complexes A and B. More in detail, $\Delta \rho(x, y, z)$ (calculated as difference between the electron density of the complex and those of the individual monomers) is a measure of the electronic charge that is accumulated or depleted at each point within the complex and provides directly the whole spatial extent of the charge fluctuation. In this way, the chemical meaning of $\Delta \rho(x, y, z)$, is free from the arbitrariness inherent in any charge decomposition model. The isosurfaces of the $\Delta \rho(x, x)$ y, z) maps for complexes A and B are plotted in Figure 3 and clearly show that in complex A the charge shift occurs only within the region of the two hydrogen bonds. On the contrary, due to the close proximity between monomers in complex B, the charge shift is not restricted to the four



Figure 3. (Colour online) Calculated isosurfaces at 0.0008 *el* bohr³ of the charge displacement $\Delta \rho(x, y, z)$ in complex A (top) and B (bottom). The total displaced charge is 0.61 and 1.57 *e*, respectively. Colours: violet, positive $\Delta \rho$ values (accumulation of charge); brown, negative $\Delta \rho$ values (depletion of charge).



Figure 4. (Colour online) Stick view of 27 unit cells $(3a \cdot 3b \cdot 3c)$ showing the self-assembly of 5 in the crystal lattice. The voids left by the tubular pores running along the crystallographic *a*-axis are evidenced by dashed circles.

hydrogen bonds but it spreads as far as the macrocycles, suggesting that the mutual polarisation between monomers also contributes to stabilise the complex. This is also supported by the calculation of the total amount of displaced electric charge: 0.61 and 1.57e in the two complexes. All these theoretical results support the hypothesis that the final observed crystal structure is the result of the polymerisation process after dimerisation. The symmetry expansion extended to 27 unit cells $(3a \cdot 3b \cdot 3c)$ shows a tertiary structure generated by the self-assembly of the one-dimensional polymeric chains in the crystal lattice as depicted in Figure 4. The polymeric chains, elongated parallel to the crystallographic bc plane, generate a porous structure with the channels running along the crystallographic a-axis. This justifies the calculated density value $(0.899 \text{ g} \times \text{cm}^{-3})$ lower than what could be expected for an organic compound. The estimated percentage of volume of the tubular pores does correspond to the 10% of the cell.

3. Conclusions

The urea-type moieties attached to the wide rim of a calyx [6]arene have been exploited to make the conformation of the macrocycles pre-organised for their self-assembly in infinite polymeric chains. X-ray diffraction analysis on single crystal has shown that thiourea groups are not only responsible of the 1,2,3-alternate conformation of the macrocycle via intramolecular hydrogen bonds, but also of the formation of one-dimensional polymeric chains of dimers via intermolecular hydrogen bonds. A porous crystalline structure is generated as tertiary structure by the

self-assembly of the polymeric chains in the crystal lattice. Quantum mechanical calculations have been carried out to demonstrate that polymerisation process should follow the formation of the dimers, the latter being more energetically favoured with respect to the polymerisation.

4. Experimental

4.1 General

All reactions were carried out under nitrogen; all solvents were freshly distilled under nitrogen and stored over molecular sieves for at least 3 h prior to use. Chemical shifts reported are referred either to the tetramethylsilane or residual solved resonances. ESI-MS spectra were recorded with a Waters Acquity UPLC system (Waters Corporation, Milford, MA, USA). Melting points are uncorrected and were recorded with an Electrothermal instrument (Bibby Scientific Limited, Stone, Staffordshire, UK). Silica gel layers (SiO₂, Merck 60 F254, Merck KGaA, Darmstadt, Germany) were used for thin layer chromatography. A 60 Å silica gel (Merck, 0.04– 0.063 mm, 230-240 mesh) were used for column chromatography. Compounds 3 and 4 were synthesised according to reported procedures (11). All other reagents were of reagent grade quality as obtained from commercial suppliers and were used without further purification.

4.2 Synthesis

4.2.1 Tris-(N-phenylthioureido)calix[6]arene (5)

To a solution of calix[4]arene 5 (0.8 g, 0.7 mmol) in dry CH_2Cl_2 (25 ml), phenyl isothiocyanate (0.5 g, 3.7 mmol)

was added. After stirring overnight at room temperature, the reaction was quenched by the addition of 20 ml of water. The organic phase was separated, dried over anhydrous Na₂SO₄ and evaporated to dryness under reduced pressure. Pure compound **5** was obtained in 20% yield after chromatographic separation of the residue (*n*-hexane:ethyl acetate = 3:2) as pale yellow solid. mp > 300°C; ¹H NMR (300 MHz, CDCl₃): δ 8.5 (br. s, 3H), 8.2 (br. s, 3H), 7.8–7.7 (m, 6H), 6.4 (br. s, 6H), 4.7 (br. s, 6H), 4.0 (br. s, 6H), 3.6 (br. s, 6H), 3.6–3.5 (m, 12H), 2.6 (br. s, 9H); 1.36 (s, 27H), 1.25 (t, 9H, J = 7 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 154.6, 153.5, 146.7, 138.0, 136.4, 132.8, 129.5, 128.9, 127.9, 125.9, 124.7, 118.2, 72.3, 69.8, 66.9, 60.8, 34.3, 31.6, 15.3; MS (ESI): *m/z* (%): 1537 (100) [M + Na]⁺.

4.3 X-ray crystallographic analysis

Crystal data and experimental details for data collection and structure refinement are reported in Table 3. The crystal structure of **5** was determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at 190(2) K on a Bruker APEX II (Mo K α radiation $\lambda = 0.71073$ Å) equipped with a charge-coupled device (CCD) area detector and a graphite monochromator. Orientation matrices and unit-cell parameters were improved by least-square refinement of reflections, integrated with SAINT (*12*) taken from the entire data-

Table 3. Crystal data and structure refinement information for **5**.

Chemical formula	$C_{90}H_{108}N_6O_9S_3$
Formula weight	1514.058
Crystal system	Triclinic
Space group	P - 1
a (Å)	15.401(9)
b (Å)	15.986(9)
<i>c</i> (Å)	24.510(9)
α (°)	82.96(1)
β (°)	78.21(1)
γ (°)	71.64(1)
$V(Å^3)$	5595(5)
Z	2
$\rho_{\text{calc.}}$ (g/cm ³)	0.899
$\mu (\mathrm{cm}^{-1})$	1.111 (Mo Kα)
2θ max for data collection (°)	49.35
Temperature (K)	190
Data collected (h, k, l)	(-17, -18, -28) to $(17, 18, 28)$
Total reflections	56,093
Unique reflections	56,093 $(R_{\rm int} = 0)$
Observed reflections	$13,795 [F_{o} > 4.0\sigma(F_{o})]$
Data/restraints/parameters	56,093/15/881
Goodness-of-fit on F^{2a}	0.510
Final <i>R</i> indices (obs. data) ^b	$R_1 = 0.0652, wR_2 = 0.0066$
Largest diff. peak and hole $(e/Å^{-3})$	0.40/-0.26

^a Goodness-of-fit $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters. ^b $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

set. Final unit cell constants were calculated using SAINT on the final merged data-sets. All the data were corrected for Lorenz, polarisation and absorption using SADABS (13). The structure was solved by direct methods using the SIR2004 program (14) and refined on F_0^2 by full-matrix least-squares procedures using the SHELXL-97 program (15) in the WinGX suite (16). All non-hydrogen atoms were refined with anisotropic atomic displacements excepting the carbon atoms of the benzene ring attached to N2C and the five carbon atoms of the ether chains which were refined with isotropic atomic displacements. The hydrogen atoms were included in the refinement at idealised geometry (C-H 0.95 Å) and refined 'riding' on the corresponding parent atoms with isotropic atomic displacement 1.2 times that of the parent atom. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_0^2]$. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication no. CCDC-928852 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk).

4.4 Calculations

All calculations were carried out with the Gaussian 09 program (17) using the semiempirical PM6 method. The calculation of the electron density difference $\Delta \rho(x, y, z)$ three-dimensional map was carried out with the pixel method: the cubes of the electron densities of the dimer and of those of the two individual monomers were generated at the PM6 level using a grid of $0.2 \times 0.2 \times 0.2$ Å (the volume of each pixel was of 0.008 Å³) and the $\Delta \rho(x, y, z)$ z) cube was calculated by subtracting pixel by pixel the electron densities of the two monomers from the electron density of the dimer, and this leads to regions where the electron density increases (positive $\Delta \rho$ values) and regions depleted of electron density (negative $\Delta \rho$ values). The total displaced charge in a dimer was calculated as a sum over all the positive $\Delta \rho$ values in the cube of the $\Delta \rho(x, y, z)$. This value is of course equal to the sum over all the negative $\Delta \rho$ values in the cube.

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