

Three conformational polymorphs and order–disorder phase transition in a calix[4]arene bis(crown)

PIERRE THUÉRY,^{a,*} MARTINE NIERLICH,^a ROBERTO CALEMCZUK,^b MOHAMED SAADIOUI,^c ZOUHAIR ASFARI^c
AND JACQUES VICENS^c

^aCEA/Saclay, DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France, ^bCEA/Grenoble, DRFMC/SPSMS, Laboratoire de Cryophysique, 17 rue des Martyrs, 38054 Grenoble, France, and ^cECPM, Laboratoire de Chimie des Interactions Moléculaires Spécifiques (CNRS URA 405), 1 rue Blaise Pascal, 67008 Strasbourg, France. E-mail: thury@drecam.cea.fr

(Received 15 January 1998; accepted 7 July 1998)

Abstract

Three polymorphs of a calix[4]arene fixed in the 1,3-alternate conformation by two bridges, a crown-6 on one side and a crown-6 including a photoisomerizable azobenzene unit on the other, 8,11,14,28,31,34,37,40,-43,57,60,63-dodecaoxa-2,3-diazanonacyclo[62.2.2.2^{4,7}.-1^{16,45}.1^{26,55}.0^{15,20}.0^{22,27}.0^{44,49}.0^{51,56}]doheptaconta-1(66),2,-4,6,15,17,19,22,24,26,44,46,48,51,53,55,64,67,69-nonadecene, have been characterized by single-crystal X-ray diffraction. In all the polymorphs the azobenzene group is in the more stable *trans* conformation. The polymorphism arises from the high conformational flexibility of the bridges, which are arranged differently and are highly disordered in the two monoclinic forms (1) and (2a). Form (2a) presents a phase transition near 268 (2) K, leading to a triclinic form (2b), differing from the high-temperature form by some ordering of the chains and a subsequent reduction in crystallographic site multiplicity. The evolution of the cell parameters and peak width with temperature has been investigated down to 173 (2) K. Adiabatic calorimetry measurements indicate a smooth transition centered at 265.0 (1) K, with a heat capacity jump of 60 mJ g⁻¹ K⁻¹, suggesting a second-order nature for the transition.

1. Introduction

The design and synthesis of macrocyclic molecules directed to the selective binding of metal cations has been a field of continuous interest since the discovery of crown ethers and cryptands. The extensively investigated family of calixarenes provides a wide range of derivatives available for such a purpose (Gutsche, 1989; Vicens & Böhmer, 1991). Among these compounds, calix[4]arene fixed in the 1,3-alternate conformation by crown-6 ether bridges has been shown to be a cation extractant with a high selectivity for caesium over sodium, which could be used for caesium recovery from

radioactive waste resulting from nuclear reprocessing (Ungaro *et al.*, 1994; Casnati *et al.*, 1995; Asfari *et al.*, 1995; Asfari, Nierlich *et al.*, 1996). We have determined the crystal structures of some of these ligands and their alkali-metal-ion complexes, with the aim of better understanding the origins of this selectivity, which we have attributed to high complementarity and pre-organization of the ligands in the case of caesium complexation (Thuéry, Nierlich, Bressot *et al.*, 1996; Asfari, Naumann *et al.*, 1996; Thuéry, Nierlich, Lamare *et al.*, 1996, 1997; Thuéry, Nierlich, Bryan *et al.*, 1997). More recently we have investigated the crystal structures of such compounds in which one of the ether bridges includes a *cis/trans* photoisomerizable azobenzene unit (Saadioui, Asfari, Thuéry *et al.*, 1997; Thuéry, Lance *et al.*, 1997): the introduction of such a photo-responsive group could lead to photocontrol of ion complexation. The crown ether chains in all these compounds always retain high flexibility in solution. Molecular dynamics simulations have shown that, in the absence of interactions with complexed solvent molecules or metal cations, the crown conformation was fluctuating among the many possibilities (Thuéry, Nierlich, Bryan *et al.*, 1997). However, in the crystal structures reported up to now, concerning uncomplexed as well as solvent or cation complexed forms, little disorder has been observed. This is not the case for the three polymorphs of an azobenzene-containing calix[4]arene bis(crown) reported here. Polymorphism in organic substances, a far more general trend than once imagined, has been the subject of some recent reviews (Bernstein, 1987; Dunitz, 1995; Dunitz & Bernstein, 1995) and has also been discussed in relation to crystal engineering (Desiraju, 1989). Concerning phase transitions, it has been reported recently that only 65 cases of structure determinations of more than one phase were present in the Cambridge Structural Database (Hager *et al.*, 1998). To our knowledge, the present case is the first report of polymorphism and phase transition phenomena in the domain of calixarene chemistry.

2. Experimental

2.1. Synthesis

The azobenzene-containing calix[4]arene bis(crown), represented in Fig. 1, was prepared as described elsewhere (Saadioui, Reynier *et al.*, 1997). Orange single crystals of low crystallographic quality were obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ [compound (1)]. To improve their quality these crystals were further recrystallized from CHCl_3 , which gave a polymorphic modification (2). As often seen with such compounds (and particularly in this case involving highly disordered molecules, see later), it has not been possible to obtain the high-quality crystals necessary for accurate crystal structure determinations to be performed.

2.2. Structure determinations

For the diffraction experiments the crystals were encapsulated in Lindemann glass capillaries. Low-temperature measurements were performed with an Enraf–Nonius FR558NH nitrogen cryostat. An interval of ~ 1 h was allowed before each variable temperature measurement to enable equilibrium to be reached.

All structures were solved by direct methods with *SHELXS86* (Sheldrick, 1985, 1990) and refined with *SHELXTL93* (Sheldrick, 1993). Whereas the calixarene moiety itself is in all cases perfectly ordered, the bridges, affected by an important disorder and high displacement parameters, have proven difficult to model. In several parts of the crowns two fragments have been identified, including up to six atoms. All atoms were refined anisotropically, except those of the disordered parts of

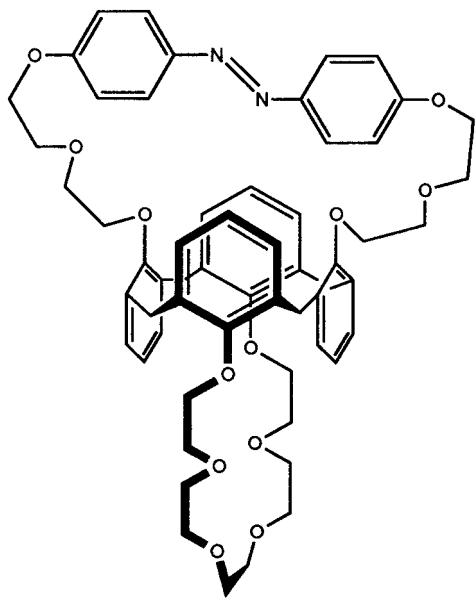


Fig. 1. Schematic representation of the calix[4]arene bis(crown) under study.

the molecules. These were refined isotropically, with occupation factors constrained to sum to unity (the occupation factors were also constrained to be equal for atoms pertaining to the same fragment of a disordered part). Soft restraints were applied to displacement parameters when necessary. For the three compounds the low data quality resulted in some abnormal bond lengths in the disordered parts of the crowns; these bond lengths were restrained to standard values: O–C 1.426 (10) and C–C 1.53 (1) Å (Allen *et al.*, 1995). Some angles were also abnormal: the 1··3 distances defining such angles were thus restrained to 2.36 (1) (C··C) or 2.39 (1) Å (O··C). These restraints resulted in satisfactory geometries, at the expense of an increase (up to 0.015) in the agreement factors. H atoms were introduced, except for the disordered parts, at calculated positions and constrained to ride on their parent C atoms (C–H 0.97 Å for CH_2 , 0.93 Å for $\text{C}_{\text{ar}}\text{—H}$, displacement factor equal to 1.2 times that of the parent C atom). Experimental details are given in Table 1.† Special details concerning the refinements are listed below.

(1): The geometry of the azobenzene group was particularly unsatisfactory, the two N atoms having an N–N distance shorter than usual. Being unstable on refinement, they were fixed in the last refinement cycles. The last difference Fourier map shows a single peak at $1.49 \text{ e } \text{Å}^{-3}$ which could be attributed to a second position for N(1), in agreement with high values of the displacement parameters for the phenyl rings: two positions of N(1) and of the attached aromatic ring, symmetrical with respect to the C–N(2) bond direction and both corresponding to *trans* geometries, could exist, but the poor data did not enable this disorder to be resolved. The bond distances in the aromatic rings of the diazo moiety were restrained to 1.39 (1) Å and the N– C_{ar} distances to 1.43 (1) Å.

(2a): The two positions of C(28) [bonded to O(11)] were unstable on refinement. They were given fixed occupation factors (0.5) and displacement parameters (0.15 Å^2).

(2b): The asymmetric unit comprises two independent molecules (*A* and *B*), in which the disordered atoms are labelled *I*, *J* and *K*, *L*, respectively. Owing to the low temperature used for data collection (213 K), the refinement is more satisfactory than the preceding ones.

2.3. Calorimetric measurements

The calorimeter design allows an improved version of the adiabatic continuous heating technique. The heat capacity c is given by $c = P/(dT/dt)$. The approximately constant power P is set to obtain a predetermined average heating rate. The instantaneous heating rate

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0547). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

	(1)	(2a)	(2b)
Crystal data			
Chemical formula	C ₅₈ H ₆₄ N ₂ O ₁₂	C ₅₈ H ₆₄ N ₂ O ₁₂	C ₅₈ H ₆₄ N ₂ O ₁₂
Chemical formula weight	981.11	981.11	981.11
Cell setting	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.667 (4)	20.341 (6)	20.285 (8)
<i>b</i> (Å)	18.647 (11)	11.709 (3)	11.608 (4)
<i>c</i> (Å)	20.188 (6)	23.875 (8)	23.894 (6)
α (°)	90	90	92.22 (3)
β (°)	90.72 (2)	112.39 (2)	112.32 (2)
γ (°)	90	90	87.81 (3)
<i>V</i> (Å ³)	5144 (4)	5258 (3)	5199 (3)
<i>Z</i>	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.267	1.239	1.253
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25
θ range (°)	8–12	8–12	8–12
μ (mm ⁻¹)	0.088	0.086	0.087
Temperature (K)	243 (2)	273 (2)	213 (2)
Crystal form	Parallelepiped	Parallelepipedic	Parallelepipedic
Crystal size (mm)	0.70 × 0.60 × 0.50	0.65 × 0.60 × 0.50	0.65 × 0.60 × 0.50
Crystal color	Orange	Orange	Orange
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None
No. of measured reflections	6514	7559	13 177
No. of independent reflections	6301	7304	12 513
No. of observed reflections	2449	3495	8852
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	0.02	0.017	0.0209
θ _{max} (°)	22	23	23
Range of <i>h, k, l</i>	0 → <i>h</i> → 14 0 → <i>k</i> → 19 –21 → <i>l</i> → 21	0 → <i>h</i> → 22 0 → <i>k</i> → 12 –26 → <i>l</i> → 24	–22 → <i>h</i> → 22 0 → <i>k</i> → 12 –26 → <i>l</i> → 26
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 60 min	Every 60 min	Every 60 min
Intensity decay (%)	4.7	0.4	5.6
Refinement			
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$	0.1273	0.1074	0.0797
<i>wR</i> (<i>F</i> ²)	0.3155	0.2800	0.2086
<i>S</i>	1.363	1.227	1.015
No. of reflections used in refinement	4701	5696	12 460
No. of parameters used	628	636	1290
H-atom treatment	See text	See text	See text
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1798P)^2 + 16.0150P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1516P)^2 + 13.1365P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1351P)^2 + 11.9644P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.019	0.016	0.019
$\Delta\rho$ _{max} (e Å ⁻³)	1.493	0.564	0.659
$\Delta\rho$ _{min} (e Å ⁻³)	–0.597	–0.334	–0.501
Extinction method	None	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1995, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1995, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1995, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	<i>CAD-4 Software</i> (Enraf–Nonius, 1989)	<i>CAD-4 Software</i> (Enraf–Nonius, 1989)	<i>CAD-4 Software</i> (Enraf–Nonius, 1989)

Table 1 (*cont.*)

	(1)	(2a)	(2b)
Cell refinement	CAD-4 Software (Enraf-Nonius, 1989)	CAD-4 Software (Enraf-Nonius, 1989)	CAD-4 Software (Enraf-Nonius, 1989)
Data reduction	MolEN (Fair, 1990)	MolEN (Fair, 1990)	MolEN (Fair, 1990)

reflects the variations of the heat capacity. The sample is attached to a sapphire sample holder using Rhodorsil grease. A platinum film thermometer and a heater made from a chip resistor are glued to the back of the sapphire. A chromel-constantan thermocouple monitors the temperature difference between the sapphire and the inner adiabatic shield. A second thermocouple measures the temperature difference between the inner and the outer shields. The assembly is mounted on a plug that ensures both electrical and thermal connections. The thermal shields are independently regulated. The inner one follows the temperature of the sample and the outer one is kept a few degrees lower. Uncontrolled heat exchange occurs as a result of thermal e.m.f.'s in the thermocouple circuits, gas desorption, radiation through pumping lines, AC heating (RF and/or 50 Hz), temperature gradients in the shields *etc.* The residual power is measured every 25 K, interpolated and taken into account. The resulting correction affects the specific heat typically by 0.3%, using a 0.2 g sample and a heating rate of approximately 0.01 K s^{-1} . The heat capacity of the empty sample holder was measured repeatedly for evaluation of the reproducibility. Approximate values are 0.02 J K^{-1} at 100 K and 0.1 J K^{-1} at 300 K. The r.m.s. (root mean square) scatter is typically below 0.1% and more than 1500 independent data may be obtained from a single run. The difference between two runs is $\pm 0.2\%$ (peak-to-peak) between 60 and 250 K. Accuracy was estimated by measuring a 0.3 g high-purity copper sample (99.990%) between 20 and 300 K. The deviation with respect to published values (Martin, 1987) is a smooth S-shaped curve with zero values at 40, 100 and 300 K. It never exceeds $\pm 1\%$ (peak-to-peak) between 25 and 300 K.

The heat capacity measurement in the present case has been performed three times, with satisfying reproducibility, in the increasing temperature mode (0.5 to 1 K min^{-1}). A 5.40 mg sample of the compound under study, composed of several single crystals attached to a glass holder by small quantities of Dow Corning high-vacuum grease, was used. The contribution of the sample environment has been removed from the data.

3. Results and discussion

At room temperature two polymorphic modifications, corresponding to (1) and (2a), are observed. Polymorph (1) retains its structure at least down to 243 (2) K, the temperature at which the structure was determined: no

cell measurement has been performed at lower temperatures, the crystals of (1) having been transformed to (2a) upon recrystallization. The structure of (2a) was determined at 273 K, since this compound undergoes a phase transition at 268 K, leading to another polymorphic modification (2b).

3.1. Comparison of polymorphs (1) and (2a)

As is often the case (Dunitz & Bernstein, 1995) the conditions for obtaining a particular polymorphic form are unfortunately not clear and probably depend on the solvent used and the temperature of crystallization. Both polymorphs crystallize in the monoclinic system, with the same space group, but unrelated cell parameters. The cell volumes at 295 K are 5197 (4) and 5298 (3) \AA^3 for (1) and (2a), respectively: this 2% difference and the corresponding density difference, although small, are significant. Empirically, the internal energy among polymorphs is inversely proportional to the crystal density (Dunitz, 1995), which may indicate a slightly lower internal energy for polymorph (1) in our case.

The azobenzene group is in the more stable *trans* conformation in both (1) and (2a). We have shown previously that the azobenzene conformation depends on the chain length and the calixarene conformation (Thuéry, Lance *et al.*, 1997): the *trans* conformation has already been found to be more stable for a chain containing six O atoms and a calixarene in the 1,3-alternate conformation; on the other hand, shorter chains (four O atoms) or the calixarene cone conformation can stabilize the *cis* form.

As illustrated in Figs. 2 and 4, the molecules in the two phases differ in a clear cut manner by the crown conformations. The crown including the azobenzene group is bent more towards the calixarene moiety in (1) than in (2a). In (1) it adopts a geometry comparable to that already observed for the same chain and a similar 1,3-alternate calixarene conformation (Thuéry, Lance *et al.*, 1997). The crown conformation in (2a) is more unusual, such a 'vertical' position being restricted up to now to shorter chains. Some atoms of the azobenzene-containing crown ether chain are disordered over two sites in both structures. This is also the case for the unsubstituted crown-6 bridge, for which the overall differences between the two structures are less important than for the azobenzene-containing chain.

The crystal packings of (1) and (2*a*) are unrelated to each other. However, the molecular conformations are so strongly different that the polymorphism cannot be considered, as for rigid molecules, as the manifestation of alternative ways of close packing of an unchanged molecule. The present case clearly belongs to the category of conformational polymorphism: the intermolecular interactions from which the crystal stabilization derives are known to be sufficient to bring

about torsional or conformational changes in the molecular structure (Desiraju, 1989), the conformation found in the solid state not necessarily being the lowest energy in solution. Such a phenomenon is likely to happen in highly flexible compounds such as that under study, in which numerous conformations of the crown ether chains, which differ in their torsion angles, are close on the energy scale.

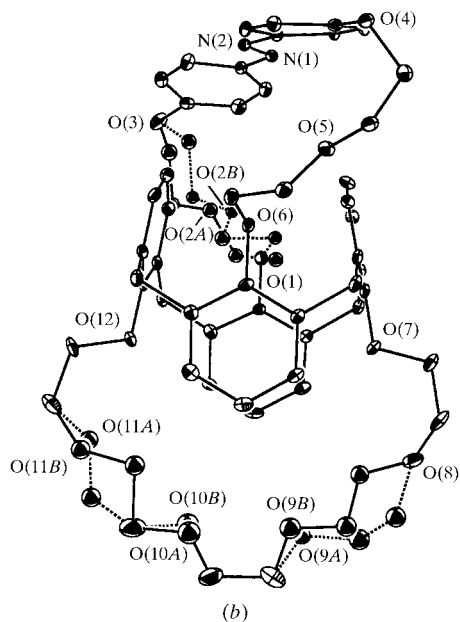
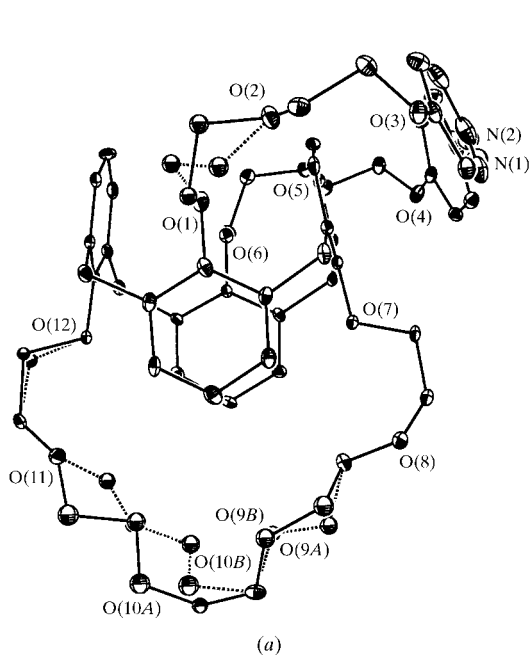


Fig. 2. Molecular units in (a) (1) and (b) (2*a*). H atoms have been omitted. One of the disordered positions is represented by dashed lines.

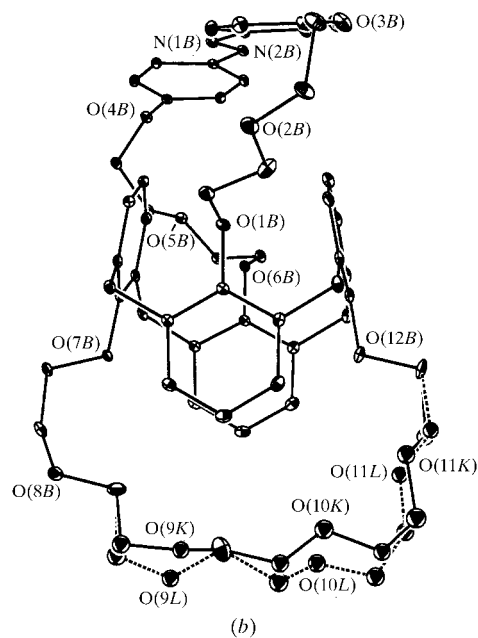
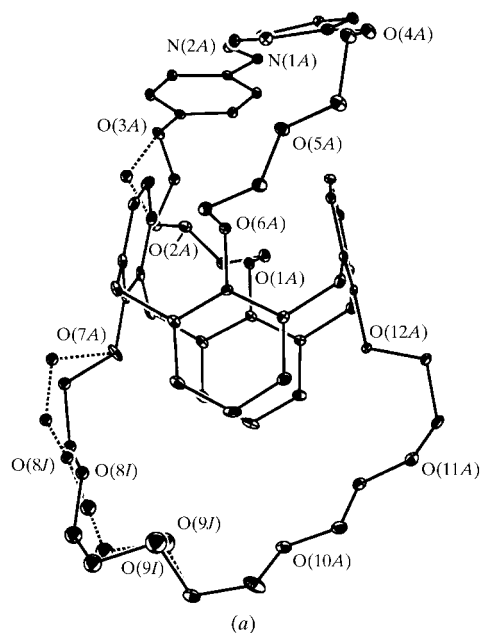


Fig. 3. Molecular units in (2*b*) [(a) molecule A, (b) molecule B]. H atoms have been omitted. One of the disordered positions is represented by dashed lines.

3.2. Comparison of polymorphs (2a) and (2b): order-disorder phase transition

3.2.1. *Crystal structures.* Near 268 (2) K, polymorph (2a) undergoes a phase transition from the monoclinic high-temperature form to a triclinic low-temperature one. As can be seen in Figs. 3 and 4, the differences between (2a) and (2b) [structures determined at 273 (2) and 213 (2) K, respectively] are far less important than between (1) and both (2a) and (2b). The number of molecules per asymmetric unit increases from one in (2a) to two in (2b) [(2bA) and (2bB)] upon the transition. Some ordering in the azobenzene-substituted crown is obvious: whereas five atoms are disordered in (2a), only one is disordered in (2bA) and none in (2bB). As can be seen in Fig. 4, each of the geometries of the two fragments of the disordered part of this crown in (2a) is found, with slight distortions, in one of the molecules of (2b): that shown with continuous lines in (2bB) and that with dashed lines in (2bA). Furthermore, the overall geometry of the crown with respect to the calixarene moiety is slightly different in (2bA) and (2bB): the projection of the center of the N1–N2 bond onto the mean plane of the calixarene coincides

approximately with the calixarene center in (2bB), whereas it is displaced on one side in (2bA). In (2a) this projection is similar to that in (2bB), but slightly displaced on the same side as in (2bA), which suggests that this displacement is associated with the crown geometry observed in (2bA) and in one of the disordered fragments of (2a). As a consequence, the two phenolic rings of the calixarene moiety attached to this crown are slightly more tilted towards the mean plane defined by the four methylene bridges in (2bA) [mean dihedral angle $79.3 (1)^\circ$] than in (2bB) [$84.8 (1)^\circ$], the value in (2a) being intermediate between these [$82.1 (3)^\circ$]. The situation is less clear in relation to the unsubstituted crown-6 bridge, which is far from being perfectly ordered even at 213 K. The disorder in (2a) is not clearly related to those in (2bA) and (2bB) and does not correspond to a mere superposition of both geometries. Despite those differences, the gross aspect of molecular conformation is similar in the three molecules [(2a), (2bA) and (2bB)]. The disorder present near room temperature has given rise to two slightly different conformations: the low-temperature form can thus be considered as an example of conformational isomerism (Bernstein, 1987). Owing to the reduced

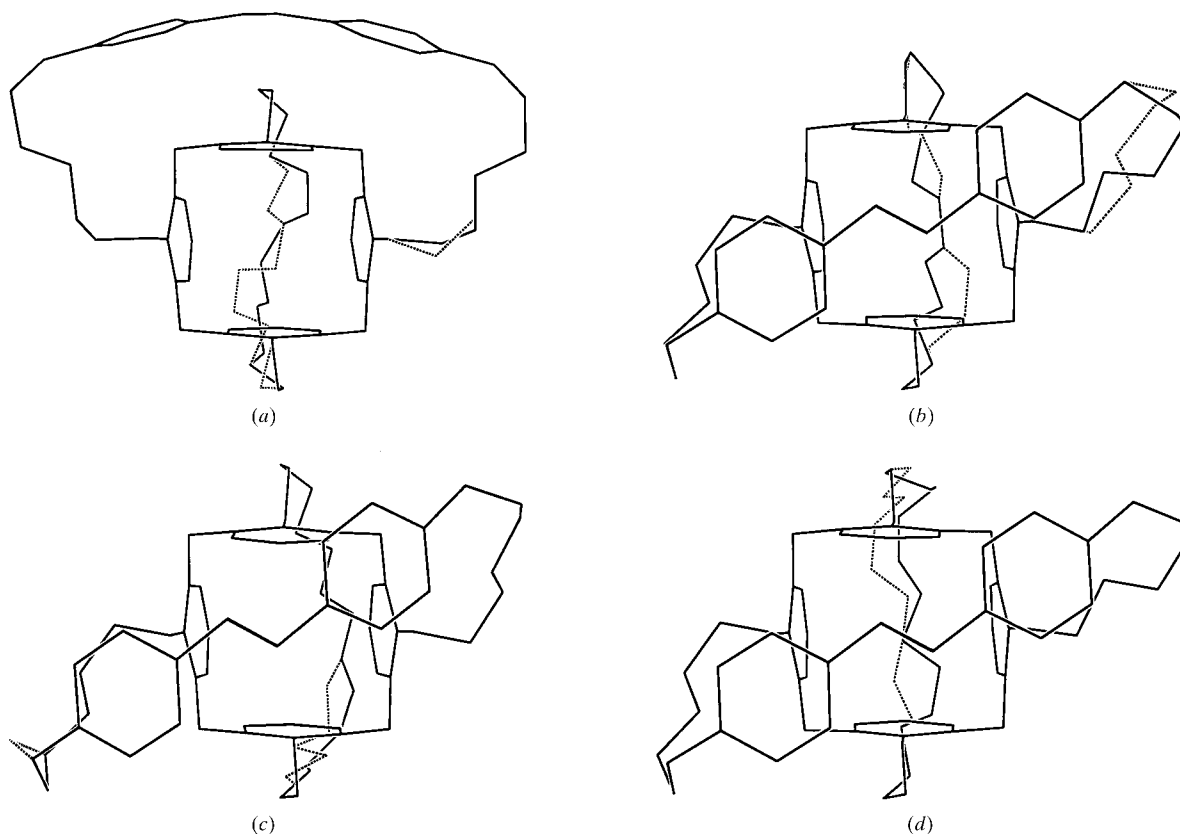


Fig. 4. Molecular units in (a) (1), (b) (2a), (c) (2bA) and (d) (2bB). Views are along the calixarene main axis, perpendicular to the calixarene methylene bridges mean plane. One of the disordered positions is represented by a dashed line in each case.

Table 2. Thermal dependence of the cell parameters, angle β and volume in (2a) and (2b)

Temperature (K)	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
Decreasing temperature					
293	20.348 (8)	11.772 (6)	23.889 (8)	112.18 (3)	5299 (4)
283	20.344 (6)	11.741 (6)	23.900 (8)	112.30 (3)	5282 (4)
273	20.345 (7)	11.724 (4)	23.903 (6)	112.30 (2)	5275 (3)
268	20.348 (9)	11.715 (6)	23.904 (6)	112.36 (4)	5270 (4)
263	20.326 (7)	11.689 (10)	23.903 (8)	112.40 (4)	5250 (5)
258	20.293 (12)	11.684 (11)	23.905 (7)	112.37 (4)	5240 (6)
253	20.314 (8)	11.667 (5)	23.930 (7)	112.38 (3)	5241 (4)
248	20.313 (12)	11.666 (7)	23.922 (6)	112.36 (4)	5239 (5)
243	20.305 (9)	11.651 (4)	23.904 (7)	112.32 (3)	5228 (4)
213	20.289 (9)	11.614 (3)	23.899 (5)	112.34 (3)	5203 (3)
173	20.243 (11)	11.588 (7)	23.832 (4)	112.36 (3)	5164 (4)
Increasing temperature					
213	20.290 (9)	11.612 (6)	23.899 (5)	112.30 (3)	5204 (4)
228	20.302 (7)	11.629 (3)	23.916 (4)	112.30 (2)	5219 (3)
243	20.321 (7)	11.654 (7)	23.930 (6)	112.34 (3)	5238 (4)
253	20.330 (9)	11.680 (3)	23.929 (5)	112.34 (3)	5253 (3)
263	20.364 (13)	11.701 (12)	23.925 (10)	112.33 (4)	5273 (7)
268	20.356 (10)	11.718 (4)	23.929 (5)	112.35 (3)	5279 (4)
273	20.355 (9)	11.732 (4)	23.914 (6)	112.34 (3)	5282 (3)

rearrangements involved, the crystal is able to cross the transition line several times without any detectable loss of crystallinity.

This phase transition thus appears as an order-disorder one, connecting a disordered high-temperature phase with high crystal symmetry and a relatively more ordered low-temperature phase with lower crystal symmetry. The variation of the crystallographic parameters with temperature is given in Fig. 5 (angles α and γ) and in Table 2 (a , b , c , β and V). A clear transitional effect appears in the variation of the cell angles α and γ , which in the low-temperature phase depart from their preceding value in the high-temperature phase (90°) to reach values of 92.24 (5) and 87.64 (4)° at 173 (2) K (the evolution is seemingly not terminated at this temperature). This evolution represents a bending of the triclinic

b axis towards the plane defined by the two largest parameters. Within experimental error, the departure of both α and γ from 90° is the same, as evidenced in Fig. 5 ($180 - \alpha$ is represented instead of α in order to facilitate the comparison), which indicates that b remains in or near the plane bisecting a and c . The experimental resolution is not sufficient to decide on the existence of a discontinuity at the transition temperature. When the temperature of 268 (2) K is reached in the decreasing temperature mode the crystal is in the monoclinic system, whereas it is in the triclinic system when reached in the increasing temperature mode: however, this cannot be considered as evidence for a hysteresis effect owing to the low accuracy of the temperature control. No further evidence for hysteresis in all the temperature ranges in which the parameters vary continuously can be

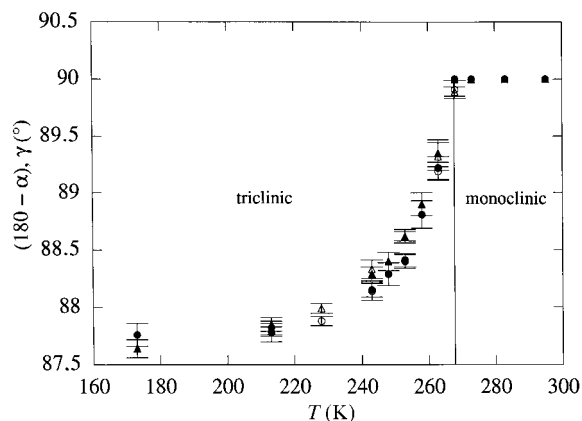


Fig. 5. Thermal dependence of $(180 - \alpha)$ (triangles) and γ (circles) in (2a) and (2b). Full symbols: decreasing temperature; empty symbols: increasing temperature.

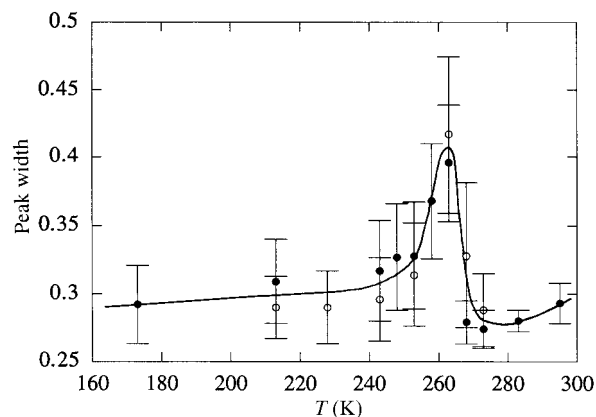


Fig. 6. Thermal dependence of the mean diffraction peak width in (2a) and (2b) (arbitrary units) for 25 reflections between $\theta = 8$ and 12° . Full symbols: decreasing temperature; empty symbols: increasing temperature. The line is a guide for the eye.

found. The β angle presents a flat maximum near the transition temperature. The parameters a and b show a mere thermal contraction between room temperature and 173 K, but c presents a reproducible (both for increasing and decreasing temperatures, and for repeated experiments) maximum, not at the onset temperature but near 250 K. The variation of the cell volume is almost linear, within experimental error: no discontinuity appears and the accuracy of the measurements is not sufficient to show the effect of the maximum on the c parameter. The thermal variation of the diffraction peak widths (as defined in Enraf–Nonius, 1989), represented in Fig. 6, shows a significant enlargement near the onset temperature [268 (2) K]. Such an enlargement could be attributed to the coexistence of the two phases in a first-order transition process or to a transient increase in disorder in a second-order one: no definitive conclusion on this point can be drawn from the crystallographic investigation alone.

3.2.2. Calorimetric measurements. Order–disorder transitions are generally second-order: this hypothesis is supported in our case by the adiabatic calorimetry measurements (the investigation of the variation of order parameters, which would be necessary to further characterize the phenomenon, is beyond the scope of this paper). As can be seen in Fig. 7, a single heat capacity jump appearing as a rounded lambda point is apparent, with a critical temperature (taken at the inflexion point) of 265.0 (1) K, in agreement with the less precise value determined from the crystallographic study. A Δc_p value of $\sim 60 \text{ mJ g}^{-1} \text{ K}^{-1}$ can be deduced from the data (transition line assimilated to a vertical line in a mean-field approximation). The smooth character of the transition (in agreement with the crystallographic investigation, which shows that the evolution goes on down to the lowest temperatures used), at which some disorder still remains, suggests that the ordering process is rather sluggish and gradual.

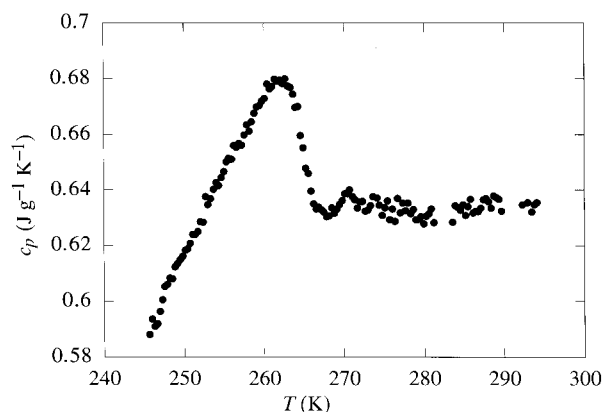


Fig. 7. Thermal dependence of the heat capacity around the transition point between (2a) and (2b) [265.0 (1) K].

4. Conclusion

In spite of the low accuracy of the structure determinations owing to the inherent disorder and low crystal quality, the present work illustrates the phenomena of conformational polymorphism and phase transition in a rather large and highly deformable organic molecule. However, as already stated, the conformational mobility of calix[4]arene bis(crown ethers) is significantly reduced by solvent or cation complexation, with all the O-atom lone pairs being directed towards the crown center in these cases. Owing to the presence of the azobenzene substituent in the compound under study, the complexation of caesium ions by the unmodified crown ether chain has another peculiar effect in solution: it induces, by an allosteric effect likely mediated by slight geometrical modifications of the calixarene core, some cation-dependent changes in the *cis/trans* ratio of the azobenzene group (Saadioui, Asfari & Vicens, 1997), which is further evidence for the high deformability of the molecule.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, edited by A. J. C. Wilson, Vol. C, Part 9.5, pp. 685–706. Dordrecht: Kluwer Academic Publishers.
- Asfari, Z., Bressot, C., Vicens, J., Hill, C., Dozol, J. F., Rouquette, H., Eymard, S., Lamare, V. & Tournois, B. (1995). *Anal. Chem.* **67**, 3133–3139.
- Asfari, Z., Naumann, C., Vicens, J., Nierlich, M., Thuéry, P., Bressot, C., Lamare, V. & Dozol, J. F. (1996). *New J. Chem.* **20**, 1183–1194.
- Asfari, Z., Nierlich, M., Thuéry, P., Lamare, V., Dozol, J. F., Leroy, M. & Vicens, J. (1996). *An. Quím. Int. Ed.* **92**, 260–266.
- Bernstein, J. (1987). *Organic Solid State Chemistry*, edited by G. R. Desiraju, pp. 471–518. *Studies in Organic Chemistry* 32. New York: Elsevier.
- Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M. J., Egberink, R. J. M., de Jong, F. & Reinhoudt, D. N. (1995). *J. Am. Chem. Soc.* **117**, 2767–2777.
- Desiraju, G. R. (1989). *Crystal Engineering, the Design of Organic Solids*, pp. 285–301. New York: Elsevier.
- Dunitz, J. D. (1995). *Acta Cryst.* **B51**, 619–631.
- Dunitz, J. D. & Bernstein, J. (1995). *Acc. Chem. Res.* **28**, 193–200.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Gutsche, C. D. (1989). *Calixarenes. Monographs in Supramolecular Chemistry*, edited by J. F. Stoddart. Cambridge: The Royal Society of Chemistry.
- Hager, O., Foces-Foces, C., Llamas-Saiz, A. L. & Weber, E. (1998). *Acta Cryst.* **B54**, 82–93.
- Martin, D. L. (1987). *Rev. Sci. Instrum.* **58**, 639–648.

- Saadioui, M., Asfari, Z., Thuéry, P., Nierlich, M. & Vicens, J. (1997). *Tetrahedron Lett.* **38**, 5643–5646.
- Saadioui, M., Asfari, Z. & Vicens, J. (1997). *Tetrahedron Lett.* **38**, 1187–1190.
- Saadioui, M., Reynier, N., Dozol, J. F., Asfari, Z. & Vicens, J. (1997). *J. Incl. Phenom.* **29**, 153–165.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXTL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Thuéry, P., Lance, M., Nierlich, M., Reynier, N., Lamare, V., Dozol, J. F., Saadioui, M., Asfari, Z. & Vicens, J. (1997). *An. Quím. Int. Ed.* **93**, 324–331.
- Thuéry, P., Nierlich, M., Bressot, C., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *J. Incl. Phenom.* **23**, 305–312.
- Thuéry, P., Nierlich, M., Bryan, J. C., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4191–4202.
- Thuéry, P., Nierlich, M., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1996). *Acta Cryst. C* **52**, 2729–2731.
- Thuéry, P., Nierlich, M., Lamare, V., Dozol, J. F., Asfari, Z. & Vicens, J. (1997). *Supramol. Chem.* **8**, 319–332.
- Ungaro, R., Casnati, A., Ugozzoli, F., Pochini, A., Dozol, J. F., Hill, C. & Rouquette, H. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1506–1509.
- Vicens, J. & Böhmer, V. (1991). Editors. *Calixarenes: a Versatile Class of Macrocyclic Compounds*. Dordrecht: Kluwer Academic Publishers.