SHORT PAPER

J. Chem. Research (S),
2001, 468–469

An uncommon calix[4]azacrown-4 dimer assembled by hydrogen-bonded interaction[†]

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A novel calix[4]azacrown-4 (**2**) was prepared, and its single crystal X-ray crystallographic analysis revealed that the carbonyl groups O atoms in **2** interact with amide H in another molecule of **2** by hydrogen bonds in the crystal, thus giving rise to a dimer possessing three "crown ether" rings.

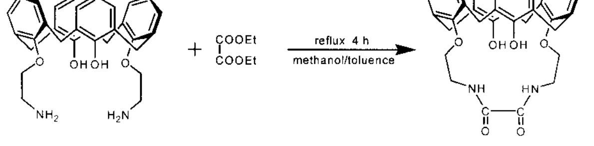
Keywords: calixarenes, crown ethers, aza-crowns, hydrogen bonding, X-ray crystal structures

Recently, a great deal of effort has been devoted to the investigation of calix[4]arene dimers in order to gain insights into factors controlling molecular aggregates from the viewpoints of multiple recognition and the cooperative working of several weak intermolecular interactions.[1-9] Indeed, calixarene derivatives possessing carboxylic acids and pyridyl groups can form dimers in apolar solvents by intermolecular hydrogen bonds, which have been proved by many research groups through ^{1}H NMR spectroscopy. More recently, Rebek *et al.*[1,8] have reported that calixarene dimers assembled in solution by hydrogen bond interaction between four urea functions attached on the wide rim of calixarene. Unfortunately, calixarene dimers formed by hydrogen bonds in the solid state are still rare, except for recent studies by Böhmer *et al.*[9] In the present study, we report firstly the synthesis of a novel calix[4]azacrown-4 compound (**2**), and secondly its single crystal X-ray structure, which not only confirms unambiguously the existence of a hydrogen-bonded dimer in the crystalline state, but also provides an exact description of its geometry.

An alternative strategy has been developed for the synthesis of calix[4]azacrown-4 in which the 1,3-(distal) positions of *p*-*tert*-butylcalix-[4]arene are linked with two amide bridges. The easily accessible 1,3-distally substituted calix[4]arene amine **1**[10] was condensed with diethyl oxalate in a mixture of methanol and toluene to obtain the novel calix[4]azacrown **2** as a white powder in 40% yield (Scheme 1). A small amount of **2** was dissolved in hot chloroform–methanol mixture to make a saturated solution, which was then cooled to room temperature. After removing the precipitates by filtration, the resultant solution was kept at 10 °C for a week. A crystal so formed was collected along with its mother liquor for X-ray crystallographic analysis.

The molecular structure of **2** is shown in Fig. 1. As reported in previous papers,[11,12] the calix[4]arene derivative **2** displays a flattened, pseudo C_2-symmetrical cone conformation, but the two phenyl rings which support the azacrown chain are pushed towards the interior of the cavity consisting of the four phenyl groups because of an intramolecular hydrogen-bond between the O(3)H and C(47)=O(5) functions, which results in their lying almost perpendicular to the least squares plane defined by the methylene groups (δ = 72.3°, and 75.7°). As a consequence the other two phenyl rings are pushed to the exterior of the cavity (δ = 55.4°, and 50.1°). The dihedral angles between opposite phenyl rings are 32° and 74.5° respectively. Thus the opening of the cavity becomes elliptical with slight differences between the two distances between opposite central carbon atoms of the *tert*-butyl groups. The two adjacent amide groups involved in the crown ring are arranged in an anti-configuration which is the conformation of lowest energy. These structural characteristics maybe provide the possibility for the self-assembly of **2** by intermolecular hydrogen bonding in the solid state (Fig. 2).

Though possessing similar structure with previous work,[12] calix[4]azacrown **2** formed a dimmer. As can be readily seen from Fi. 2, the dimer is composed of two crystallographically independent calix[4]azacrown-4 with same shape. One of carbonyl groups O atoms in a calix[4]azacrown-4 molecule interacts with one of amide functions H in another molecule **2** by hydrogen bond, and meanwhile, the amide functions H atom divided from the carbonyl group in the first molecule forms another hydrogen bond with the carbonyl groups O in the second calix[4]arenecrown-4. The two hydrogen bonds possess



Scheme 1

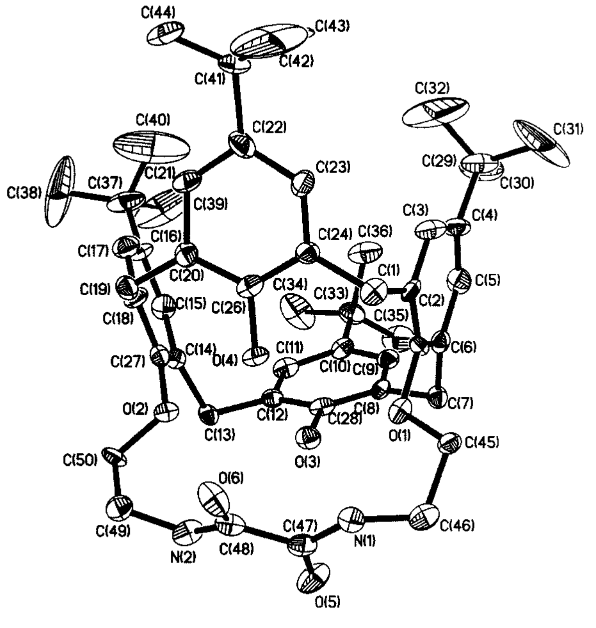


Fig. 1. ORTEP representation of the molecular structure of **2**.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

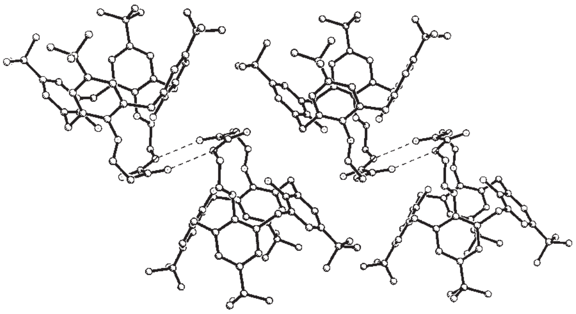

Fig. 2. The dimer crystal structure of **2**.

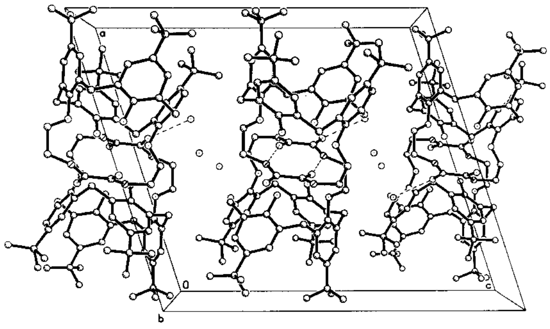

Fig. 3. Crystal packing of **2** viewed along the **b** axis.

the same bond lengths and bond angles, *i.e.*, $d_{[H1\cdots O2]} = d_{[H2\cdots O1]} = 2.024$ Å; $\Phi_{[N1—H1\cdots O2]} = \Phi_{[N2—H2\cdots O1]} = 151.04°$, and they are nearly parallel each other. Unlike common 3m-crown-m, the pseudo 10-crown-4 formed by two N–H···O hydrogen bond almost displays an exact plane ring, which becomes visually the face of the "chair" composed of three "crown ether " rings in the dimer.

It is interesting to note that many water molecules fill the lattice space (Fig. 3), though the crystal formed does not come from aqueous solution. One possible explanation is that the chloroform–methanol mixture solvent contained a few water molecules. In fact, the carbonyl group O not forming a hydrogen bond with the amide function H exists in hydrogen-bonded interaction with water molecules, and thus the crystal provides a hydrophilic microenvironment. These results above indicate that the several weak interactions including the hydrogen bond, hydrophobic/hydrophilic *etc*. play the important roles in molecular assembly or aggregate, which will promote further understanding of significant contributions of several weak interactions in process of biologic receptors selective binding substrates.

Experimental

A solution of **1** (10 mmol) and diethyl oxalate (15 mmol) in a mixture of methanol (100ml) and toluene (100 ml) were refluxed for 48 h. After completion of the reaction the solution was concentrated at reduced pressure. The remaining solid residue was suspended in water, filtered and recrystallized from methanol and ethyl ether to obtain **2** in 40% yield. m.p.: >280°C; FAB-MS: *m/z* 788 (M^+); FT-IR (KBr): ν/cm^{-1} 3493, 3372, 3047, 2959, 2905, 2871, 1677, 1599, 1510, 1485, 1465, 1362, 1301, 1242, 1202, 1125, 1097, 1045, 976, 920, 871, 821, 780, 762; ^{1}H-NMR ($CDCl_3$, TMS): δ (ppm) 7.67 (s, 2H, NH), 7.02 (s, 4H, ArH), 6.93 (s, 2H, OH), 6.77 (s, 4H, ArH), 4.24 (d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 4.11 (t, 4H, J = 5.2 Hz, OCH_2), 3.89(t, 4H, J = 5.2 Hz, NCH_2), 3.33(d, 4H, J = 13.2 Hz, $ArCH_2Ar$), 1.26(s, 18H, $C(CH_3)_3$), 0.90(s, 18H, $C(CH_3)_3$); Anal.: Calcd. for $C_{50}H_{64}N_2O_6$: C, 75.95; H, 8.35; N, 3.54; Found: C, 75.98; H, 8.35; N, 3.46.

The X-ray intensity data of **2** were collected on a Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube (λ = 0.71073 Å) and a graphite monochromator. Data were collected to $2\theta_{max} = 50.06°$. Crystal data for **1**: $C_{50}H_{64}N_2O_6$: M = 788 (excluding solvent molecules), monoclinic, P2(1)/c, a = 18.881(7) Å, b = 13.551(5) Å, c = 21.248(8) Å, V = 5180(3) Å^3, Z = 4, D_m= 1.058 g/cm^3. T = 293(2) K. The structure was solved by using direct method and refined employing full-matrix least-squares on F^2. Convergence was achieved with R_1 = 0.0775 and wR2 = 0.0831 for 7630 data having $I > 2\sigma(I)$ (of 12588 independent reflections).

Supporting information available

Crystallographic details (tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters) are available on request from the authors.

This work was supported by the National Outstanding Youth Fund (Grant No. 29625203), Natural Science Foundation of China (Grant No. 29992590-8 and 29972029), and Natural Science Fund of Tianjin Municipality (Grant No. 993601311), which are gratefully acknowledged.

Received 18 April 2001; accepted 16 August 2001
Paper 01/845

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