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NOTE

Structure of Thiacalix[4]crown-5 Derivative

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The single crystal of 1,3-alternate-25,27-*bis*(2-phthalimidoethoxy) thiacalix[4]crown-5 (**1**) was obtained by recrystallization from its chloroform-methanol (2:1 v/v) solution. Its structure was confirmed by single crystal X-ray analysis. It crystallizes in the triclinic system (space group, P-1) and the chloroform solvent molecular occupies interstitial lattice space between two calixarene molecules. It displays 1,3-alternate conformation. The crystal packing is stabilized by weak C-H···π contacts.

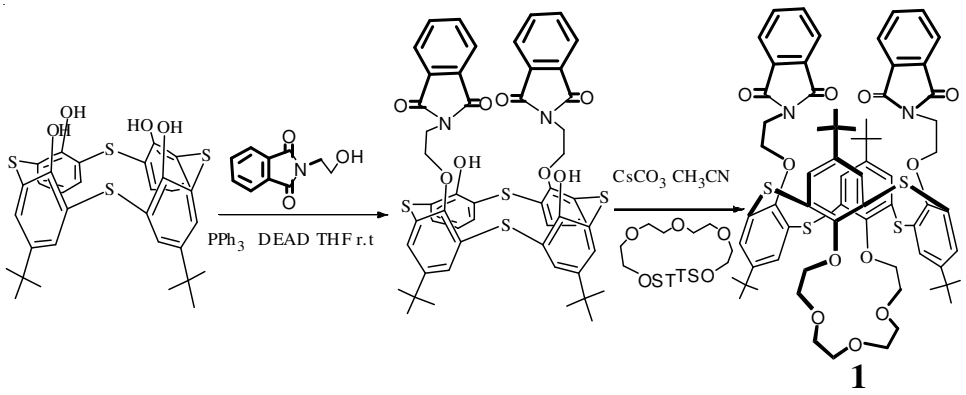
Key Words: Thiacalixarene, Crown ether, X-Ray structure.

Calix[4]arenes are macrocycles which provide an ideal scaffold to reorganize functional units for application in catalysis or molecular recognition[1]. They are available in large quantities and can be easily modified by selective reactions involving the up or low rim of the molecule[2]. The compound **1** is a highly useful synthetic intermediate for 1,3-disubstitution of thiacalix[4]arene at the lower rim[3]. In this paper, the structure of 1 have studied and reported.

Compound **1** was sythesized following the literature procedure (**Scheme-I**)[4]. Colourless prisms of the solvated calixarene suitable for X-ray diffraction were obtained by recrystallization from chloroform-methanol (2:1 v/v) solution (m.p. 482-483 K). The X-ray data were collected on a Bruker Apex-II CCD diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073 Å) at 293 (2) K with crystal size 0.23 mm^3 × 0.18 mm^3 × 0.14 mm^3. A total of 12738 (R_{int} = 0.027) independent reflections were collected by ϕ and ω scans technique in the range 1.6 = θ = 25º from which 9948 [I > σ2(I)] reflection were corrected for Lorentz and polarization factors. The structure was solved by direct method using SHELXS-97 and refined using a full-matrix least-squares procedure on F^2 in SHELXS-97. All non-hydrogen atoms were refined wits anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed with isotropic thermal parameters.

The molecular stucture of compound **1** is illustrated in Fig. 1. It crystallizes in the triclinic system (space group P-1), a = 13.229(5) Å, b = 15.676(5) Å, c = 18.582(5) Å, α = 79.507(5)°, β = 88.225(5)°, γ = 77.387(5)°. Its molecular geometry is best described by a 1,3-alternate conformation with two opposite aromatic rings: ring 1 (C27-C28-C29-C30-C31-C32) and ring 3 (C19-C20-C21-C22-C23-C24), ring 2

(C39-C40-C41-C42-C43-C44) and ring 4 (C33-C24-C35-C36-C37-C38), which differing only little [dihedral angles 50.16° and 49.71°, respectively]. The size of the thiacalixarene cavity could be defined by the distances between the adjacent sulfur atoms, 5.575, 5.570, 5.545 and 5.559 Å, respectively. The observed C-S distance, in the range of 1.773-1.780 Å, is in agreement with the one observed for the parent *p-tert*-butyl-thiacalixarene (1.785 Å)[5]. Due to their hydrophobic surface, the packing of the calixarene molecules is primary stabilized by vander Waals interactions and weak C-H···π contacts[6].



Scheme-I: Sythesis of compound **1**

The crystal packing is shown in Fig. 2. Interestingly, the chloroform solvent molecule occupies interstitial lattice space between two calixarene molecules. Unlike the normal calixarene structure whose chloroform molecular was including in the cavity[7]. Further details of the structure analysis are given in Table-1.

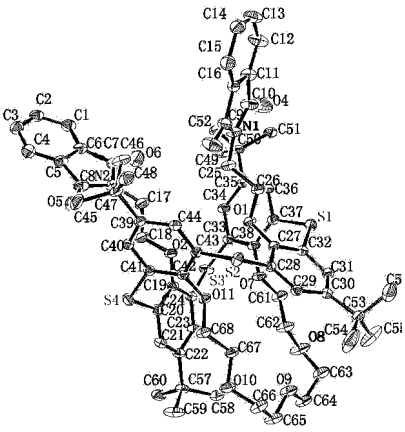


Fig. 1. Structure of compound **1**

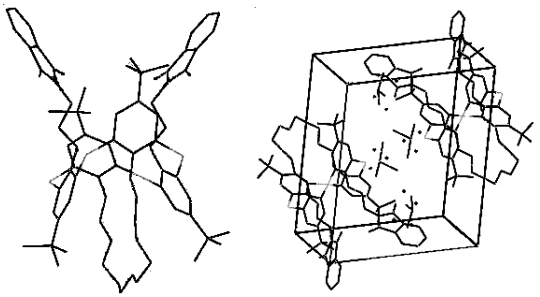


Fig. 2. Structure packing of compound **1**

TABLE-1
CRYSTALLOGRAPHIC DATA AND SUMMARY OF DATA
COLLECTION AND STRUCTURE REFINEMENT

	Compound **1**		Compound **1**
Formula	$C_{68}H_{76}N_2O_{11}S_4 \cdot 2CHCl_3$	Volume ($Å^3$)	3697(2)
Formula weight	1464.28	Z	2
Crystal system	Triclinic	D(calc) (Mg cm^{-3})	1.315
Space group	P-1	? (mm^{-1})	0.40
Temperature (K)	293	$2\theta_{max}$ (deg)	50
Number of parameters	901	N measd	36852
R	0.058	N ind	12738
Rw	0.176	GOF	1.089

Conclusion

In summary, the structure of compound **1** has been first determined, which was shown to be in a fixed 1,3-alternate conformation by X-ray single-crystal structure determination. And the chloroform solvent molecular occupies interstitial lattice space between two calixarene molecules. It is very different from the former calixarene structure which had been observed. This may be affords an additional method for the study of interaction in calixarene.

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