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Synthesis and Structure of a 1,3-*alternate*-Thiacalix[4]arene Diamide Derivative

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Abstract

A novel receptor possessing two complexation sites and bearing 1,3-*alternate* conformation based on thiacalix[4]arene, confirmed by single crystal X-ray analysis, was prepared. The tetrathiacalix[4]arene diamide shows strong intramolecular hydrogen bonding. The binding behavior towards K^+ and halides has been examined by ^1H NMR titration experiments.

Introduction

From both a biological [1] and an environmental [2] viewpoint the synthesis of anion receptors is one of the most challenging targets in supramolecular chemistry. Calixarenes [3] and more recently thiacalixarenes [4] have been widely used in molecular recognition due to their unique three-dimensional structure with almost unlimited derivatisation. Despite of the importance of the molecular recognition of anions, little work has been done, whereas that of cations has been studied intensively. Selective complexation of anions is more demanding than that of cations due to the many reasons such as size, charge density, polarizability, solvation energy and pH-dependent acid-base equilibria [5].

A number of examples of substituted calixarenes have been used for anion complexation [6]. Thus, introduction of activated amides [7], amines [7a], urea [8], and thiourea [8b] into the calixarene platform, led to receptors capable of interacting with anions. Such receptors are able to form ditopic systems capable of ion-pair recognition [9] which show significant relevance to the selective extraction and/or transport of metals salts across lipophilic membranes. A number or receptors with multiple binding sites, which can be tailored to exhibit novel cooperative and allosteric behavior, have appeared in the literature [10].

Moving from our interest on the synthesis of heteroditopic receptors that function as not only an anion binder but also as a cation binder, we have introduced amide functions into the lower rim of the thiacalix[4]arene. Amide functions have been used as efficient extractants for both cations and anions due to their high stability and hydrophobicity. Furthermore, the presence of acetate functions in the opposite side and the sulphur atoms in the calix framework possess high affinity toward K^+ and Ag^+ ions, respectively. We thus report, herein, the synthesis and complexation studies of diamide **4**, Figure 1, which possesses a 1,3-*alternate* conformation, using ^1H NMR titration experiments in $CDCl_3$.

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Results and discussion

Synthesis

The synthesis of 1,3-*alternate*-**4** was conducted as shown in Scheme 1. Thus *O*-alkylation of tetrathiacalix[4]arene **1** carried out with 2 equiv. of bromoethyl acetate in the presence of 1 equiv. of Na_2CO_3 according to the reported procedure produces exclusively the disubstituted product *distal*-**2a** [11]. The corresponding acid chloride *distal*-**2c** was prepared by hydrolysis of *distal*-**2a** with KOH aq. in a mixture of ethanol and water, followed by treatment with thionyl chloride in $CHCl_3$ at room temperature for 4 h in good yield. The reaction of *distal*-**2c** with *p*-methylbenzyl amine carried out in the presence of Et_3N in CH_2Cl_2 afforded *distal*-**3** in 83% yield. *O*-alkylation of *distal*-**3** with bromoethyl acetate in the presence of Cs_2CO_3 afforded the tetrasubstituted 1,3-*alternate*-**4** in 84% yield. The product structures were supported by their spectral and analytical data.

The ^1H NMR spectrum of 1,3-*alternate*-**4** shows two singlets for the *tert*-butyl protons at δ 1.00 and 1.30 ppm, in which the former peak can be observed at a

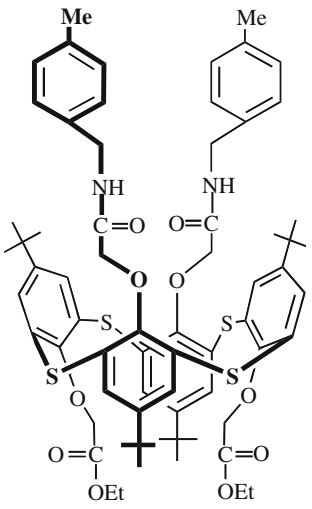


Figure 1. Structure of 1,3-*alternate*-**4.**

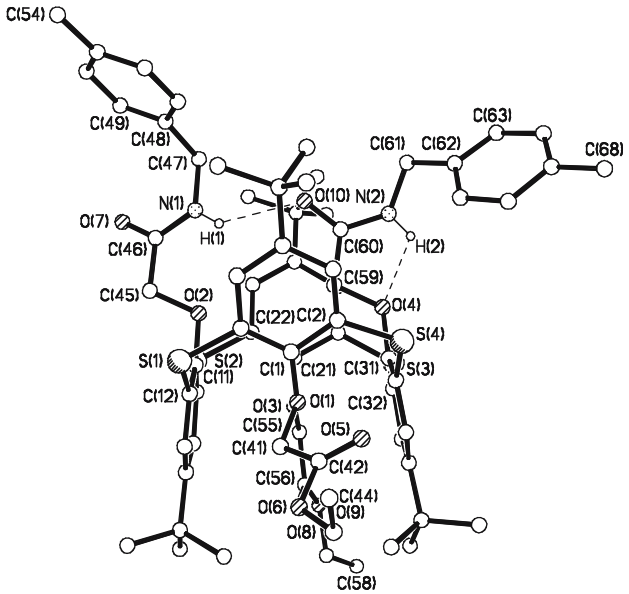
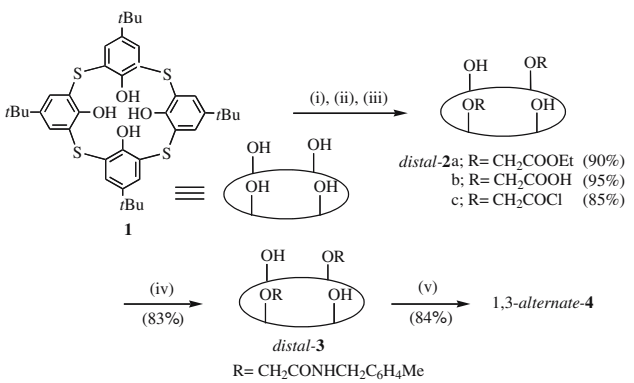


Figure 2. Ball and stick drawing of 1,3-*alternate*-**4.**

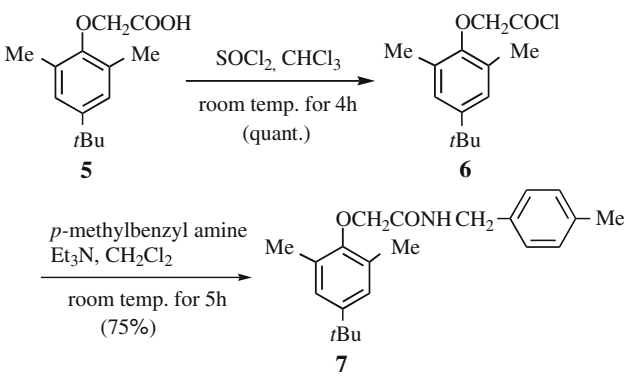
higher field due to the ring current effect arising from the benzene ring of two inverted *p*-methylbenzyl groups. Other signals in the ^{1}H NMR spectrum may correspond to both the *cone* or 1,3-*alternate* conformer differing only slightly in their observed chemical shifts. Fortunately, recrystallization from MeOH and $CHCl_3$ produces X-ray quality colorless crystals of 1,3-*alternate*-**4**. The ORTEP drawing of 1,3-*alternate*-**4** analyzed by single crystal X-ray is shown in Figure 2. In the solid state, it is clear that compound **4** adopts a "1,3-*alternate* conformation" and the orientations of the carbonyl oxygens of the acetates are outwardly orientated with respect to the cavity because of the electron repulsion between oxygens. Interestingly, the structure of 1,3-*alternate*-**4** reveals the existence of intramolecular hydrogen bonding between the carbonyl oxygen of amide and NH proton (C = O···HN, 2.35 Å), and between the phenolic oxygen and the NH protons (ArO···HN, 2.05 Å).

The diamide 1,3-*alternate*-**4** has, at first glance, two possible binding sites because of the1,3-*alternate* conformation [12]. Furthermore, the NH group can bind anions by hydrogen bonding while the carbonyl and phenolic oxygens are available for cation binding. In particular, the presence of the acetate function might provide the possibility to complex cations and could work as a controller for the recognition of cation and/or anions by the amide function placed at the other site of the thiacalix[4]arene cavity. It is therefore possible that the various binding sites of 1,3-*alternate*-**4** could participate simultaneously and cooperatively upon ion binding producing higher forms of molecular behavior.

Several examples of intramolecular hydrogen-bonding among opposing urea groups which can bind anionic species in calix[4]arenes have been reported [13]. As a consequence, intramolecular hydrogen bonding may be anticipated between the NH and CO groups. In order to investigate the existence of intramolecular hydrogen bonding in 1,3-*alternate*-**4** the reference compound **7** was synthesized from phenoxylacetic acid **5** as shown in Scheme 2. Compared with the chemical shift of the NH protons of **7**, the corresponding chemical shift of 1,3-*alternate*-**4** is a downfield (i.e. $\Delta\delta = +0.25$ ppm). The much larger down field shift of the NH proton for *distal*-**3** as ($\Delta\delta = +0.39$ ppm) can be expected for the *cone*-structure of *distal*-**3**, which allows for strong



Scheme 1. Reagents and conditions: (i) $BrCH_2CO_2Et$, Na_2CO_3, acetone, reflux for 48 h; (ii) KOH, ethanol/water, reflux for 3 h; (iii) $SOCl_2$, $CHCl_3$ for 4 h; (iv) *p*-methylbenzyl amine, Et_3N, CH_2Cl_2, r.t. for 5 h; (v) $BrCH_2CO_2Et$, Cs_2CO_3, acetone, reflux for 36 h.



Scheme 2.

intramolecular hydrogen-bonding between NH and CO groups due to the much closer contact of the chains $OCH_2CONHAr$.

The secondary amide group with the donor unit and acceptor unit can form not only intramolecular bonding but also intermolecular hydrogen bonding depending on the solvent. The compound 1,3-*alternate*-**4** was dissolved in the strongly hydrogen-bonding solvent DMSO-d_6. The downfield shift of NH protons ($\Delta\delta = +0.10$ ppm) of 1,3-*alternate*-**4** indicates the formation of relatively weak intermolecular hydrogen-bonding.

Binding studies

The recognition properties of receptor 1,3-*alternate*-**4** were investigated by ^{1}H NMR titration experiments in $CDCl_3$ toward selected anions (tetrabutylammonium (TBA) chloride and bromide) and cations (silver and potassium trifluoromethanesulfonate). In general, the titration experiments were carried out by the increasing addition of ion (0.1 mol dm^{-3}) into 5×10^{-6} mol of the receptor in 0.5 cm^3 of $CDCl_3$. The association constansts (K_{ass}) were calculated by nonlinear least squares fitting [14] and the stoichiometry was determined by using Job's method. Addition of 1 equiv of KSO_3CF_3 into *distal*-**3** solution did not cause significant chemical shift (i.e. >0.01 ppm) even in the presence of an excess of K^+ ion. In contrast, upon titration of 1,3-*alternate*-**4** significant chemical shifts were observed. The acetate protons (i.e. OCH_2 $\Delta\delta = +0.19$) shifted to lower magnetic field and a slight chemical shift change was observed in the rest of protons (*NH* $\Delta\delta = +0.06$). Upon addition of an extra equiv. of K^+ no significant changes were observed, supporting the 1:1 solution stoichiometry (1,3-*alternate*-**4**$\supset K^+$; $K_{ass} = 1.3\times10^2\ M^{-1}$). Titration of 1,3-*alternate*-**4** with 1 equiv. or an excess of $AgSO_3CF_3$ did not caused any detectable change of chemical shift.

On the other hand, titration of 1,3-*alternate*-**4** with 1 equiv. or excess of TBACl or TBABr led to no significant shifts indicating that there is little interaction or no interaction between these molecules and the anionic species. This fact together with the weak intermolecular hydrogen-bonding formed in DMSO-d_6 and the negligible chemical shift change upon complexation of K^+ by the acetate group implies that preorganization of the amide groups in the calix framework is unfavorable towards anion complexation.

Conclusion

A novel receptor possessing two complexation sites and bearing 1,3-*alternate* conformation for the thiacalix[4]arene, as confirmed by single crystal X-ray analysis, has been prepared. The NH protons of each amide made two different intramolecular hydrogen bonds with carbonyl oxygen of amide and the the phenolic oxygen. The original C_{2V}-symmetry has been remained after complexation of 1,3-*alternate*-**4** with K^+, however such complexation does not induce any enhancement for anion recognition. Further studies on the application to the synthetic receptors for use in metal controlled biomimetic systems are now in progress.

Experimental

All mps (Yanagimoto MP-S_1) are uncorrected. ^{1}H NMR spectra were determined 300 MHz with a Nippon Denshi JEOL FT-300 NMR spectrometer with $SiMe_4$ as an internal reference: *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by Shimadzu 240 spectrophotometer. Elemental analyses were performed by Yanaco MT-5.

Materials

5,11,17,23-Tetra-*tert*-butyl-25, 27-bis[(ethoxycarbonyl) methoxy]-26,28-dihydroxy-2,8, 14,20-tetrathiacalix[4] arene (*distal*-**2a**) and 5,11,17, 23-tetra-*tert*-butyl-25,27-bis- [carboxylmethoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (*distal*-**2b**) were prepared according to the reported procedure [11a].

*5,11,17,23-Tetra-tert-butyl-25,27-bis[(chlorocarbonyl) methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix [4]arene (distal-**2c**)*

A mixture of *distal*-**2b** (120 mg, 0.125 mmol) and thionyl chloride (2 ml) in chloroform (6 ml) was reflux for 4 h under argon. Removal of the solvent and residual thionyl chloride under reduce pressure furnished the acid chloride *distal*-**2c** as an off-white solid in quantitative yield. Despite the normal incompatibility of acid chloride and phenol, the compound was moderately stable if stored under nitrogen. No attempts were made to purify the crude product *distal*-**2c** as a white solid, the NMR spectrum having indicated it was already of sufficient quality for further use. IR ν (KBr)/cm^{-1} 3480 (OH), 1800 (CO). ^{1}H NMR δ ($CDCl_3$) 0.70 (18, s *t*Bu), 1.35 (18H, s, *t*Bu), 5.08 (4H, s, OCH_2), 6.92 (4H, s, Ar–*H*), 7.67 (4H, s, Ar–*H*), 8.02 (2H, s, *OH*).

*25,27-Bis[(p-methylbenzylaminocarbonyl) methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene (distal-**3**)*

The dichloromethane solution of the acid chloride was dropped to a dichloromethane solution of *p*-methylbenzyl amine and triethylamine (1 ml) at 0°C. After dropping was complete, the mixture was stirred at room temperature for further 5 h. The reaction was terminated by addition of HCl solution at 0°C. After extracting, the organic layer was evaporated to dryness to obtain crude product, which was purified by column chromatography (350 g silica gel 2:1 ethyl acetate:hexane) to give pure compound *distal*-**3** (1.73 g, 83%) as colorless prisms. Mp 195–200°C. IR ν (KBr)/cm^{-1} 3382,

3319 (NH, OH), 1679 (CO). ^{1}H NMR δ ($CDCl_3$) 1.10 (18, s *t*Bu), 1.31 (18H, s, *t*Bu), 2.20 (6H, s, Ph–CH_3), 4.57 (4H, d, J = 6.91, NHCH_2), 4.60 (4H, s, OCH_2), 6.90 (4H, d, J = 7.92, Ph–*H*), 7.17 (4H, m, Ph–*H*), 7.35 (4H, s, Ar–*H*), 7.60 (4H, s, Ar–*H*), 7.68 (2H, s, *OH*), 8.92 (2H, t, *NH*). MS m/z 1042.41 (M^+). Anal. Calcd. For $C_{60}H_{70}N_2O_6S_4$ (1043.47): C, 69.06; H, 6.76; N, 2.68. Found: C, 69.16; H, 6.66; N, 2.64%.

*5,11,17,23-Tetra-tert-butyl-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-bis-[(p-methylbenzylaminocarbonyl)methoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-alternate-**4**).*

To a solution of *distal*-**3** (1.73 g, 0.60 mmol), Cs_2CO_3 (1.17 g, 3.61 mmol) in dry acetone (100 ml) was added ethylbromo acetate (0.60 g, 3.61 mmol). The mixture was reflux for 36 h under argon, cooled at room temperature and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with 1 N HCl. The organic layer was separated, washed with brine (2×15 ml) and dried over $MgSO_4$ anhydrous. After filtration, the solvent was evaporated to dryness to obtain crude product 1,3-*alternate*-**4** as a white solid (1.68 g, 84.2%). Mp 135–140°C. IR ν (KBr)/cm^{-1} 3376 (NH), 1768 (CO). ^{1}H NMR δ ($CDCl_3$) 1.00 (18H, s, *t*Bu), 1.28 (6H, m, CH_2CH_3), 1.30 (18H, s, *t*Bu), 2.33 (6H, s, Ph–CH_3), 3.80 (4H, s, OCH_2), 4.22 (4H, m, CH_2CH$_3$), 4.40 (4H, d, J = 6.91, NHCH_2), 4.62 (4H, s, OCH_2), 7.10 (8H, m, Ph–*H*), 7.28 (4H, s, Ar–*H*), 7.61 (4H, s, Ar–*H*), 7.92 (2H, t, J = 6.91, *NH*). MS m/z 1214 (M^+). Anal. Calcd. For $C_{68}H_{82}N_2O_{10}S_4$ (1215.66): C, 67.18; H, 6.80; N, 2.30. Found: C, 67.36; H, 6.71; N, 2.27%.

*Preparation of 4-tert-butyl-2,6-dimethyl[(4-methylbenzylaminocarbonyl)- methoxy]benzene (**7**)*

To a solution of (4-*tert*-butyl-2,6-dimethyl)phenoxyacetic acid **5** (200 mg, 0.86 mmol) was dissolved in dry $CHCl_3$ (10 ml) under nitrogen and thionyl chloride (5 ml) and pyridine (3 drops) were added. The solution was stirred at room temperature for 4 h, following which all volatiles were removed at reduced pressure to afford acid chloride **6** as a white solid, which was used without further purification. Triethylamine (2 ml) was added to a solution of *p*-methylbenzyl amine (114 mg, 0.94 mmol) in CH_2Cl_2 (6 ml) over 10 min at 0°C and the mixture was stirred for 5 h. A solution of acid chloride in CH_2Cl_2 (6 ml) was added and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with CH_2Cl_2 (10 ml) and washed with 2 M hydrochloric acid. The combined extracts were washed with water (5 ml), saturated brine (5 ml), dried over Na_2SO_4 and condensed under reduce pressure. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane-EtOAc (1:1, v/v) as eluent to give 218 mg (75%) of **7** as a colorless oil. IR ν (KBr)/cm^{-1} 3277(NH), 2950, 2928, 2865, 1667 (CO), 1533, 1515, 1484, 1458, 1443, 1408, 1360, 1322, 1310, 1195, 1124, 1050, 870, 819. ^{1}H NMR δ ($CDCl_3$) 1.30 (9H, s, *t*Bu), 2.31 (3H, s, Ar′-CH_3), 2.34 (6H, s, Ar–CH_3), 4.44 (2H, s, ArOCH_2), 4.46 (2H, s, Ar′CH_2), 7.12 (2H, d, J = 8.8, Ar′-H_a), 7.16 (2H, s, Ar–*H*), 7.34 (2H, d, J = 8.8, Ar′-H_b), 7.73 (1H, s, *NH*). MS m/z 339 (M^+). Anal. Calcd. For $C_{22}H_{29}O_2N$ (339.22): C, 77.84; H, 8.61; N, 4.13. Found: C, 77.58; H, 8.53; N, 4.17%.

^{1}H NMR complexation experiment

To a $CDCl_3$ solution (4×10^{-3} M) of 1,3-*alternate*-**4** in the NMR tube was added a CD_3CN solution (4×10^{-3} M) of $AgSO_3CF_3$ or KSO_3CF_3. The spectrum was registered after addition and the temperature of NMR probe kept constant at 27°C.

Determination of association constants

The measurements were performed by ^{1}H NMR titration experiments in a varying guest concentration of 0–50 mM and a constant concentration of host receptors with 5 mM. As a probe the chemical shift of the amide protons [C(O)*NH*] signal was used. The association constant values were calculated by the integral intensity of *NH* protons in the complex and free host molecules.

*Crystallographic data for 1,3-alternate-**4***

Crystal data for 1,3-*alternate*-**4**: $C_{68}H_{82}N_2O_{10}S_4$, M = 1215.60, triclinic, $P\bar{1}$, a = 12.921(3), b = 14.978(3), c = 17.944(4) Å, α = 101.704(3), β = 103.670(3), γ = 90.599(3) °, V = 3298.0(13) Å^3, Z = 2, D_c = 1.224 g cm^{-3}, μ = 0.202 mm^{-1}, T = 120(2) K, colorless needle; 19941 reflections measured on a Bruker APEX 2 CCD diffractometer at Daresbury Laboratory SRS, Station 9.8, using silicon 111 monochromated synchrotron radiation. 19941 independent reflections were corrected for Lp effects and for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.933, 0.996). The structure was non-merohedrally twinned with two domains; major occupancy = 0.5422(9)%. The structure solved by direct methods (Bruker SHELXTL), F^2 refinement, R_1 = 0.0705 for 12656 data with $F^2 > 2\sigma(F^2)$, wR_2 = 0.2042 for all 19941 data, 800 parameters. One of the ^{t}Bu groups was modeled with 2-fold disorder of the three Me groups; major sites occupied 66.8(7)%. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 608136. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-1223-3360336033 or e-mail: deposit@ccdc.cam.ac.uk].

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