



Computational study of ion-pair recognition by heteroditopic calix[4]diquinone derivative [☆]



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ABSTRACT

The complexation characteristics of isophthalamide diether calix[4]diquinone macrobicycle (**1**) with ion-pairs (alkali metal or ammonium cation and halide anion) were investigated by quantum mechanical calculation methods. The total electronic and Gibbs free energies of the various (monotopic, heteroditopic, and contact motifs) complexes of alkali metal and ammonium cations and/or halide anions with **1** were analyzed and compared. The structures of the endo- or exo-complexes of the various cations and anions with the host (**1**) were optimized using the mPW1PW91/6-31G(d,p) method, followed by DFT B3LYP/6-31G(d,p) calculations. Although the cone conformer is less stable than the partial cone and 1,3-alternate conformers of the free host (**1**), the cone-type complexes are more stable than the partial cone and 1,3-alternate analogues. The contact-complexation efficiencies of the sodium-halide ion-pair inside the cavity of the lower rim of the cone-type hosts were better (~20 kcal/mol) than those of the potassium ion-pair. These calculated outcomes agree with the experimental results of the anion-binding behavior of **1** · M⁺. The contact-complexation efficiencies of the ion-pairs inside the lower rim pocket of the host **1**(cone) were much better (45–50 kcal/mol) than those of its heteroditopic-complexation with host **1**.

The exo-complexation of the cone isomer with the ion-pair could be clearly confirmed by differences in the diagnostic C=O bands in the free host and the infrared spectra of its complexes.

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1. Introduction

Calixarenes [1–4] have a well-defined molecular framework and are attractive as a basic skeleton for constructing new supra-molecular systems [5–10]. The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms of the calix[4]aryl receptor [11–17].

Historical developments in the field of cation recognition and sensing [18] have been recently emulated in the emergence of a large number of systems for the recognition and sensing of anions. [19–24] However, the designs of ion receptors studied to date have almost universally focused on the selective recognition of either a cation or an anion, which may be achieved through careful consideration of the size, geometry, and solvation properties of the target guest species. In these systems, the cation can be bound using a number of common motifs, while the anion is coordinated using Lewis acidic, electrostatic, or hydrogen bonding interactions [25–28]. Therefore, this approach implicitly neglects the obviously

important role of the counterion in controlling the strength and selectivity of the recognition process; such a shortcoming is commonly compensated for by making the counterion “non-coordinating”.

However, an alternative paradigm for ion recognition exists and involves the design of systems wherein the binding of both cation and anion, an ion-pair, can be achieved. The design and application of new heteroditopic receptor systems capable of simultaneous coordination of both anionic and cationic guest species has recently attracted a great deal of interest [29]. Such an approach offers considerable benefits as the overall receptor/ion-pair complex is charge neutral and should prove advantageous for salt solubilization, extraction, detection, and membrane-transport applications [30–39].

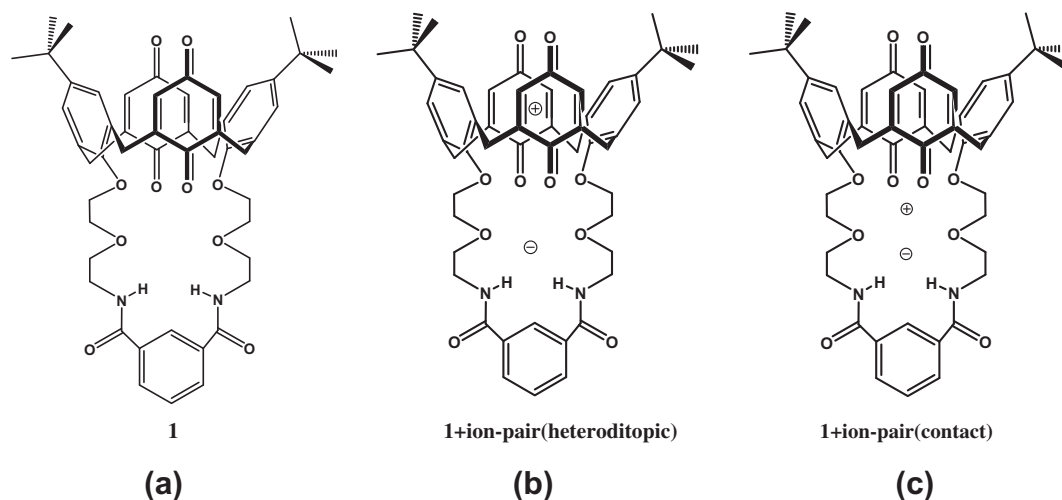
Interest in a contact ion-pair binding approach, wherein the anion and cation are bound essentially as one moiety, is particularly noteworthy as this avoids the energetically unfavorable separation of the two ions [40,41]. Importantly, the geometry of the ditopic receptor must be optimized so that the anion and cation binding sites are located in proximity to enhance this interaction, as an incorrect orientation could lead to the ion pair associating outside of the receptor, or solvent-separated ion binding.

Beer's group reported the design, synthesis and binding properties of one such rare system, which demonstrates a dramatic

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Scheme 1. Chemical structures of (a) isophthalamide diether calix[4]diquinone macrobicycle (**1**) and its ion-pair (b) heteroditopic and (c) contact complexes.

Table 1
mPW1PW91/6-31G(d,p) Calculated Energies of the Conformers of the Free Host (**1**).

Conformer ^a	Total electronic energy		Gibbs Free energy	
	E^b (a.u.)	ΔE^c (kcal/mol)	G^d (a.u.)	ΔG^c (kcal/mol)
CONE	-2876.3842	12.9	-2875.4806	8.6
PC	-2876.4025	1.5	-2875.4931	0.8
13ALT	-2876.4049	0.0	-2875.4944	0.0

^a Abbreviations of conformers: PC denotes a partial conformation, one ring inverted out of the two 1,4-benzoquinones of the lower rim of the host; 13ALT is the 1,3-alternate, both the benzoquinones are inverted from the mean plane of the calix[4]aryl skeleton.

^b The error limits of these calculated total electronic energies are about 0.00001 a.u. (0.01 kcal/mol).

^c ΔE or ΔG (kcal/mol) is defined as the energy of the conformer minus the energy of the most stable 13ALT conformation of **1** obtained using 1 a.u. = 627.50955 kcal/mol.

^d Sum of total electronic and thermal Gibbs free energies at 298 K.

enhancement of anion binding by a cobound cation and, in some cases, strong binding with associated ion pairs where no affinity for the free ions is observed [42,43]. A heterotopic receptor (Scheme 1b) relies on the incorporation of distinct anion and cation binding sites within the same molecule to recognize multiple ions [44–49,25,50–59]. The ion-pair recognition process is ideally

cooperative in nature, such that the binding of one ion enhances the binding of the other and vice versa. The design of these heteroditopic receptors commonly relies on separating the two ions, which incurs an unfavorable Coulombic energy penalty. To circumvent this event, it is desirable to coordinate the ion pair such that the components are in contact (Scheme 1c). Such a requirement places severe restrictions on the receptor design that can be employed, and consequently such systems are extremely rare, but recently Smith et al. [60–65] and Rissanen et al. [66] demonstrated the power of such an approach.

The calix[4]diquinone unit has well-documented cation binding properties that may be readily probed by electrochemical and UV-visible spectroscopic methods [67]. The isophthalamide cleft has been widely utilized as an anion binding unit in a variety of systems [68–70]. It was hoped that a considerable enhancement of anion recognition would take place in the presence of a bound cationic guest species by using a combination of these two moieties.

We report herein the computational analysis of a new class of ion-pair receptors reliant on the proximal inclusion of calix[4]diquinone cation binding and isophthalamide-based anion binding fragments within the same macrobicycle. The complexation characteristics of the heteroditopic calix[4]diquinone derivative (**1**) with ion-pairs (alkali metal or ammonium cation and halide anion) were investigated using mPW1PW91 (hybrid HF–DF) and DFT

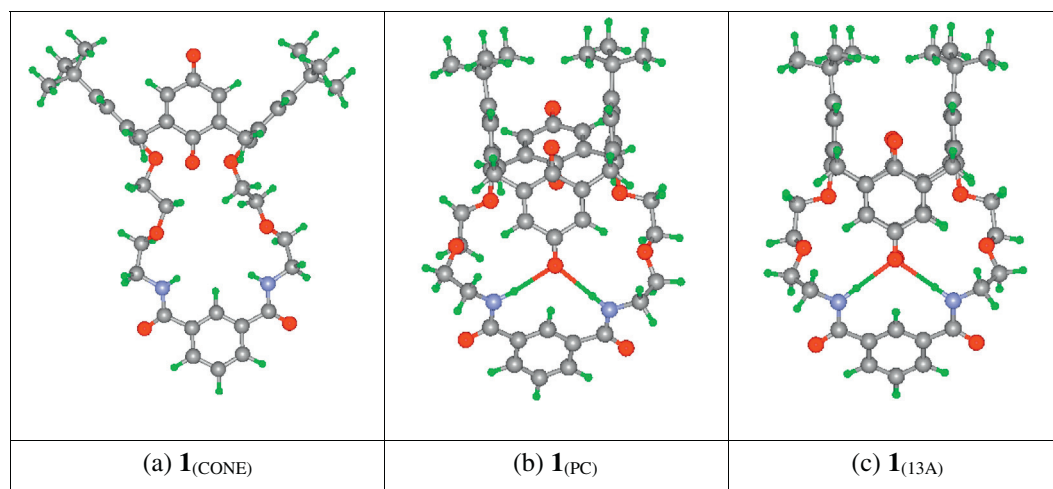


Fig. 1. mPW1PW91/6-31G(d,p) calculated structures of various conformations (cone, PC and 13ALT) for the free host **1**. (a) CONE, (b) PC, and (c) 13ALT.

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