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Guest Discrimination in Complexes of Alkali Metal Cations with the $C_{36}H_{36}$ Spheriphane: An ab Initio Electronic Structure Study

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Abstract: Large-scale electronic structure calculations, carried out at the HF/6-311G** level of theory, reveal qualitative differences among the complexes of the $C_{36}H_{36}$ spheriphane with alkali metal cations. Although both endohedral and exohedral isomers are found to be energy minima for the Li^+, Na^+, and K^+ guests, the formation of endohedral species proceeds without a barrier only in the first two cases. In the endohedral isomers, the Li^+ cation is displaced from the cage center, whereas the Na^+ and K^+ cations are not. The size of the guest cation is also a controlling factor for the complexation energies, which decrease in magnitude from Li^+ to K^+. The endohedral isomers are predicted to be more stable than their exohedral counterparts in the gas phase, but this order of stabilities is expected to be reversed in solvents that form strong complexes with the guest cations. Bonding in the inclusion complexes of $C_{36}H_{36}$ is analyzed in terms of electrostatic, polarization, and steric effects and compared to that in the endohedral complexes of the C_{60} fullerene.

Introduction

Supramolecular systems, such as clathrates, inclusion complexes, and endohedral complexes, are of great importance to diverse disciplines of science. They are involved in processes of interest to biochemistry (enzymatic reactions), meteorology (formation of water clathrates in clouds and droplets), organic chemistry (template-effect syntheses), physical chemistry (catalysis involving zeolites), solid-state physics (ferroelectrics based on endohedral fullerites), and chemical engineering (formation of alkane clathrates in gas pipes). Although the recent years have witnessed several theoretical studies of supramolecular systems,[1] predictions of their properties have remained mostly a domain of molecular mechanics and low-level semiempirical methods, the notable exceptions being endohedral complexes of fullerenes[2] and a few small species.[3] Three factors have been impeding more widespread application of *ab initio* electronic structure methods to supramolecular systems. First, the host molecules are in most cases quite large, making rigorous calculations prohibitively expensive if not impossible at present. Second, the complexes usually lack high molecular symmetry, rendering savings in computational effort due to elimination of symmetry-redundant quantities impossible. Third, host cages (such as calixarenes) are often quite flexible, giving rise to a large totality of possible energy minima that dramatically increases the cost of calculations.

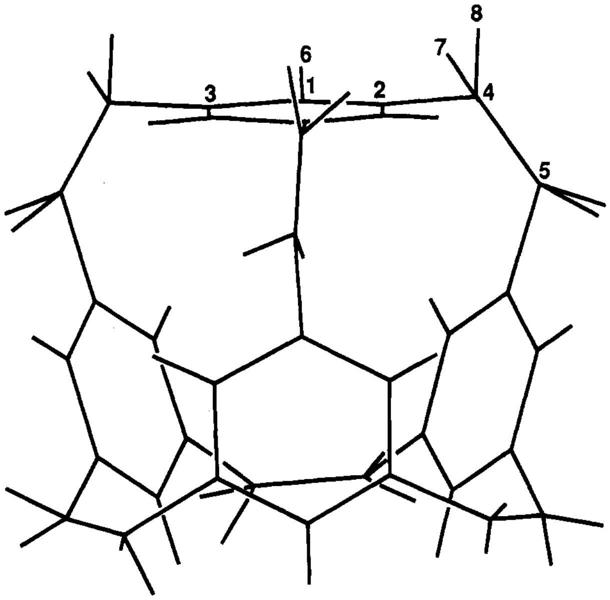

Figure 1. Molecular skeleton of the $C_{36}H_{36}$ spheriphane molecule.

Although the last two of these factors are not an issue in the case of fullerene host cages, the resulting endohedral complexes possess several properties, such as very high barriers to formation, that are atypical of other supramolecular systems.[4] For this reason, we have recently embarked upon research on species that are more representative of common guest−host complexes yet are amenable to theoretical treatment. Complexes of alkali metal cations with heptacyclo[$13.13.2^{1,15}.2^{8,22}.1^{3,27}.1^{6,10}.1^{13,17}.1^{20,24}$]hexatriaconta-1,3(33),6,8,10(34),13,15,17(35),20,22,24(36),27-dodecaene (the $C_{36}H_{36}$ spheriphane, Figure 1), which has been recently synthesized by Vögtle et al.,[5] are good examples of such species. In this paper, we report large-scale Hartree−Fock calculations on complexes with the composition of $C_{36}H_{36}\cdot M^+$, where M = Li, Na, and K. These

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calculations, which to our knowledge constitute the first *ab initio* electronic structure theoretical study of inclusion complexes of this size, provide interesting predictions of guest discrimination, stabilities, relative energies of endohedral and exohedral isomers, and barriers to encagement of the guests.

Details of the Calculations

The geometry of the $C_{36}H_{36}$ spheriphane molecule was initially optimized within the constrains of T symmetry at the HF/STO-3G level of theory. The GAUSSIAN 90 suite of programs[6] was used. All of the corresponding vibrational frequencies were found to be positive, indicating that a genuine energy minimum was obtained despite the symmetry constraints. Subsequent calculations were carried out at the HF/6-311G** level of theory with the TURBOMOLE system of programs.[7] For the potassium atom, an uncontracted (17s11p1d) even-tempered basis set was used. The parameters that determine the orbital exponents were optimized, yielding the Hartree–Fock energy of the K^+ cation equal to −599.014 072 hartrees.

With these basis sets, geometry optimizations within T symmetry were performed for the pristine host and its complexes with the guests placed at the host cage center. The resultant optimized geometries of the $C_{36}H_{36}$ cage were frozen in a series of single-point calculations (carried out within C_3 symmetry) in which the guests were displaced along the C_3 symmetry axes. The NMR shifts in the $C_{36}H_{36}$ hydrocarbon were computed using a CPHF GIAO program[8] interfaced with TURBOMOLE and modified in order to avoid disk storage of two-electron integrals.[9] The benzene molecule (the ^1H and ^{13}C shifts measured respectively at 7.37 and 128.5 ppm in $CDCl_3$[10]) was used as a standard in conversions between the absolute shieldings and the shifts.

Results and Discussion

The aesthetically appealing $C_{36}H_{36}$ spheriphane molecule (Figure 1) consists of four benzene rings connected by six $-CH_2CH_2-$ chains. The resulting host cage possesses four openings through which sufficiently small guests can enter. The size of each opening is determined by hydrogen atoms protruding from three benzene rings. These hydrogens are located ca. 2.0 Å from the C_3 symmetry axis that passes through the centers of the fourth benzene ring and the opening. Within T molecular symmetry, the geometry of $C_{36}H_{36}$ is fully determined by seven bond lengths, six bond angles, and five torsional angles. The optimized values of bond lengths and angles (Table 1) are close to those encountered in common hydrocarbons. The benzene rings are essentially planar, as reflected in values of the $C_4-C_2-C_1-H_6$ and $C_3-C_1-C_2-C_4$ torsional angles that do not deviate significantly from 0 and 180°, respectively. The computed vibrational frequencies testify to substantial stiffness of the cage with respect to expansion. At the HF/6-311G** level of theory, the predicted ^1H and ^{13}C NMR shifts equal 2.26, 2.59 (protons of the CH_2 groups), 6.53 (protons of the benzene rings), 27.2 (carbons of the CH_2 groups), 125.3, and 141.5 ppm (carbons of the benzene rings). The good agreement between these values and the experimentally determined shifts of 2.89, 2.89, 6.47, 33.3, 126.5, and 138.7 ppm indicates the closeness of the optimized geometry to that of the real molecule in solution.

Table 1. The HF/6-311G** Optimized Geometries of $C_{36}H_{36}$ and Its Complexes[a]

atoms[b]	$C_{36}H_{36}$	$C_{36}H_{36}\cdot Li^+$	$C_{36}H_{36}\cdot Na^+$	$C_{36}H_{36}\cdot K^+$
C_1-C_2	1.382	1.385	1.385	1.387
C_1-C_3	1.393	1.396	1.396	1.397
C_1-H_6	1.076	1.076	1.076	1.076
C_2-C_4	1.517	1.515	1.516	1.519
C_4-C_5	1.542	1.541	1.542	1.545
C_4-H_7	1.085	1.084	1.084	1.084
C_4-H_8	1.088	1.086	1.086	1.087
$C_2-C_1-H_6$	119.02	119.03	119.02	118.99
$C_3-C_1-H_6$	119.48	119.45	119.43	119.37
$C_1-C_2-C_4$	120.27	120.45	120.40	120.27
$C_2-C_4-H_7$	108.55	108.74	108.67	108.48
$C_2-C_4-H_8$	109.27	109.05	109.01	108.88
$C_2-C_4-C_5$	115.73	114.95	115.28	116.25
$C_4-C_2-C_1-H_6$	−0.40	0.08	0.28	0.90
$C_3-C_1-C_2-C_4$	180.52	178.76	179.35	181.02
$C_1-C_2-C_4-H_7$	4.87	4.58	4.43	3.92
$C_1-C_2-C_4-H_8$	249.81	249.40	249.35	249.12
$C_1-C_2-C_4-C_5$	128.30	128.06	128.01	127.82

[a] All bond lengths in Å, bond angles and torsional angles in deg. T symmetry assumed for complexes with the guests located at the center of the host cage. See the text for the description of the basis set for K. [b] See Figure 1.

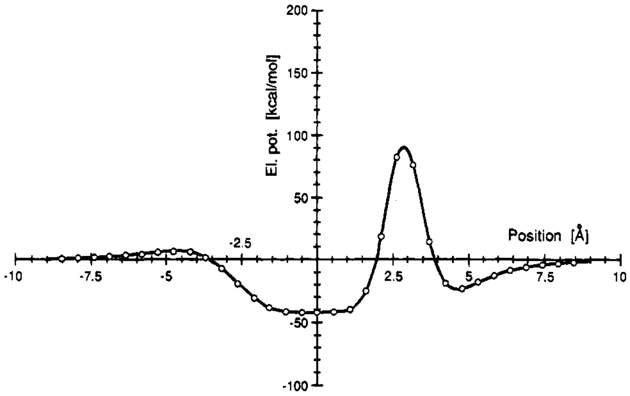

Figure 2. Electrostatic potential (converted to energy units) along the C_3 symmetry axis in $C_{36}H_{36}$.

Table 2. The Stationary Points in the HF/6-311G** Electrostatic Potential of the $C_{36}H_{36}$ Spheriphane

point	R^a (Å)	$U(R)$ (kcal/mol)
maximum 1	−4.683	7.18
minimum 1	0.000	−41.67
maximum 2	2.876	90.00
minimum 2	4.606	−24.37

[a] Distance from the host cage center.

The HF/6-311G** electrostatic potential along the C_3 symmetry axis of $C_{36}H_{36}$ (Figure 2) possesses two minima and two maxima (Table 2). An electrostatic energy barrier of ca. 7 kcal/mol is encountered as one approaches each opening of the host cage. Past this shallow barrier, a broad and deep minimum of ca. −42 kcal/mol is reached at the cage center, followed by a steep increase in the electrostatic potential as one passes through the center of each benzene ring. A secondary minimum of ca. −24 kcal/mol is located on the top of each benzene ring.

The location and depth of the electrostatic potential minima have been widely used in the past to infer the magnitude and the orientational preference of interactions between small charged guests (such as protons and metal cations) and organic molecules.[11] In light of the calculated electrostatic potential in the $C_{36}H_{36}$ host, one predicts the $C_{36}H_{36}\cdot M^+$ species to exist in two forms, namely the endohedral one with the alkali metal cation located close to the cage center and the exohedral one

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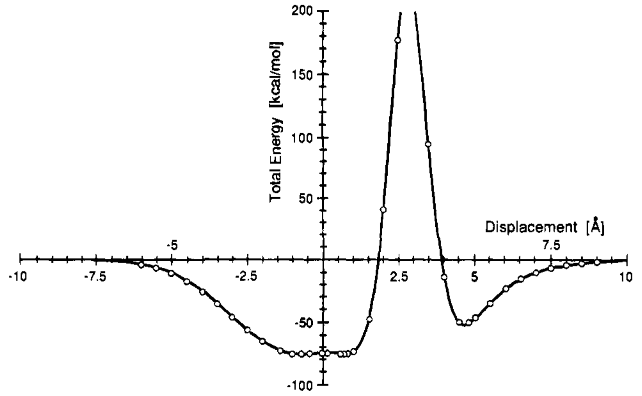

Figure 3. The HF/6-311G** total energy of the $C_{36}H_{36} \cdot Li^+$ system (relative to isolated $C_{36}H_{36} + Li^+$) vs displacement of the guest from the host cage center.

Table 3. The Stationary Points in the HF/6-311G** Total Energy of the $C_{36}H_{36} \cdot Li^+$ System

point	R^a (Å)	$E(R)^b$ (kcal/mol)
minimum 1	−0.786	−76.48
maximum 1	0.000	−75.49
minimum 2	0.659	−76.45
maximum 2	2.848	220.03
minimum 3	4.646	−52.18

[a] Displacement of the guest from the host cage center. [b] Energy relative to isolated $C_{36}H_{36} + Li^+$.

with the guest hovering above one of the benzene rings. The latter isomer is expected to be less stable than the former.

Inspection of our results for the $C_{36}H_{36} \cdot Li^+$ system (Figure 3 and Table 3) confirms the above predictions in a qualitative sense. The endohedral isomer is essentially a π-electron complex, as indicated by the distance of 1.807 Å between the Li^+ cation and the benzene ring, which is similar to that of 2.022 Å calculated at the HF/6-31G level of theory for the benzene · Li^+ species.[12] Relative values of these two distances suggest that the Li^+ cation binds more strongly to $C_{36}H_{36}$ than to C_6H_6—a difference than can be attributed to the higher polarizability of the former guest and/or the better basis set used in our calculations. The difference in binding strength is also evident in the respective complexation energies (−52.2 vs −36.1 kcal/mol). One should note that the potential energy curve is relatively steep in the vicinity of the exohedral minimum, implying small amplitudes of the Li^+ librations.

Bonding in the endohedral isomer of $C_{36}H_{36} \cdot Li^+$ is very similar in nature to that in the $Li^+@C_{60}$ endohedral complex.[2,4] As one may conclude from the data compiled in Tables 2 and 3, the electrostatic component contributes only about 55% to the total interaction energy in the endohedral $C_{36}H_{36} \cdot Li^+$. The remaining 45% is a sum of the stabilizing electrostatic polarization and destabilizing steric repulsion components, the former one being obviously predominant. As in $Li^+@C_{60}$, the dipole—dipole part of the electrostatic polarization component is responsible for the propensity of the guest to move from the cage center. Because of this propensity, placing the Li^+ cation at the center of the $C_{36}H_{36}$ cage gives rise to an energy maximum. The actual minima are attained for Li^+ located either −0.786 or 0.659 Å from the host cage center, the evident asymmetry caused by steric repulsion that favors displacement away from the benzene ring. The minima are only ca. 1 kcal/mol lower in energy than the maximum and the potential energy curve is very flat for small values of the guest displacement, meaning that the Li^+ cation can rattle freely inside the host cage at room temperature. The direct barrier separating the exohedral isomer from its endohedral counterpart is formidable (272 kcal/mol), as it involves penetration of the benzene ring. However, there is no energy barrier to the insertion of the Li^+ cation through any of the host cage openings. Therefore, one expects the isomer interconversion reaction to involve "sliding" of the Li^+ cation from the benzene ring into one of the cage "windows".

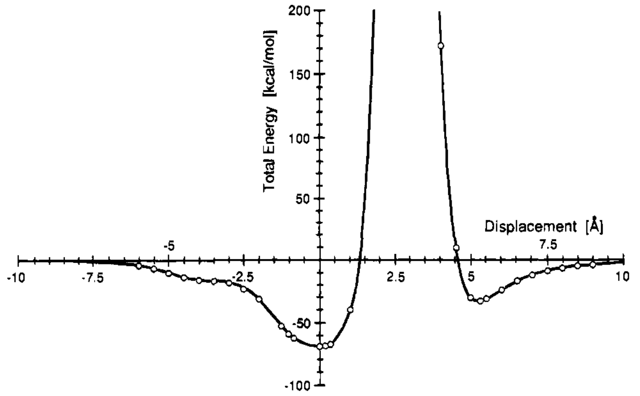

Figure 4. The HF/6-311G** total energy of the $C_{36}H_{36} \cdot Na^+$ system (relative to isolated $C_{36}H_{36} + Na^+$) vs displacement of the guest from the host cage center.

Table 4. The Stationary Points in the HF/6-311G** Total Energy of the $C_{36}H_{36} \cdot Na^+$ System

point	R^a (Å)	$E(R)^b$ (kcal/mol)
minimum 1	0.000	−68.75
maximum 1	2.861	910.11
minimum 2	5.234	−32.50

[a] Displacement of the guest from the host cage center. [b] Energy relative to isolated $C_{36}H_{36} + Na^+$.

The $C_{36}H_{36} \cdot Na^+$ system (Figure 4 and Table 4) is qualitatively similar to its $C_{36}H_{36} \cdot Li^+$ congener, the only difference being the fact that placing the guest at the host cage center produces an energy minimum rather than a maximum. This qualitative change in the potential energy hypersurface is in sharp contrast to the situation encountered in endohedral complexes of the C_{60} cluster, for which electronic structure calculations find the displacement of the Na^+ cation to be finite (although less than half that of Li^+).[2,4] Apparently, the cage radius of the $C_{36}H_{36}$ spheriphane is sufficiently small to entirely suppress the displacement of the relatively large Na^+ cation. The difference in guest sizes also has a direct effect on the complexation energies. In comparison with the $C_{36}H_{36} \cdot Li^+$ species, the endohedral and exohedral isomers of $C_{36}H_{36} \cdot Na^+$ are respectively ca. 8 and 22 kcal/mol less stable. The insertion into the host remains barrier-free for the Na^+ guest.

Replacing the Na^+ guest by the markedly larger K^+ cation brings about substantial changes in the potential energy curve of the corresponding complex (Figure 5). These changes include the appearance of a new shallow minimum that corresponds to the guest cation located in front of the host cage opening. The minimum, which is only ca. 5 kcal/mol deep (Table 5), is the result of the competition between the attractive interactions that increase steadily as the guest enters the cage and strong steric repulsions that rise sharply as the guest approaches the ridges of the cage opening. This competition is also responsible for the left-side shoulder in the potential energy curve of the $C_{36}H_{36} \cdot Na^+$ system (Figure 4). The new minimum lies in the vicinity of a large energy barrier. Since this barrier is absent

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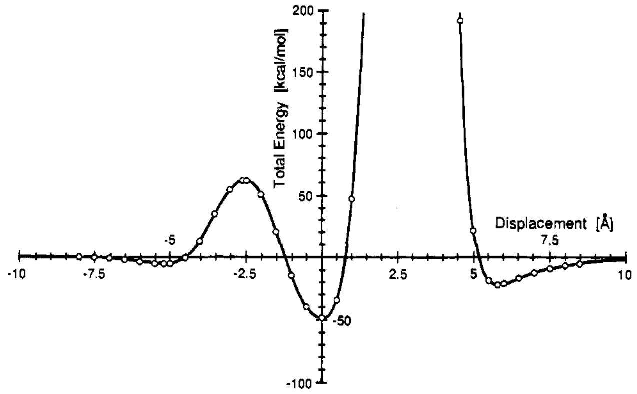

Figure 5. The HF/6-311G** total energy of the $C_{36}H_{36} \cdot Na^+$ system (relative to isolated $C_{36}H_{36} + K^+$) vs displacement of the guest from the host cage center.

Table 5. The Stationary Points in the HF/6-311G** Total Energy of the $C_{36}H_{36} \cdot K^+$ System

point	R^a (Å)	$E(R)^b$ (kcal/mol)
minimum 1	−5.192	−5.18
maximum 1	−2.530	62.75
minimum 2	0.000	−48.48
maximum 2	2.910	2170.30
minimum 3	5.816	−20.66

[a] Displacement of the guest from the host cage center. [b] Energy relative to isolated $C_{36}H_{36} + K^+$; see the text for the description of the basis set for K.

in the complexes involving Li^+ and Na^+, one expects the $C_{36}H_{36}$ spheriphane to exhibit the property of guest discrimination, i.e. formation of inclusion compounds that is facile with lighter alkali metal cations and hindered with heavier alkali metal cations. Conversely, once formed, the endohedral $C_{36}H_{36} \cdot K^+$ is predicted to be less labile than either of its Li^+ and Na^+ analogs.

Several potential sources of error should be considered before assessing the relevance of the aforedescribed theoretical predictions to experimental research. First of all, one has to address the issues of the basis set superposition error (BSSE) and the neglect of correlation energy. Because of the reasonably large basis sets employed in the present calculations, BSSE should ge negligible for all practical purposes. The lack of electron correlation effects is a more serious problem, as it gives rise to the exclusion of the London interactions. However, as the guest polarizabilities are relatively small, these interaction are expected to neither alter the shapes of the potential energy curves nor significantly contribute to the relative stabilities of the $C_{36}H_{36} \cdot M^+$ isomers.

The freezing of the host geometries at those of complexes with the guests located at the cage center should also be addressed here. This freezing, which had to be imposed in order to make the calculations computationally feasible, does not alter the energies of the endohedral isomers and its impact on the energies of the exohedral isomers is minimal. In fact, inspection of Table 1 reveals that the host geometry undergoes only small, although systematic, changes upon the placement of the guests, suggesting that even the bond lengths and angles of the pristine $C_{36}H_{36}$ hydrocarbon could have been used throughout the calculations without seriously affecting the computed properties. Allowing the host cage to relax fully would lower the energies along the potential energy curve. Therefore, such a geometry relaxation could not generate barriers to the guest insertion in complexes with Li^+ and Na^+. Although the barrier present in the $C_{36}H_{36} \cdot K^+$ system would be lowered, it would not be entirely eliminated because of the substantial stiffness of the host cage.

Finally, one should be reminded that the above calculations do not include solvent effects. Reversal of the predicted orders of stability, which are valid for gas-phase reactions, could conceivably occur in some solvents. This is so, because the formation of endohedral isomers requires stripping all molecules of solvent from the guest cations, whereas retention of some solvent molecules is possible for exohedral species. On the other hand, nonspecific effects due to solvent polarization (reaction field), which are commonly described with continuum models, are expected to be negligible because of the large size of the host cage.

Conclusions

Properties of complexes formed between the $C_{36}H_{36}$ spheriphane and alkali metal cations are strongly affected by the guest size. For each of the Li^+, Na^+, and K^+ guests, two minima on the potential energy hypersurface are found, corresponding to endohedral and exohedral isomers, respectively. The endohedral isomers (inclusion complexes), which are more stable in the gas phase than their exohedral counterparts, are similar to the analogous endohedral complexes of the C_{60} fullerene. However, the displacement of the guest from the cage center is suppressed in the endohedral $C_{36}H_{36} \cdot Na^+$ species, whereas it is not in $Na^+@C_{60}$. The less stable exohedral isomers are essentially π-complexes between one of the benzene rings of the spheriphane and the guest cation. Their conversion to the corresponding endohedral structures is predicted to be barrier-free in complexes with Li^+ and Na^+ and involve "sliding" of the cation along the benzene ring into one of the host cage openings. On the other hand, the formation of the analogous endohedral $C_{36}H_{36} \cdot K^+$ species is predicted to be hindered by a high-energy barrier and proceed through an intermediate with the guest located in front of the host cage opening.

The present study, which uncovers the phenomenon of guest discrimination in complexes of alkali metal cations with the $C_{36}H_{36}$ spheriphane, demonstrates that useful theoretical predictions can be obtained with rigorous *ab initio* electronic structure methods for supramolecular systems, provided the host molecule is inflexible enough to rule out the possibility of a large number of conformational isomers.

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