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Ammonium Ion Complexes of Tetraethyl Resorcarene: An *Ab Initio* Study

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The complexation of various ammonium ions with a resorcarene host was evaluated by *ab initio* calculations. The approximations of the binding locations and the interaction energies for each guest are reported. The supramolecular complex formation also affects the conformation of the resorcarene host.

Keywords: Resorcarenes; *Ab initio* calculations; Supramolecular complexes; Ammonium ions

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INTRODUCTION

Host–guest chemistry is a rapidly developing area of chemistry. The one-pot synthesizable resorcarenes are a relatively new class of artificial host compounds [1,2] that have been described as hosts for ammonium ions [3–9] and especially for acetylcholine [10–13]. The C_4 crown conformation with a homodirectional circular array of intramolecular hydrogen bonds between the OH-groups is the most stable conformation [14] and was used in our complexation calculations. Methylammonium ions were used as guests, and other ammonium ions were used to produce supplementary data. These particular ions were chosen because of their previous use in our mass spectrometric experiments [8]. Complex formation occurs mainly in the cavity of the host resorcarene: the upper rim of the cavity is at the level of the resorcinol OH-hydrogens and the lower rim is at the level of the resorcinol hydrogens pointing 'down'. The tetraethyl resorcarene and the guests under investigation are presented in Fig. 1.

EXPERIMENTAL

The starting geometry of the host resorcarene was the most stable conformation, the C_4 crown, observed in our earlier study [14]. The ammonium guests were positioned randomly inside the cavity of tetraethyl resorcarene and the whole host-guest system was fully preoptimized several times. The final optimization calculations were made to the starting geometries, producing promising preliminary results. In addition, some single-point energy calculations were undertaken for verification of other systems. Thus, the final geometries reported are assumed to have a global minimum energy configuration. It is unlikely that significantly more stable structures occur when the positioning of the guests or the directions of the H-bonds of the resorcarene host are altered. Additional density functional theory (DFT) calculations were made for comparison of binding energies by two different methods.

Preoptimization calculations were performed with Gaussian 98 [15] using the Hartree–Fock (HF) method with generic basis sets 6-31G++(d,p) for the eight resorcinol OH-groups and 3-21G for the rest of the molecular skeleton and the ammonium guests. Despite the limitations of the relatively small basis set 3-21G, it is thought to account reasonably for the structures [16]. Final optimization calculations were performed with Gaussian 03 [17] using the HF method with generic basis sets 6-31G++(d,p) for the eight resorcinol OH-groups and 6-31G(d) for the rest of the molecular skeleton and the ammonium guests. DFT calculations were performed as single-point energy calculations with B3LYP/6-311G++(d,p) to the optimized structures from HF calculations.

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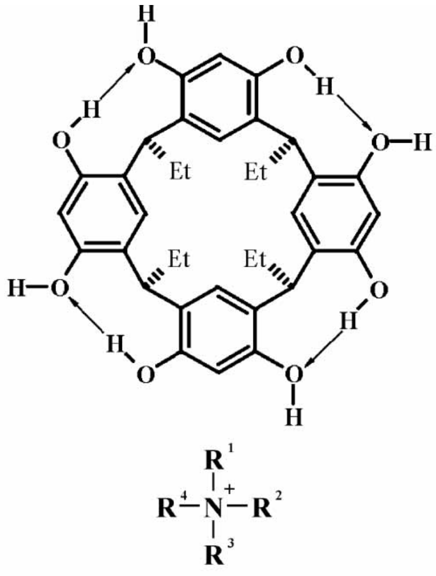

A: $R^1 = R^2 = R^3 = R^4 = H$
MM; ME; MP: $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$; CH_2CH_3; $CH_2CH_2CH_3$
DM; DE: $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$; CH_2CH_3
TrM; TrE: $R^1 = H$; $R^2 = R^3 = R^4 = CH_3$; CH_2CH_3
TeM; TeE: $R^1 = R^2 = R^3 = R^4 = CH_3$; CH_2CH_3

FIGURE 1 Tetraethyl resorcarene with homodirectional array of hydrogen bonds and the ammonium ions as guests.

TABLE I Effect of ammonium ion complexation on the resorcarene skeleton. The distances shown are internuclear between the opposite upper rim resorcinol hydrogens. The counterpoise corrected relative binding energies of the ammonium ions are given

	Length (Å)	Width (Å)	Energy (kJ/mol) HF	Energy (kJ/mol) B2LYP
C_4 crown	9.89	9.89	—	—
MM1	10.72	8.81	− 137.3	− 156.5
DM	10.09	9.78	− 111.9	− 126.3
TrM	10.07	9.87	− 95.4	− 105.8
TeM	10.25	9.58	− 76.3	− 83.4
ME	10.80	8.69	− 131.7	− 148.8
DE	10.81	8.77	− 110.9	− 111.4
TrE	10.31	9.61	− 61.9	− 66.6
TeE	10.45	9.44	− 60.8	− 65.1
MP	9.95	9.86	− 128.0	− 142.5
A	10.93	8.35	− 154.0	− 174.1

The calculations provided: (a) the conformational change of the host resorcarene, (b) the relative energies of the interactions, and (c) the approximation of the most favorable docking location for each ammonium ion. The counterpoise corrected [18] interaction energies should be considered as approximate because of the lack of electron correlation effects.

RESULTS AND DISCUSSION

In every case, the complexation of the guest affected the molecular skeleton of the host resorcarene, causing a conformational change from C_4 crown to C_2 boat. These conformational changes and the relative interaction energies are presented in Table I. The interaction energies of the guest are the sum of several possible noncovalent interactions, for example electrostatic interactions, H-bonding and interactions with π-clouds.

The most favorable location for the monomethylammonium ion is in the center of the cavity. The orientation of the guest ion is vertical, with the ammonium end pointing down in the cavity. The complexation induces a conformational change in the host resorcarene, causing the complex formed to appear as a boat with a tiny mast, as depicted in Fig. 2. The binding energy of the methylammonium ion is strongest in this series (Table I).

On the contrary, the dimethylammonium ion is located approximately at the level of the upper rim such that the methyl group is in the middle of the cavity and the ammonium is near the wall of the cavity. The two ammonium hydrogens are pointing towards two resorcinol rings and the other methyl group is pointing up from the cavity (Fig. 2). This complexation induces a minor conformational change in the host resorcarene.

The complex with the trimethylammonium ion is unlike all other methylammonium complexes. The guest is not located in the middle of the cavity but near to the cavity wall in such a way that one ammonium hydrogen is pointing directly towards the aromatic ring. This particular location causes only a minor conformational change in the molecular skeleton of the resorcarene host (Fig. 3).

The complexation of quaternary ammoniums, including tetramethylammonium, to the cavity of

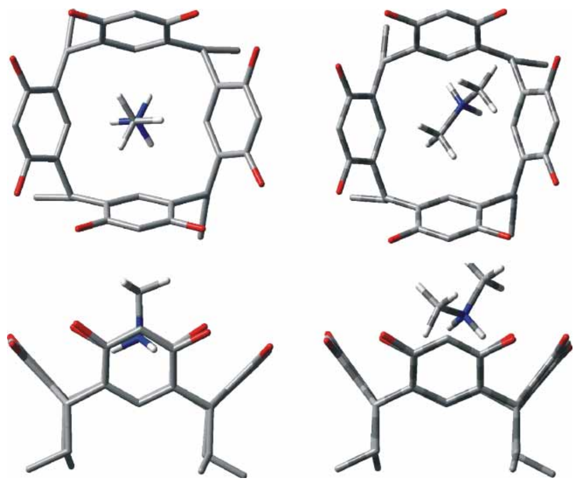

FIGURE 2 Methyl- (left) and dimethylammonium (right) complexes of tetraethyl resorcarene. The hydrogens of the host are omitted for clarity.

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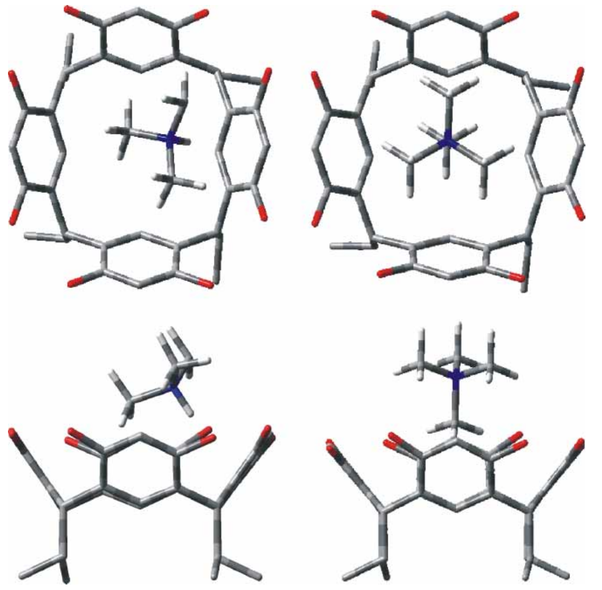

FIGURE 3 Tri- (left) and tetramethylammonium (right) complexes of tetraethyl resorcarene. The hydrogens of the host are omitted for clarity.

the resorcarene tetraanion has been depicted earlier by Schneider and Schneider [3]; the guest ammoniums are orientated in such a way that one methyl group is located in the cavity. Our calculations led to the same result, with one methyl group located in the cavity (Fig. 3). With this orientation the cavity becomes effectively filled. However, the overall size of the guest ion is very large relative to the volume of the cavity so that a large part of the guest ion is in fact located above the cavity. Even so, it induces a conformational change in the host.

With the methylammonium ions, the binding energies decrease while the degree of ammonium ion substitution increases, thus correlating with the ability to form intermolecular H-bonds with the host resorcarene. In addition, the methylammonium ion is located, at least partially, inside the cavity, while the other methylammonium ions seem to 'float' above the cavity.

Ethylammonium ions were also investigated for comparison. The ethylammonium ion has an elongated structure, which means that both vertical and horizontal guest orientations are possible. According to the calculations, a relatively stable complex is formed in both orientations but the vertical orientation of the guest is slightly favored. The ammonium end lies inside the cavity, which makes the complex look like a boat with a long and angular mast (Fig. 4).

The diethylammonium ion is located almost above the cavity as seen in Fig. 4. The methyl end is inside the cavity and the ammonium hydrogens are pointing towards the upper rim of the cavity. The structure is remarkably similar to that of the dimethylammonium complex. In addition, a correlation of the locations between trimethyl- and triethylammonium ions is clearly present: the triethylammonium is located above the cavity and the ammonium hydrogen is pointing towards the resorcinol unit (Fig. 5). Again the conformational change caused by this ion is the smallest in the series of ethylammonium ions.

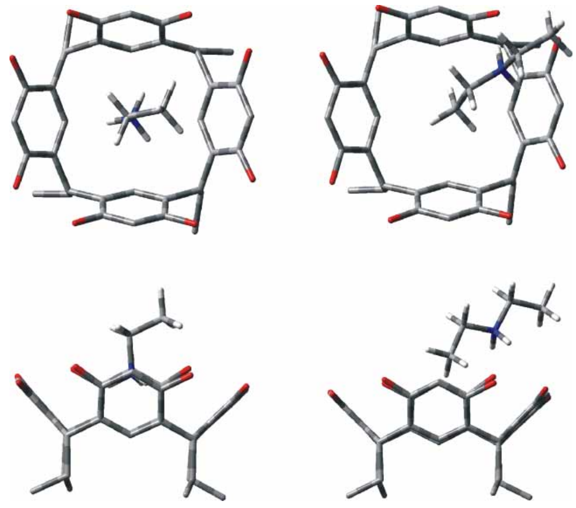

FIGURE 4 Ethyl- (left) and diethylammonium (right) complexes of tetraethyl resorcarene. The hydrogens of the host are omitted for clarity.

With tetraethylammonium the large size of the cation affects the binding. The branched and spherical structure of the guest reduces the complex formation ability. Because of steric hindrance, only a minor part of one hydrocarbon chain is located in

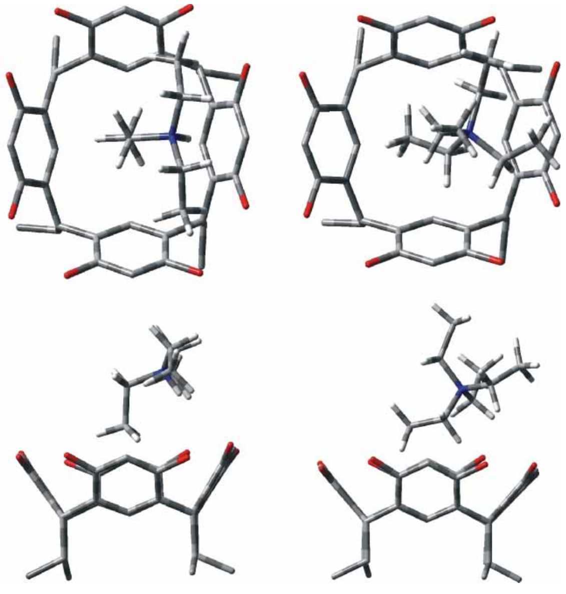

FIGURE 5 Tri- (left) and tetraethylammonium (right) complexes of tetraethyl resorcarene. The hydrogens of the host are omitted for clarity.

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the cavity, while the rest of the guest ‘floats’ above the cavity and the resorcarene skeleton (Fig. 5). The guest causes only a minor conformational change but there seem to be some interactions strong enough to maintain the supramolecular complex. The appearance of the complex is remarkably similar to the crystal structure reported [19].

With the ethylammonium series, the size of the guest increases rapidly. Thus, the guests are mainly floating above the cavity, although there are still sufficient holding interactions present. As with the methylammoniums, the interactions decrease when the size of the guest increases. With these docking locations of the tri- and tetraethyl ions the energy difference is extremely small.

The propylammonium ion behaves in a similar way to the ethylammonium ion. The orientation of the guest ion is vertical and the ammonium end lies inside the cavity (Fig. 6). Surprisingly, this particular guest did not induce significant conformational changes in the host. With monosubstituted ammonium ions the trend remains: the increase in the length of the hydrocarbon chain slightly decreases the relative binding energy. In addition, the positions inside the cavity are increasing when the length of the carbon chain increases.

Complexation of the ammonium ion NH_4^+ was also determined for comparison. This guest induces a drastic conformational change in the resorcarene skeleton. Two of the hydrogens are pointing down towards the bow and stern, and the remaining two are pointing up towards the sides of the boat. This particular position seems to be energetically favored, even though the relatively small size should also enable other possible orientations. The four hydrogen bonds make the binding energy the strongest of the ions investigated. As seen in Fig. 6, the ammonium ion is located approximately in the middle of the cavity, that is deeper inside the cavity when compared to the ammonium guests with hydrocarbon chains.

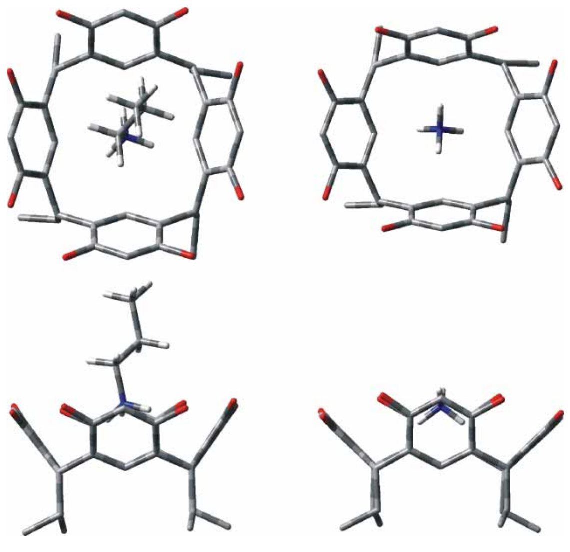

FIGURE 6 Propylammonium (left) and ammonium (right) complexes of tetraethyl resorcarene. The hydrogens of the host are omitted for clarity.

CONCLUSIONS

Complex formation between resorcarene as host and various ammonium ions as guests was evaluated with the Hartree–Fock method. The results suggest that, because of the differences in the structure of the ions, the most favorable orientation of the guest varies widely within the ammonium series. The stability of the complexes seems to correlate with the ability to form intermolecular H-bonds. This trend remains whatever the calculation method used. Complexation of the ammonium guest also induces a conformational change in the host.

Acknowledgements

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References

[1] Högberg, A. G. S. *J. Org. Chem.* **1980**, *45*, 4498.

[2] Niederl, J. B.; Vogel, H. J. *J. Am. Chem. Soc.* **1940**, *62*, 2512.

[3] Schneider, U.; Schneider, H.-J. *Chem. Ber.* **1994**, *127*, 2455.

[4] Schneider, H.-J.; Güttes, D.; Schneider, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 647.

[5] Lippmann, T.; Wilde, H.; Pink, M.; Schäfer, A.; Hesse, M.; Mann, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1195.

[6] Schneider, H.-J.; Güttes, D.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6449–6454.

[7] Murayama, K.; Aoki, K. *Chem. Lett.* **1998**, 301.

[8] Mäkinen, M.; Nissinen, M.; Rissanen, K.; Vainiotalo, P. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 143.

[9] Kobayashi, K.; Asakawa, Y.; Aoyama, Y. *Supramol. Chem.* **1993**, *2*, 133.

[10] Schneider, H.-J.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 1613.

[11] Murayama, K.; Aoki, K. *Chem. Commun.* **1997**, 119.

[12] Inouye, M.; Hashimoto, K.; Isagawa, K. *J. Am. Chem. Soc.* **1994**, *116*, 5517.

[13] Schneider, H.-J.; Schneider, U. *J. Inclusion Phenom. Mol. Recogn.* **1994**, *19*, 67.

[14] Mäkinen, M.; Jalkanen, J.-P.; Vainiotalo, P. *Tetrahedron* **2002**, *58*, 8591.

[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.;

Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.9*; Gaussian, Inc. Pittsburgh, PA, 1998.

[16] Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1996.

[17] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03; Revision B.01*; Gaussian, Inc. Pittsburgh, PA, 2003.

[18] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

[19] Atwood, J. L.; Szumna, A. *J. Supramol. Chem.* **2002**, *2*, 479.

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