Theoretical investigation of the complexation of crown ethers and crown ethers of fulleropyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4†‡

Demeter Tzeli,* Ioannis D. Petsalakis and Giannoula Theodorakopoulos

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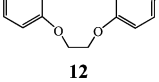
The electronic and geometric structures of dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and their complexes with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4 were investigated by employing density functional theory (B3LYP, M05-2X, M06-2X, MPWBIK and B2PLYP-D) in conjunction with three basis sets. Different energetic minima have been identified for all of the above molecules and complexes in the gas phase as well as in $CHCl_3$ solvent. We report geometries, complexation energies and some thermochemical data. For increasing values of x, the complexation energies, corrected for the basis set superposition error range from 3.29 to 0.73 eV in the gas phase and from 1.56 to 0.13 eV in the $CHCl_3$ solvent. In the case of the largest crown ethers, the 24-crown-8 ethers are folded around the ammonium cation so as to maximize the number of hydrogen bonds formed and present the largest complexation energies. Finally, the presence of fullero-N-methylpyrrolidine, attached to the crown ethers, does not change the complexation energies substantially.

I. Introduction

Macrocyclic polyethers (crown ethers, CrE) have stimulated considerable interest since their discovery.[1,2] It is well known that CrE are particularly adaptable hosts for a large number of guests.[4–6] Their ability to bind to neutral[5] and cationic[3,4] substrate species with a high degree of selectivity has motivated the use of CrE in many diverse fields; such as in membrane separation of cationic species, in enantiomer resolution, and in catalysis.[7] The strength of their binding with various species and its specificity are determined both by the conformations of the CrE, the size of the guest, the nature of the intermolecular interactions, and in solution depend also on the solvating ability of the solvent with respect to the cation and the complex. Thus, the investigation of the conformations and the complexation behavior of CrE and their derivatives are motivated both by potential technological applications and by scientific questions regarding the specificity of their binding.

During recent years the complexation of crown ethers with many guests has been investigated both experimentally and theoretically.[3–5] Guests such as substituted ammonium ions have received considerable attention. The $(CH_3)_xNH^+_{4-x}$ ammonium cations complexation by 12-crown-4 and 18-crown-6 ethers have been studied experimentally[8–14] and theoretically[7,15] in the gas phase[8,15] and in different solvents such as H_2O,[7,12] MeOH,[11] H_2O–MeOH[13] iPrOH,[11] tBuOH,[11] OctOH,[11] DMF,[11] DMSO,[11] Py,[11] HMPT,[11] Me_2CO,[11] MeCN,[11] acetonitril-dimethyl-sulfoxide,[10] $CHCl_3$,[14] and, CCl_4;[7] while, as far as we know, there is no study for complexes of 24-crown-8 ether with $(CH_3)_xNH^+_{4-x}$ cations. To the best of our knowledge, there is no experimental or theoretical information in the literature for complexes of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4 in the gas phase or in $CHCl_3$ solvent. These specific complexes are interesting because they are parts of supramolecular complexes formed by fullerene-CrE and electron donors such as π-extended tetrathiafulvalene (exTTF) derivatives. Recently, the formation of supramolecular complexes of different exTTF derivatives with fullerene crown ethers has been achieved by "threading" of the exTTF-containing ammonium salt through the CrE moiety, and in this manner stable 1 : 1 complexes between exTTF and fullerene have been achieved.[16,17] Similarly, other supramolecular systems involving CrE that can mimic the photosynthetic process, have the potential for constructing photonic, photocatalytic, and optoelectronic devices.[18]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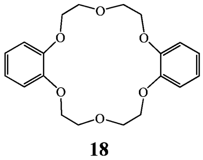
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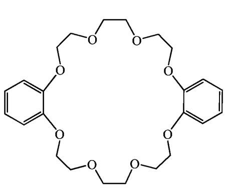
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In the present study the electronic and geometric structures of dibenzo-12-crown-4 (**12**), dibenzo-18-crown-6 (**18**), dibenzo-24-crown-8 ethers (**24**), and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and their complexes with

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Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation Address, 48 Vassileos Constantinou Ave., Athens, Greece. E-mail: dtzeli@eie.gr; Fax: 30 210 7273 794; Tel: 30 210 7273 813

† Electronic supplementary information (ESI) available: Tables 1S–3S and Fig. 1S–6S of dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and their complexes with $(CH_3)_xNH^+_{4-x}$, $x =$ 0–4. See DOI: 10.1039/c0cp00180e

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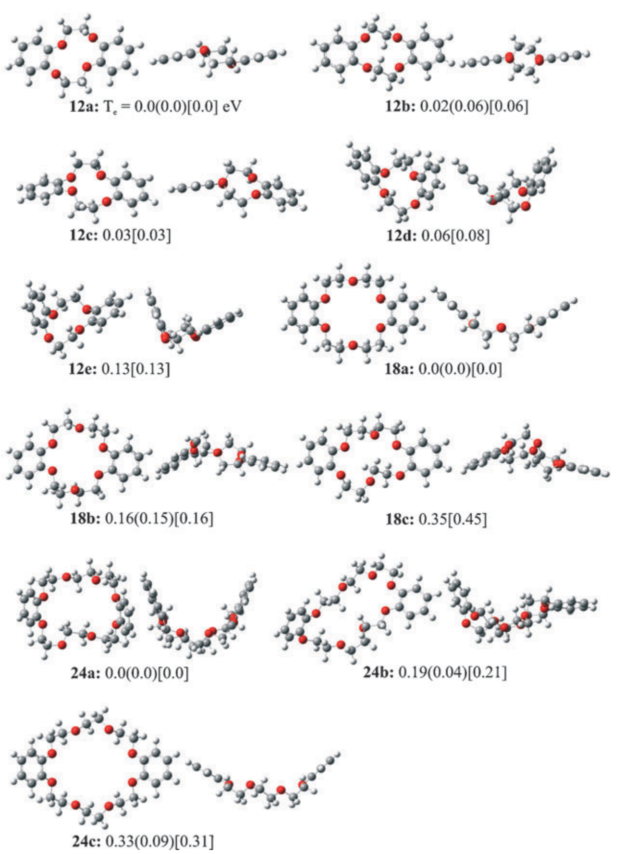
$(CH_3)_xNH_{4-x}^+$, $x = 0$–4 were studied by employing density functional theory (DFT). About 200 minima of the potential energy surface were calculated in the gas phase and in $CHCl_3$ solvent. We determined complexation energies, geometries, harmonic frequencies and some thermochemical data. We investigated the effect of the presence of fullero-N-methylpyrrolidine in the crown ethers and the solvation effect on the calculated complexation energies. In section II we define the computational procedure, in section III we discuss our results and in section IV we summarize our findings.

II. Computational procedure

Different isomers of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and their complexes with $(CH_3)_xNH_{4-x}^+$, $x = 0$–4 were investigated in the gas phase and in $CHCl_3$ solvent. 120 different minima have been identified for all of the above molecules and complexes in the gas phase and 80 in $CHCl_3$ solvent. The isomers of the crown ethers were determined as follows: first, the conformations most likely to be the energy lowest isomers of the three crown ethers were fully optimized. Second, a variety of distortions of the previous optimized isomers were introduced and the new structures were fully optimized. As a result, in some cases some new isomers were revealed. Next, the second step was repeated for the obtained isomers. Then, for all isomers found, the harmonic frequencies were calculated in order to find out which isomers are true minima. Only the true minima are given in the present study and they are presented in Fig. 1. The complexes of the minima of the crown ethers were obtained by attaching the $(CH_3)_xNH_{4-x}^+$ cations at different positions in the ring and subsequently all resulting structures were fully optimized. Again the harmonic frequencies of the complexes were calculated in order to determine the true minima, which are presented here in Fig. 2–4 and in Fig. 1S–2S of the ESI.†

Analytically, in the gas phase, five minima have been identified for dibenzo-12-crown-4 ether and four to six minima (depending on x) for its complex with $(CH_3)_xNH_{4-x}^+$; three minima for the dibenzo-18-crown-6 ether and three to four minima for its complex with $(CH_3)_xNH_{4-x}^+$; three minima for the dibenzo-24-crown-8 ether and five or six minima for its complex with $(CH_3)_xNH_{4-x}^+$. Subsequently, some of the lowest minima were also calculated in $CHCl_3$ solvent. Finally, five minima of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and 38 minima of their complexes with $(CH_3)_xNH_{4-x}^+$, $x = 0$–4 were calculated both in the gas phase and in $CHCl_3$ solvent. For the calculations in $CHCl_3$ solvent, the polarizable continuum model was employed.[19] This model is divided into a solute part, the dye, lying inside a cavity, surrounded by the solvent part represented as a structureless material characterized by its macroscopic properties, *i.e.* dielectric constants and solvent radius. This method reproduces well solvent effects.[20,21]



12a: T_e = 0.0(0.0)[0.0] eV
12b: 0.02(0.06)[0.06]
12c: 0.03[0.03]
12d: 0.06[0.08]
12e: 0.13[0.13]
18a: 0.0(0.0)[0.0]
18b: 0.16(0.15)[0.16]
18c: 0.35[0.45]
24a: 0.0(0.0)[0.0]
24b: 0.19(0.04)[0.21]
24c: 0.33(0.09)[0.31]

Fig. 1 Different minima of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers. T_e is the energy difference from the most stable structure in the gas phase (in $CHCl_3$ solvent) at B3LYP/6-31G(d,p) and [in the gas phase at B3LYP/6-311++G(d,p)]. Each structure is shown from two different viewing angles. (H atoms = white spheres, C atoms = grey spheres and O atoms = dark spheres (red online)).

All calculated minima were fully optimized using the B3LYP/6-31G(d,p) method in the gas phase and in $CHCl_3$ solvent. B3LYP is a DFT functional using Becke's three parameter gradient corrected functional[22] with the gradient corrected correlation of Lee, Yang, and Parr.[23] It is a widely used functional and generally works well for main group chemistry. Moreover, additional calculations were carried out using the M05-2X,[24] M06-2X,[25] MPWBIK,[26] and B2PLYP-D[27] functionals. The M05-2X and M06-2X are hybrid *meta* exchange correlation functionals. They are highly-nonlocal functionals with double the amount of nonlocal exchange. Both are recommended for the study of noncovalent interactions.[28] MPWBIK is based on the modified Perdew and Wang exchange functional (MPW) and Becke's 1995 correlation functional (B95). It is a hybrid *meta* functional that includes kinetic energy density and is recommended for non-covalent interactions, for hydrogen bonding and weak interaction calculations.[26,29] Finally, B2PLYP-D is a double-hybrid density functional with long-range dispersion corrections recommended for non-covalent interactions, too.

The 6-31G(d,p)[30] basis set was employed for all calculations, while additional calculations (fully geometry optimizations) for some chosen structures were carried out using the 6-311+G(d,p),[30] the 6-311++G(d,p),[30] and the 6-311++G(2df,2p)[30] basis sets for reasons of comparison. It should be noted that the latter basis set grows very quickly

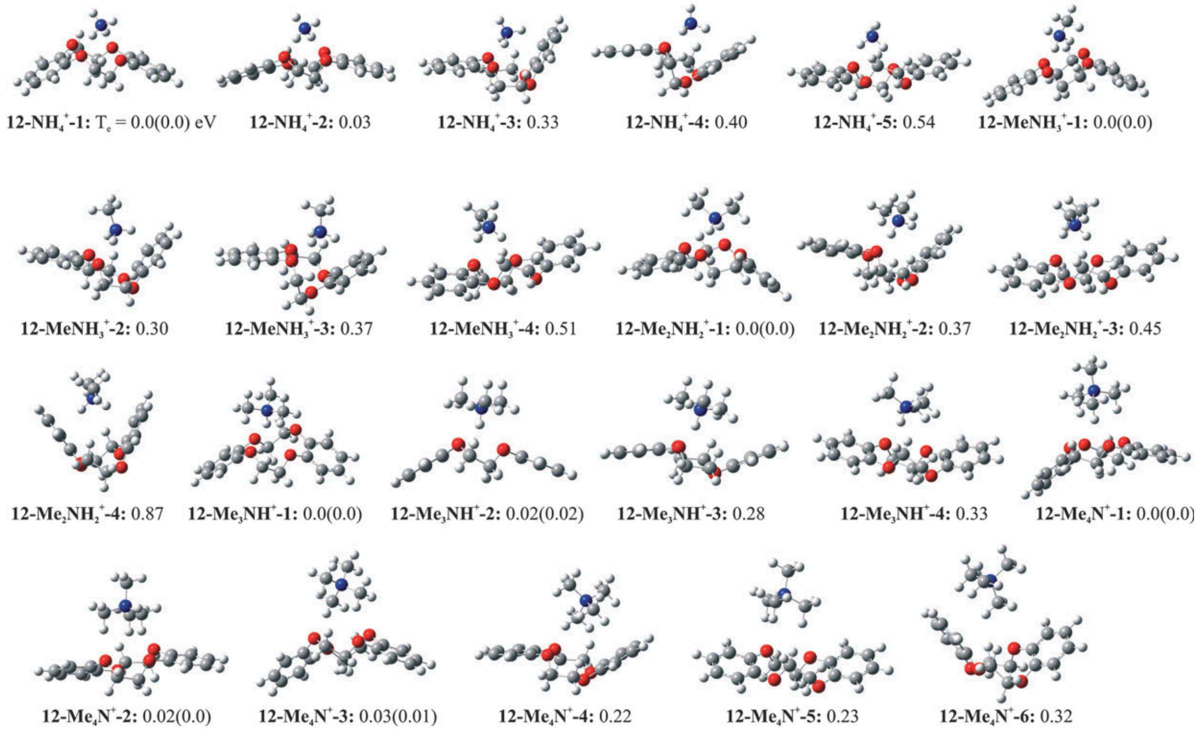


Fig. 2 Different minima and BSSE corrected relative energies with respect to the lowest minimum of dibenzo-12-crown-4 ether with $(CH_3)_xNH_{4-x}^+$, x = 0–4 in the gas phase (in $CHCl_3$ solvent). (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

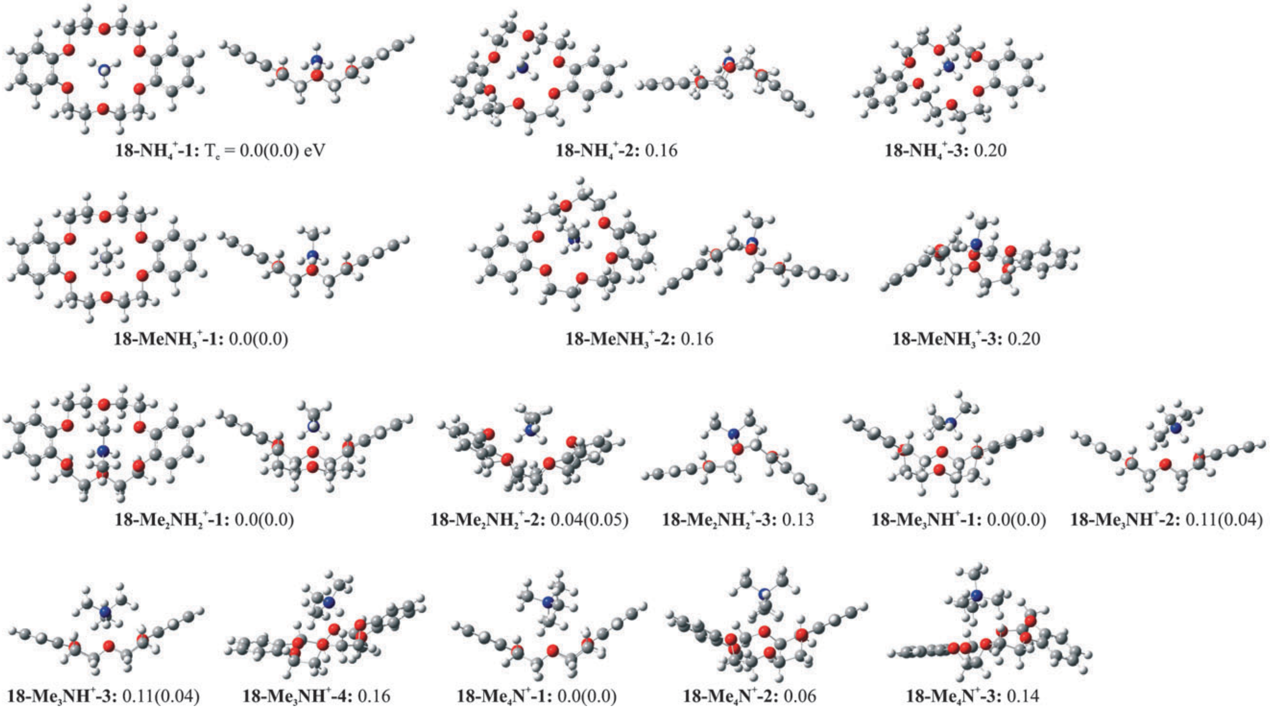


Fig. 3 Different minima and BSSE corrected relative energies with respect to the lowest minimum of dibenzo-18-crown-6 ether with $(CH_3)_xNH_{4-x}^+$, x = 0–4 in the gas phase (in $CHCl_3$ solvent). Some structures are shown from two different viewing angles. (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

with the number of atoms and was prohibitively large for calculations on the CrE-fullero-N-methylpyrrolidine clusters.

The harmonic frequencies and some thermochemical data were calculated for all calculated minima of dibenzo-12-crown-4,

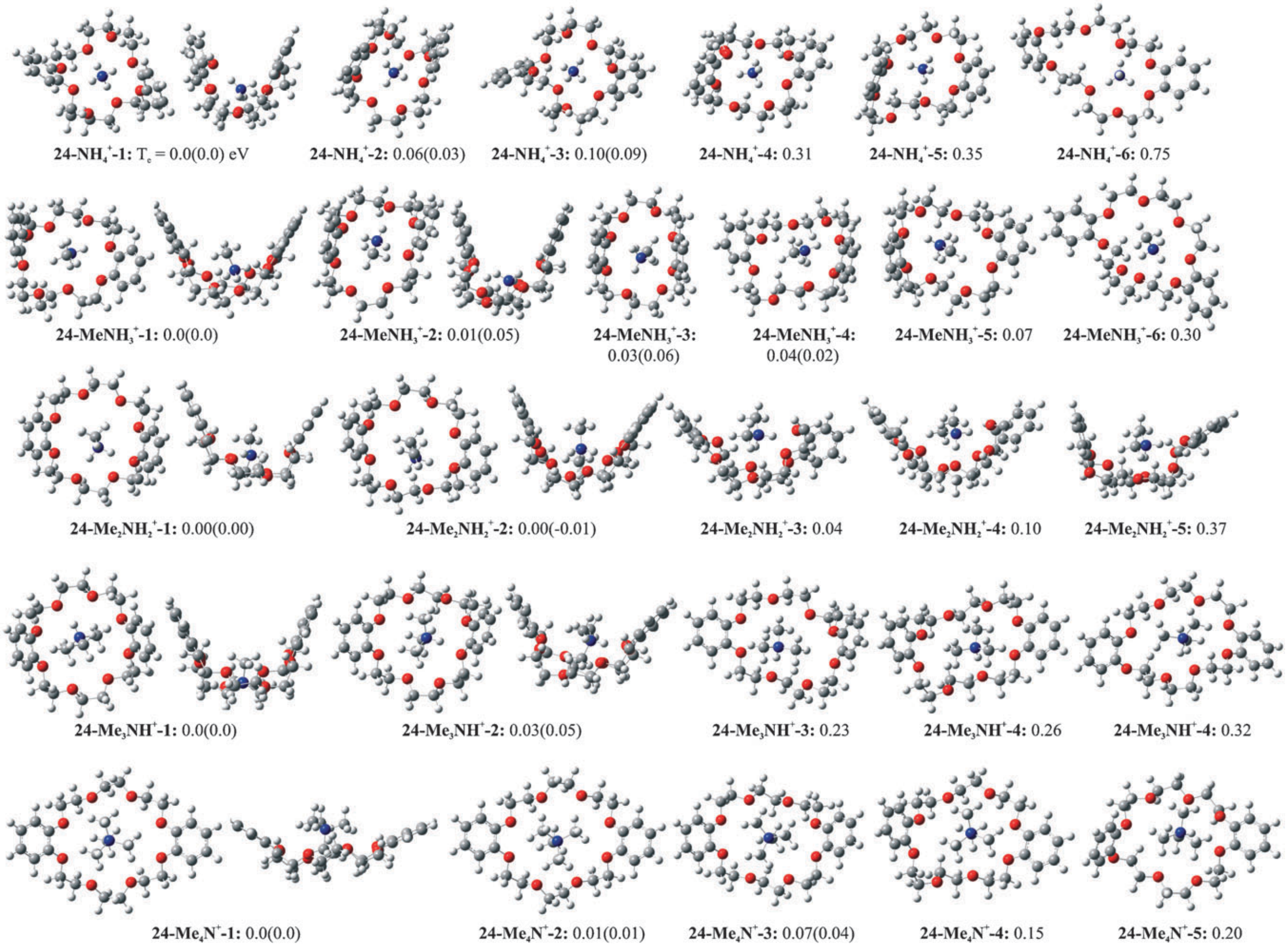


Fig. 4 Different minima and BSSE corrected relative energies with respect to the lowest minimum of dibenzo-24-crown-8 ether with $(CH_3)_xNH_{4-x}^+$, x = 0–4 in the gas phase (in CHCl$_3$ solvent). Some structures are shown from two different viewing angles. (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, of their complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4, and of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine.

For all found minima at all levels of theory, basis set superposition error (BSSE) corrections were made using the counterpoise procedure[31,32] since such corrections are especially important for van der Waals (vdW) systems[33] which is the case of the complexes calculated here. Thus, in the calculation of the all complexation energies the BSSE has been taken into account. All calculations were performed using the Gaussian 09 program package.[34]

III. Results and discussion

First, we try to select the best combination of functional and basis set for the present study. We cannot use a very large basis set because it grows very quickly with the number of atoms and will be prohibitively large for calculations on the CrE-fullero-N-methylpyrrolidine clusters.

Table 1 records the complexation energies without (CE$_u$) and with BSSE correction (CE) using different types of functionals and basis sets for the energy lowest NH_4^+·dibenzo-18-crown-6 and Me_4N^+·dibenzo-18-crown-6 complexes, *i.e.*, **18-NH$_4^+$-1** and **18-Me$_4$N$^+$-1**, respectively, see Fig. 3. We choose these two complexes because the dibenzo-18-crown-6 has a medium size among **12a**, **18a** and **24a** crown ethers (see Fig. 1) and for the case of the dibenzo-18-crown-6 ether, the **18-NH$_4^+$-1** is the most stable complex while the **18-Me$_4$N$^+$-1** has the weakest interactions (see below). We used the M05-2X, M06-2X, MPWBIK, and B2PLYP-D functionals which are recommended for non-covalent interactions, for hydrogen bonding and weak interaction calculations (see above) in conjunction with 6-31G(d,p), the 6-311++G(d,p), and the 6-311++G(2df,2p) basis sets for reasons of comparison. We can see that all the above M05-2X, M06-2X, MPWBIK, and B2PLYP-D functionals overestimate the CE values with the small 6-31G(d,p) relative to the largest 6-311++G(2df,2p) basis set by up to 0.3 eV for the **18-NH$_4^+$-1** and **18-Me$_4$N$^+$-1** complexes. Thus, the values resulting from a combination of M05-2X, M06-2X, MPWBIK, and B2PLYP-D functionals with the small basis set are not very good.

A second observation is that the CE values calculated for the **18-NH$_4^+$-1** complex are 2.90 eV at M06-2X/6-311++G(2df,2p) and 2.71 eV at MPWBIK/6-311++G(2df,2p) level of theory. We observe that using the B3LYP/6-31G(d,p) methodology,

Table 1 Complexation energies CE (eV) in the gas phase of selected complexes using different functionals and basis sets

Method	CE_u[a]	CE[b]	CE_u[a]	CE[b]
	$18\text{-}NH_4{}^+\text{-}1$		**$18\text{-}Me_4N^+\text{-}1$**	
M05-2X/6-31G(d,p)	3.26	3.09	1.71	1.49
M05-2X/6-311++G(d,p)	3.11	3.01	1.60	1.47
M06-2X/6-31G(d,p)	3.28	3.11	1.81	1.58
M06-2X/6-311++G(d,p)	3.12	3.03	1.70	1.58
M06-2X/6-311++G(2df,2p)	2.96	2.90	1.62	1.52
MPWBIK/6-31G(d,p)	3.12	2.96	1.48	1.28
MPWBIK/6-311++G(d,p)	2.92	2.82	1.34	1.22
MPWBIK/6-311++G(2df,2p)	2.76	2.71	1.24	1.15
B2PLYP-D/6-31G(d,p)[c]	3.23		1.56	
B2PLYP-D/6-311++G(d,p)[c]	3.03		1.40	
B3LYP/6-31G(d,p)	3.01	2.82	1.23	0.99
	$12\text{-}NH_4{}^+\text{-}1$		**$12\text{-}Me_4N^+\text{-}1$**	
M06-2X/6-311++G(2df,2p)	2.13	2.09	1.05	0.99
MPWBIK/6-311++G(2df,2p)	1.96	1.93	0.83	0.77
B3LYP/6-31G(d,p)	2.14	2.00	0.88	0.73
	$24\text{-}NH_4{}^+\text{-}1$		**$24\text{-}Me_4N^+\text{-}1$**	
M06-2X/6-311++G(2df,2p)	3.46	3.39	1.84	1.75
MPWBIK/6-311++G(2df,2p)	3.22	3.15	1.52	1.40
B3LYP/6-31G(d,p)	3.53	3.29	1.66	1.29

[a] BSSE uncorrected values. [b] BSSE corrected values. [c] Single point calculation at B3LYP/6-31G(d,p) geometry. There are convergence problems in the optimization procedure.

the CE is 2.82 eV which corresponds to the mean value of the M06-2X and MPWBIK functionals using the largest basis set. Similarly, for the **$12\text{-}NH_4{}^+\text{-}1$** and **$24\text{-}NH_4{}^+\text{-}1$** complexes as well, the mean CE values of the M06-2X and MPWBIK functionals using the largest basis set are very close to the data of the B3LYP/6-31G(d,p) methodology, see Table 1. Thus, for the **$12\text{-}NH_4{}^+\text{-}1$**, **$18\text{-}NH_4{}^+\text{-}1$**, and **$24\text{-}NH_4{}^+\text{-}1$** complexes the B3LYP/6-31G(d,p) technique seems to be the best compromise, since the other functionals do not give a good result when combined with the small basis sets and it is not practical to employ the largest basis set for the CrE-fullero-N-methylpyrrolidine clusters.

In the case of **$18\text{-}Me_4N^+\text{-}1$** complex the MPWBIK functional is more appropriate than the other functionals because of the type of the bonds.[26,29] At M06-2X/6-311++G(2df,2p) level of theory CE is 1.52 eV, while at MPWBIK/6-311++G(2df,2p) level is 1.15 eV. There is a difference of 0.4 eV between the two basis sets. Given that MPWBIK functional is considered a better functional for the very weak noncovalent bonds, our best result for the CE of **$18\text{-}Me_4N^+\text{-}1$** is 1.15 eV. At B3LYP/6-31G(d,p) level of theory the corresponding value is 0.99 eV. Similarly, for **$12\text{-}Me_4N^+\text{-}1$**, and **$24\text{-}Me_4N^+\text{-}1$** the CE values at MPWBIK/6-311++G(2df,2p) level are 0.77 and 1.40 eV, very close to the B3LYP/6-31G(d,p) values of 0.73 and 1.29 eV, respectively. Thus, it seems that for **$12\text{-}Me_4N^+\text{-}1$**, **$18\text{-}Me_4N^+\text{-}1$**, and **$24\text{-}Me_4N^+\text{-}1$** complexes too the B3LYP/6-31G(d,p) methodology is a resonable compromise. As a final test of its applicability we carried out B3LYP/6-31G(d,p) calculation on the acetylene–water cluster which is a reference vdW system and we found BSSE corrected interaction energy of 0.13 eV. This system has previously been calculated with high accuracy at MP4 and CCSD(T) levels using the aug-cc-pV*n*Z basis sets, $n = 2$–4 and the BSSE complete basis set limit is 0.12 eV.[35] So, we conclude that the B3LYP/6-31G(d,p) is a very good choice for the present study. In what follows we use this method for all calculations.

Table 2 records the complexation energies (CE), the CE with respect to the ZPE (CE_0), the complexation enthalpy (CH) and complexation Gibbs free energy (CG) at T = 298.15 K, P = 1 atm, the van der Waals (vdW) distances and the CE in $CHCl_3$ solvent (CE_{solv}) of the dibenzo-12-crown-4, dibenzo-18-crown-6 and dibenzo-24-crown-8 ethers complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4 at the B3LYP/6-31G(d,p) level of theory. Table 3 lists the complexation energies (CE) in the gas phase and (CE_{solv}) in $CHCl_3$ solvent of the complexes of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with $(CH_3)_xNH_{4-x}^+$, x = 0–4 at the B3LYP/6-31G(d,p) level of theory. It might be noted that BSSE has been taken into account in the calculation of all complexation energies.

Fig. 1 presents the calculated minima of dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers; Fig. 2–4 and Fig. 1S–2S of the ESI† present the complexes of the above CrE with $(CH_3)_xNH_{4-x}^+$, x = 0–4. Fig. 5 displays the CE of the lowest minima of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with $(CH_3)_xNH_{4-x}^+$, x = 0–4, in the gas phase and in $CHCl_3$ solvent. Fig. 6 presents the calculated lowest minima of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and Fig. 7 and 8 along with Fig. 3S–6S of the ESI† show their complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4. Finally, Fig. 9 displays the CE of the lowest calculated minima of complexes of the dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine with the $(CH_3)_xNH_{4-x}^+$, x = 0–4, in the gas phase and in $CHCl_3$ solvent.

In Fig. 1, the lowest calculated isomers-minima of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers are shown from two different viewing angles for clarity. As can be seen, in the case of the dibenzo-12-crown-4 ether the five lowest minima closely lie within 0.13 eV (calculations in the gas phase) of each other, while for dibenzo-18-crown-6 ether the second lowest calculated minimum structure lies 0.16 eV higher than the lowest minimum in both B3LYP/6-31G(d,p) and 6-311++G(d,p) levels of theory. For the dibenzo-24-crown-8 ether the most symmetric minimum structure (**24c**) lies 0.33 eV above the lowest minimum (**24a**) at the B3LYP/6-31G(d,p) and 0.31 eV at B3LYP/6-311++G(d,p) level of theory. The **24b** minimum lies at 0.19 eV and 0.21 eV at the corresponding levels of theory. Inclusion of solvent in the calculation does not alter significantly the relative binding energies with respect to the CE of the corresponding lowest minima (see Fig. 1, values in parentheses), except for the case of the dibenzo-24-crown-8 ether where the secondary minima are found to be more stable than in the gas phase.

Below we discuss some features of the calculated complexes. Emphasis is placed on their CEs, their geometry and the strength of the hydrogen bonds involved. In general the hydrogen bonds can be thought of as strong vdW interactions,[36] however, the bonds between the H of ammonium (H_N) and the O of the ether are stronger than the average hydrogen bond[36] with CE per H atom ranging from 0.7 to 1 eV and bond lengths ranging from 1.73 to 2.20 Å. On the other hand, there are some long $H_N \cdots O$ bonds resulting in weak interactions (typical vdW bonds). vdW bonds with CE

Table 2 Complexation energies CE (eV), with respect to the ZPE CE_0 (eV), complexation enthalpy[a] CH (eV), complexation Gibbs free energy[a] CG (eV), vdW distances R (Å) in the gas phase and complexation energies CE_{solv} (eV) in $CHCl_3$ solvent of dibenzo-12-crown-4 ether, dibenzo-18-crown-6 ether, and dibenzo-24-crown-8 ether with $(CH_3)_xNH_{4-x}^+$, $x = 0$–4 at the B3LYP/6-31G(d,p) level of theory

Structure	CE[b]	CE_0[b]	CH[b]	CG[b]	R(NH···O)	R(H···cph)	R(CH···O)	CE_{solv}[b]
12-NH_4^+-1	2.00	1.91	1.94	1.50	1.744, 1.764			0.77
12-NH_4^+-2	1.97	1.88	1.91	1.47	1.724, 1.794			
12-NH_4^+-3	1.67	1.59	1.62	1.18	1.844, 1.844	2.266		
12-NH_4^+-4	1.60	1.51	1.54	1.07	1.891, 1.740	2.343		
12-NH_4^+-5	1.46	1.41	1.43	1.02	1.733, 1.676			
12-$MeNH_3^+$-1	1.78	1.71	1.75	1.23	1.818, 1.796, 2.583		2.663	0.72
12-$MeNH_3^+$-2	1.48	1.42	1.42	0.96	1.889, 1.889	2.283		
12-$MeNH_3^+$-3	1.41	1.34	1.34	0.85	1.782, 1.946	2.367		
12-$MeNH_3^+$-4	1.27	1.23	1.23	0.79	1.788, 1.741			
12-$Me_2NH_2^+$-1	1.58	1.51	1.51	0.98	1.910, 1.882		2.373, 2.370	0.64
12-$Me_2NH_2^+$-2	1.21	1.17	1.15	0.69	1.848	2.249	2.462	
12-$Me_2NH_2^+$-3	1.13	1.10	1.08	0.63	1.840, 1.787			
12-$Me_2NH_2^+$-4	0.71	0.68	0.67	0.16		2.491, 2.496		
12-Me_3NH^+-1	1.23	1.17	1.16	0.65	2.041		2.393, 2.389, 2.817	0.44
12-Me_3NH^+-2	1.21	1.15	1.14	0.64	2.198		2.547, 2.564, 2.627	0.42
12-Me_3NH^+-3	0.95	0.91	0.89	0.42	1.853		2.584	
12-Me_3NH^+-4	0.90	0.88	0.85	0.39	1.765		2.622,[c] 2.673[c]	
12-Me_4N^+-1	0.73	0.69	0.66	0.23			2.168, 2.315, 2.357,[d] 2.505[d]	0.13
12-Me_4N^+-2	0.71	0.66	0.64	0.19			2.280,[c] 2.201, 2.542,[c,d] 2.522[d]	0.13
12-Me_4N^+-3	0.70	0.66	0.66	0.16			2.270, 2.435, 2.257, 2.577	0.12
12-Me_4N^+-4	0.51	0.47	0.44	0.01		2.736	2.274, 2.838	
12-Me_4N^+-5	0.50	0.45	0.43	0.02			2.215, 2.323,[c] 2.467[c]	
12-Me_4N^+-6	0.41	0.37	0.35	−0.12		2.683	2.758	
18-NH_4^+-1	2.82	2.69	2.73	2.24	1.826, 1.835, 1.826			1.29
18-NH_4^+-2	2.66	2.52	2.57	2.06	1.844, 1.722, 1.891			
18-NH_4^+-3	2.62	2.50	2.54	2.07	1.822, 1.762, 1.937			
18-$MeNH_3^+$-1	2.55	2.44	2.45	1.93	1.853, 1.859, 1.853			1.21
18-$MeNH_3^+$-2	2.39	2.26	2.28	1.74	1.973, 1.753, 1.888			
18-$MeNH_3^+$-3	2.35	2.25	2.26	1.75	1.845, 1.797, 1.951			
18-$Me_2NH_2^+$-1	2.08	2.01	2.01	1.45	1.847, 1.847		2.269	0.90
18-$Me_2NH_2^+$-2	2.04	1.96	1.96	1.42	1.999, 2.005		2.579, 2.814, 2.579, 2.814	0.85
18-$Me_2NH_2^+$-3	1.95	1.84	1.85	1.28	1.887, 1.887		2.480, 2.480, 2.617, 2.617	
18-Me_3NH^+-1	1.53	1.46	1.45	0.91	1.810		2.294, 2.382, 2.596,[d] 2.627[d]	0.52
18-Me_3NH^+-2	1.42	1.34	1.33	0.79	1.787		2.478, 2.200,[d] 2.641,[d] 2.294, 2.690	0.48
18-Me_3NH^+-3	1.42	1.34	1.34	0.78	1.937		2.446, 2.446, 2.230, 2.230	0.48
18-Me_3NH^+-4	1.37	1.29	1.28	0.73	1.768		2.426, 2.215,[d] 2.705,[d] 2.338	
18-Me_4N^+-1	0.99	0.94	0.92	0.41			2.308, 2.220, 2.392, 2.685, 2.719, 2.837	0.24
18-Me_4N^+-2	0.93	0.86	0.85	0.33			2.487, 2.348,[d] 2.354,[d] 2.759, 2.556, 2.516, 2.356, 2.643	
18-Me_4N^+-3	0.85	0.78	0.77	0.25			2.451, 2.456, 2.323, 2.623, 2.447, 2.458, 2.675, 2.627	
24-NH_4^+-1	3.29	3.15	3.20	1.90	1.916, 1.849, 1.890, 1.945			1.56
24-NH_4^+-2	3.23	3.07	3.13	2.56	1.906, 1.879, 1.943, 1.885			1.53
24-NH_4^+-3	3.19	3.04	3.09	2.55	1.914, 1.836, 1.933, 1.919			1.47
24-NH_4^+-4	2.98	2.89	2.96	2.36	2.048, 1.942, 1.920, 2.488[d]			
24-NH_4^+-5	2.94	2.83	2.87	2.38	1.800, 1.877, 1.877, 2.567[d]			
24-NH_4^+-6	2.54	2.41	2.45	1.95	1.754, 1.824, 1.727			
24-$MeNH_3^+$-1	2.63	2.52	2.53	1.68	1.806, 1.980, 1.918		2.344	1.20
24-$MeNH_3^+$-2	2.62	2.50	2.52	1.96	1.867, 1.932, 1.992		2.434, 2.207	1.15
24-$MeNH_3^+$-3	2.60	2.48	2.50	1.96	1.992, 2.007, 1.961		2.342, 2.435, 2.622	1.14
24-$MeNH_3^+$-4	2.59	2.48	2.49	1.94	1.986, 1.941, 1.861		2.492	1.18
24-$MeNH_3^+$-5	2.56	2.45	2.46	1.93	2.003, 1.941, 1.828		2.355	
24-$MeNH_3^+$-6	2.33	2.20	2.21	1.69	1.902, 2.102, 2.013		2.641, 2.447	
24-$Me_2NH_2^+$-1	2.22	2.11	2.11	1.52	1.951, 1.948		2.238, 2.686, 2.280, 2.543	0.94
24-$Me_2NH_2^+$-2	2.22	2.11	2.12	1.52	1.897, 1.910		2.626, 2.784, 2.352, 2.261	0.95
24-$Me_2NH_2^+$-3	2.18	2.07	2.08	1.47	1.856, 1.811		2.509, 2.369, 2.253	
24-$Me_2NH_2^+$-4	2.12	2.02	2.02	1.41	1.839, 1.809		2.391, 2.420, 2.514	
24-$Me_2NH_2^+$-5	1.85	1.75	1.75	1.16	1.979, 1.801		2.554, 2.734, 2.377, 2.340	
24-Me_3NH^+-1	1.78	1.65	1.66	1.01	1.898		2.385, 2.460, 2.543, 2.444,[d] 2.498,[d] 2.602, 2.456, 2.522	0.67
24-Me_3NH^+-2	1.75	1.64	1.64	1.03	1.942		2.322, 2.615, 2.365, 2.748, 2.488, 2.325, 2.585	0.62
24-Me_3NH^+-3	1.55	1.47	1.45	0.90	1.921		2.734, 2.379,[d] 2.600,[d] 2.407, 2.263, 2.358	
24-Me_3NH^+-4	1.52	1.43	1.42	0.84	1.887		2.461, 2.676, 2.578, 2.310, 2.389	
24-Me_3NH^+-5	1.46	1.34	1.35	0.72	1.767		2.541,[d] 2.418,[d] 2.583, 2.532, 2.442, 2.571,[d] 2.509,[d] 2.459	

Table 2 (*continued*)

Structure	CE[b]	CE$_0$[b]	CH[b]	CG[b]	R(NH···O)	R(H···cph)	R(CH···O)	CE$_{solv}$[b]
24-Me$_4$N$^+$-1	1.29	1.19	1.18	0.63			2.371, 2.373, 2.542, 2.533, 2.351, 2746, 2.775, 2.506, 2.602	0.30
24-Me$_4$N$^+$-2	1.28	1.18	1.17	0.61			2.321, 2.470, 2.525, 2.414,[d] 2.575,[d] 2.391, 2.544, 2.543, 2.390	0.29
24-Me$_4$N$^+$-3	1.22	1.12	1.11	0.54			2.269, 2.393, 2.661, 2.324, 2.205, 2.356, 2.676	0.26
24-Me$_4$N$^+$-4	1.14	1.04	1.05	0.42			2.191, 2.534, 2.676, 2.434, 2.677, 2.706, 2.450,[d] 2.386,[d] 2.793, 2.391,[d] 2.631[d]	
24-Me$_4$N$^+$-5	1.09	0.99	0.98	0.39			2.668, 2.304, 2.557, 2.432, 2.625, 2.495, 2.382	

[a] T = 298.15 K, P = 1 atm. [b] BSSE corrected values. [c] Two H atoms interact with the same O atom. [d] One H atom interacts with two O atoms.

per H atom less than 0.2 eV are also formed between the H of methyl group (H$_C$) and the O of the ether. Moreover, the interactions are not always 1 to 1 and in many cases one H atom interacts with two O atoms and in others two H atoms interact with the same O atom. In addition, vdW bonds are formed between the H of ammonium or methyl group and the π-system of the phenylene group. The solvent effect with respect to the CE, the geometry and the relevant energy ordering is discussed. The differences resulting from changes in crown ether size and the presence of fullerene are discussed. Data are given for the charges.

The isomers of the dibenzo-12-crown-4 complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4 are depicted in Fig. 2. The lowest **12-NH$_4^+$** minimum has a complexation energy, CE, and a CE corrected for the zero point energy (ZPE), CE$_0$, of CE(CE$_0$) = 2.00(1.91) eV in the gas phase which is reduced to CE = 0.77 eV in CHCl$_3$ solvent. The **12-NH$_4^+$-1**, **12-NH$_4^+$-2**, and **12-NH$_4^+$-5** minima have two hydrogen bonds between the H of NH$_4^+$ and the O of ether, while the **12-NH$_4^+$-3** and **12-NH$_4^+$-4** minima have an additional vdW bond between a third H of ammonium and the π-system of the phenylene group. The lowest **12-MeNH$_3^+$-1** minimum has two hydrogen bonds between two H$_N$ atoms of MeNH$_3^+$, two weak vdW bonds between the third H$_N$ and an O atom of ether, and between an H$_C$ of the methyl group and the fourth O atom of ether. Its complexation energy is CE(CE$_0$) = 1.78(1.71) eV. The other two minima **12-MeNH$_3^+$-2** and **12-MeNH$_3^+$-3** have two hydrogen bonds between two H$_N$ of MeNH$_3^+$ and two O of ether and a hydrogen interacrion between the third H$_N$ of ammonium and the phenylene group. The last structure, **MeNH$_3^+$-4** has only two vdW bonds. The **12-Me$_2$NH$_2^+$-1** is the lowest minimum of **12-Me$_2$NH$_2^+$** isomers with CE(CE$_0$) = 1.58(1.51) eV. It has two H$_N$···O hydrogen bonds and two between the two H$_C$···O bonds. The **12-Me$_2$NH$_2^+$-2** has one H$_N$···O, one N–H···cph (center of the phenylene group), and one C–H···O bond; the **12-Me$_2$NH$_2^+$-3** has two H$_N$···O bonds, while the **12-Me$_2$NH$_2^+$-4** has two H$_N$···cph bonds, see Fig. 2 and Table 2. The lowest **12-Me$_3$NH$^+$-1** minimum has CE(CE$_0$) = 1.23(1.17) eV and three vdW bonds, two H$_C$···O bonds and one H$_N$···O. At the last vdW bond, the H of the nitrogen is not exactly above the O to which it is connected, but resides above the rectangle that is formed by the 4 oxygen atoms and sits closer to one of them. The **12-Me$_3$NH$^+$-2** minimum looks like the **12-Me$_3$NH$^+$-1** minimum but has an additional weak H$_C$···O bond and contains a different isomer of the dibenzo-12-crown-4 ether. The **12-Me$_3$NH$^+$-3** (and **12-Me$_3$NH$^+$-4**) minima have one H$_N$···O and one(two) H$_C$···O bonds. In the case of the fourth minimum, for the H$_C$···O bond, two H atoms are directed towards the same oxygen. The lowest **12-Me$_4$N$^+$-1** minimum has CE(CE$_0$) = 0.73(0.69) eV in the gas phase while only 0.13 eV in CHCl$_3$ solvent. The three lowest **12-Me$_4$N$^+$** minima have 4 H$_C$···O bonds and in some bonds the same H can interact with two O atoms. Finally, in **12-Me$_4$N$^+$-4** and **12-Me$_4$N$^+$-6** minima a weak bond H$_C$···cph (center of the phenylene group) is also formed. It might be noted that H$_C$···cph or H$_N$···cph bonds are observed only in the dibenzo-12-crown-4 ether complexes. For the dibenzo-18-crown-6 and dibenzo-24-crown-8 ether complexes, these bonds are observed only in higher lying complexes.

The isomers of the dibenzo-18-crown-6 complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4 are depicted in Fig. 3 and Fig. 1S of the ESI.† The CE(CE$_0$) of the lowest structures of the complexes as x increases from 0 to 4 are 2.82(2.69), 2.55(2.44), 2.08(2.01), 1.53(1.46), and 0.99(0.94) eV, respectively. In the CHCl$_3$ solvent the corresponding CE values are 1.29, 1.21, 0.90, 0.52 and 0.24 eV, respectively, see Table 2. In all calculated **18-NH$_4^+$** and **18-MeNH$_3^+$** minima three H$_N$···O bonds are formed, see Fig. 3. In the **18-Me$_2$NH$_2^+$-1** minimum two hydrogen bonds (H$_N$···O) and one H$_C$···O bond are formed, while in **18-Me$_2$NH$_2^+$-2** and **18-Me$_2$NH$_2^+$-3** an additional H$_C$···O bond is formed. The hydrogen bond distances are given in Table 2. All four calculated **18-Me$_3$NH$^+$** minima have an H$_N$···O bond and four or five H$_C$···O bonds. In some cases, an H atom forms two vdW bonds with two O atoms. Finally, the three lowest **18-Me$_4$NH$^+$** minima present weak H$_C$···O bonds. It should be noted that in all above structures, the interactions are not always 1 to 1 and in many cases one H atom interacts with two O atoms and in others two H atoms interact with the same O atom.

The calculated minima of the dibenzo-24-crown-8 complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4 are depicted in Fig. 4 and Fig. 2S of the ESI.† The CE(CE$_0$) of the lowest structures of the complexes as x increases are 3.29(3.15), 2.63(2.52), 2.22(2.11), 1.78(1.65), and 1.29(1.19) eV, while in the CHCl$_3$ solvent the corresponding CE values are reduced to 1.56 1.20, 0.94, 0.67 and 0.30 eV, respectively, see Table 2.

Table 3 Complexation Energies CE (eV) in the gas phase and complexation energies CE_{solv} (eV) in $CHCl_3$ solvent of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with $(CH_3)_xNH_{4-x}^+$, x = 0–4 at the B3LYP/6-31G(d,p) level of theory

Structure	CE[a]	CE_{solv}[a]	Structure	CE[a]	CE_{solv}[a]
18A-NH$_4^+$	2.788	1.258	**18C-Me$_3$NH$^+$-1**	1.475	0.488
18A-MeNH$_3^+$	2.516	1.169	**18C-Me$_3$NH$^+$-2**	1.371	0.423
18A-Me$_2$NH$_2^+$-1	2.040	0.851	**18C-Me$_4$N$^+$**	0.930	0.195
18A-Me$_2$NH$_2^+$-2	1.658	0.533	**18D-NH$_4^+$**	2.806	1.269
18A-Me$_3$NH$^+$-1	1.465	0.472	**18D-MeNH$_3^+$**	2.535	1.164
18A-Me$_3$NH$^+$-2	1.074	0.176	**18D-Me$_2$NH$_2^+$-1**	2.101	0.864
18A-Me$_4$N$^+$	0.945	0.138	**18D-Me$_2$NH$_2^+$-2**	2.009	0.822
18B-NH$_4^+$	2.824	1.274	**18D-Me$_3$NH$^+$-1**	1.571	0.469
18B-MeNH$_3^+$	2.564	1.184	**18D-Me$_3$NH$^+$-2**	1.458	0.448
18B-Me$_2$NH$_2^+$-1	2.018	0.839	**18D-Me$_4$N$^+$**	1.045	0.210
18B-Me$_2$NH$_2^+$-2	1.791	0.620	**18*E*-NH$_4^+$**	2.736	1.245
18B-Me$_3$NH$^+$-1	1.570	0.481	**18*E*-MeNH$_3^+$**	2.463	1.156
18B-Me$_3$NH$^+$-2	1.480	0.453	**18*E*-Me$_2$NH$_2^+$-1**	2.006	0.850
18B-Me$_4$N$^+$	1.078	0.226	**18*E*-Me$_2$NH$_2^+$-2**	1.908	0.812
18C-NH$_4^+$	2.775	1.254	**18*E*-Me$_3$NH$^+$-1**	1.449	0.478
18C-MeNH$_3^+$	2.503	1.167	**18*E*-Me$_3$NH$^+$-2**	1.358	0.415
18C-Me$_2$NH$_2^+$-1	2.039	0.853	**18*E*-Me$_4$N$^+$-1**	0.900	0.188
18C-Me$_2$NH$_2^+$-2	2.014	0.820	**18*E*-Me$_4$N$^+$-2**	0.852	0.164
18C-Me$_2$NH$_2^+$-3	1.960	0.825	**18*E*-Me$_4$N$^+$-3**	0.787	0.018

[a] BSSE corrected values.

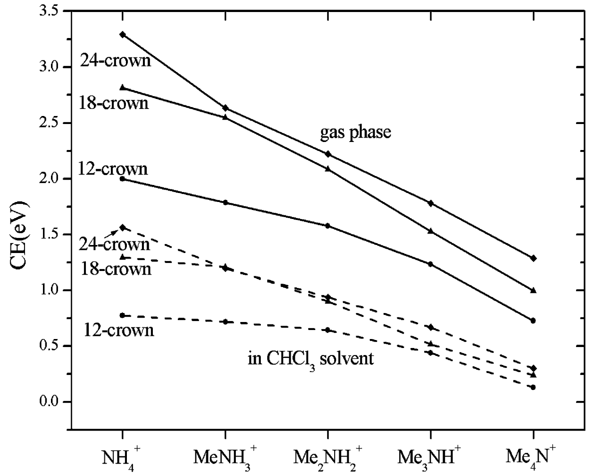


Fig. 5 Complexation energies corrected for BSSE (CE) of the lowest minima of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with $(CH_3)_xNH_{4-x}^+$, x = 0–4.

In **24-NH$_4^+$-1**, **-2**, and **-3** minima four $H_N\cdots O$ bonds are formed, in the remaining **24-NH$_4^+$-4**, **-5** and **-6** three $H_N\cdots O$ bonds, while in **24-NH$_4^+$-4** and **-5** their fourth H atom forms two week bonds with two O atoms. In all six calculated **24-MeNH$_3^+$** minima three hydrogen $H_N\cdots O$ bonds are formed, while additional C–H$\cdots$O bonds are formed, *i.e.*, in **-1**, **-4**, and **-5** one bond, in **-2** and **-6** two bonds, and in **-3** three bonds. In all **24-Me$_2$NH$_2^+$** minima two $H_N\cdots O$ bonds and three or four $H_C\cdots O$ vdW bonds are formed. Similarly, in all **24-Me$_3$NH$^+$** minima one $H_N\cdots O$ bond and five to seven $H_C\cdots O$ vdW bonds are formed. Finally, in all calculated **24-Me$_4$N$^+$** minima seven to nine $H_C\cdots O$ vdW bonds are formed. Generally the dibenzo-24-crown-8 ether is folded around the ammonium cation so as to maximize the number of hydrogen bonds and interactions formed. In the case of complexation with NH_4^+ the crown ether is the most twisted, while as the H of N are substituted with Me group, the crown ether is more relaxed.

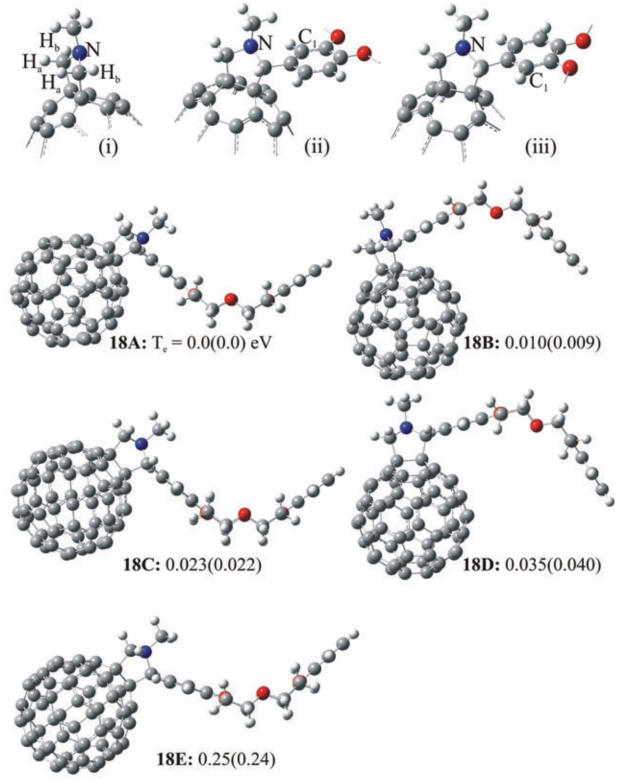


Fig. 6 Different isomers (**18A–E**) of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine. T_e is the energy difference from the most stable structure, in the gas phase (in $CHCl_3$ solvent). (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

The CE of the lowest minima of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with $(CH_3)_xNH_{4-x}^+$, x = 0–4, in the gas phase and in $CHCl_3$ solvent as the number of the constituents H change are depicted in Fig. 5. The CE of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with $(CH_3)_xNH_{4-x}^+$, x = 0–4, range from 3.29 to 0.73 eV in the gas phase, while in the $CHCl_3$ solvent the values are lower and range from 1.56 to 0.13 eV.

In the calculated complexes the $H_N\cdots O$ hydrogen bonds range from 1.73 to 2.20 Å, the H$\cdots$cph vdW bonds range from 2.25 to 2.74 Å, and the $H_C\cdots O$ vdW bonds range from 2.21 to 2.8 Å, see Table 2. Compared to the corresponding bonds of the simplest model systems $NH_4^+\cdots OMe_2$ and $CH_4\cdots OMe_2$ which are 1.47 and 2.51 Å long, respectively, the $H_N\cdots O$ bonds in our systems are elongated, while some $H_C\cdots O$ bonds are shorter, some are similar and some are elongated. The corrected for BSSE complexation energy of $NH_4^+\cdots OMe_2$ is 1.07(1.05) eV at B3LYP/6-31G(d,p)(B3LYP/ 6-311++G(d,p)) level of theory. The CEs of the **12-NH$_4^+$-1**, **18-NH$_4^+$-1**, and **24-NH$_4^+$-1** are 2.00, 2.82, and 3.29 eV and correspond to 2, 3 and 4 $H_N\cdots O$ hydrogen bonds. Thus, each bond has a CE of 1.00, 0.94 and 0.82 eV per H atom, respectively. The reduction of the CE per H atom as the size of the crown ether increases is expected and the values are consistent with a CE value of 1.07 eV of the $NH_4^+\cdots OMe_2$ complex.

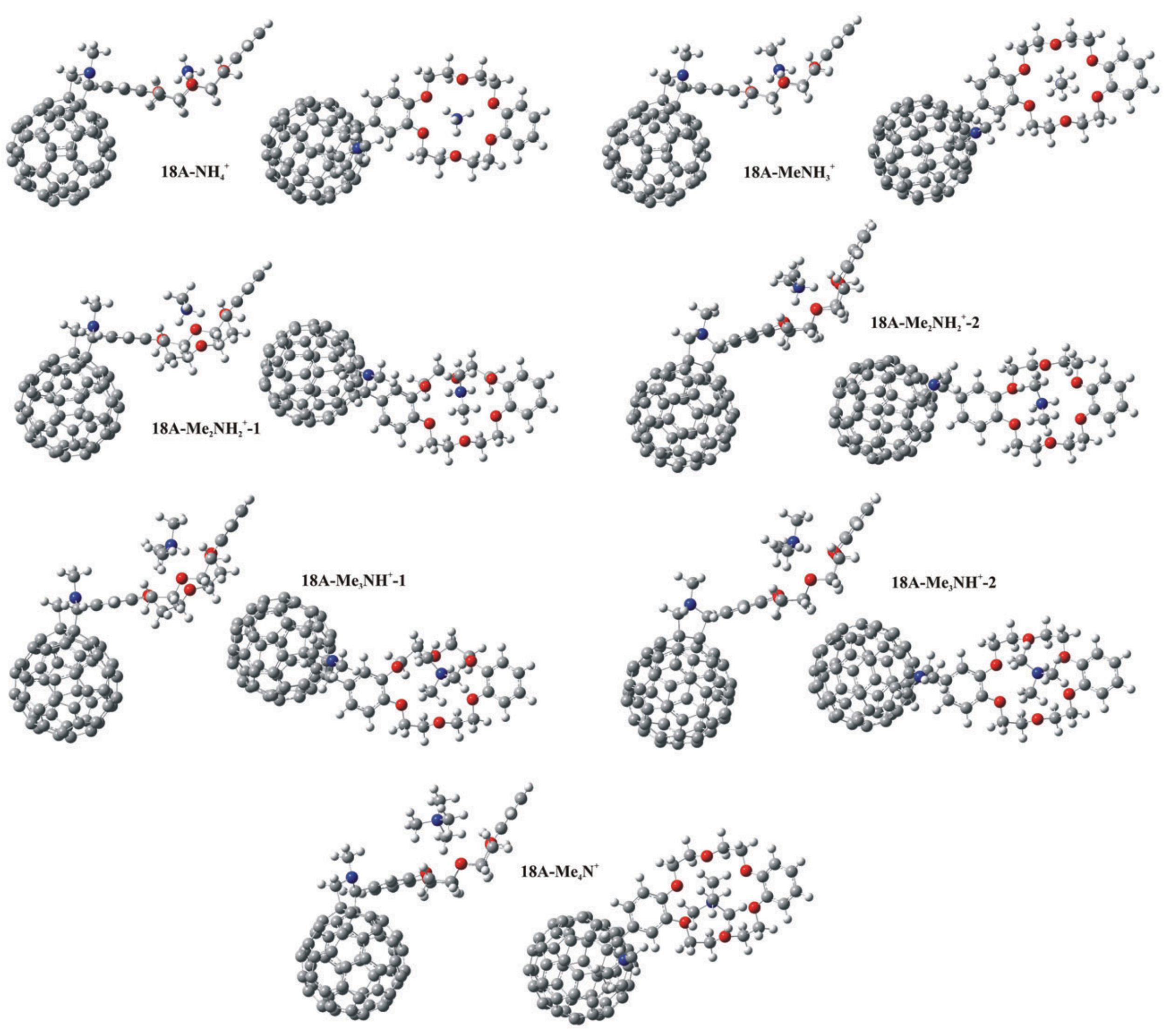


Fig. 7 Minima of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine (**18A** isomer) with $(CH_3)_xNH_{4-x}^+$. The structures are shown from two different viewing angles. (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

Mulliken population analysis of our calculated complexes shows that a larger electron charge on N is observed in the complexes than on the free ammonium cation, about 0.05 e^- in dibenzo-12-crown-4 complexes, about 0.08 e^- in dibenzo-18-crown-6 complexes, and about 0.11 e^- in dibenzo-24-crown-8 complexes. The H atoms attached to N are only slightly less positive than in the free ammonium cation. Moreover, the O atoms of the ether in the complexes are more negative by about 0.05 e^- than in the free crown ether.

Comparing the geometry in the gas phase and in $CHCl_3$ solvent, the vdW distances are similar or elongated in $CHCl_3$ solvent, see Table 2 and Table 2S of the ESI.† Moreover, some additional calculations (full geometry optimizations) for some chosen complexes with NH_4^+ and Me_4N^+ in the gas phase were carried out using the 6-311+G(d,p) and the 6-311++G(d,p) basis sets for reasons of comparison. We found small differences in geometry compared with our 6-31G(d,p) basis set. The BSSE corrected CE values employing the 6-311++G(d,p) basis set are generally smaller than the corresponding values with 6-31G(d,p) by about 4%. The calculated vdW distances at B3LYP/6-311++G(d,p) are similar to B3LYP/6-31G(d,p), only slightly elongated and in most cases by less than 1%.

Five minimum energy structures of the dibenzo-18-crown-6 CrE of fullero-N-methylpyrrolidine, namely, **18A**, **18B**, **18C**, **18D**, and **18E**, were calculated, see Fig. 6. They differ in the direction of the crown ether, namely up (**18A**, **18C**, and **18E**) or down (**18B** and **18D**) with respect to fullero-N-methylpyrrolidine. Then in the **18A**, **18C**, **18B**, and **18D** the H_b atoms of the α-C adjacent to the N atom of N-methylpyrrolidine, have been replaced by the dibenzo-18-crown-6 ether, while in **18E** minimum the H_a atom has been replaced, see Fig. 6i. Finally, in **18A** and **18B** the C_1 of the dibenzo-18-crown-6 ether and the N of N-methylpyrrolidine are on the same side (see Fig. 6ii), while in **18C** and **18D** they are in opposite sides (see Fig. 6iii).

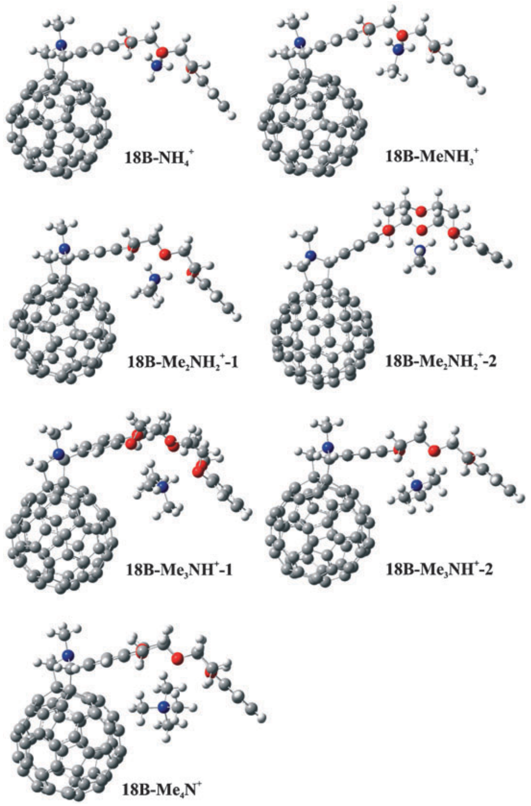


Fig. 8 Minima of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine (**18B** isomer) with$(CH_3)_xNH^+_{4-x}$. (H atoms = white spheres, C atoms = grey spheres, O atoms = dark spheres (red online) and N atoms = darker spheres (blue online)).

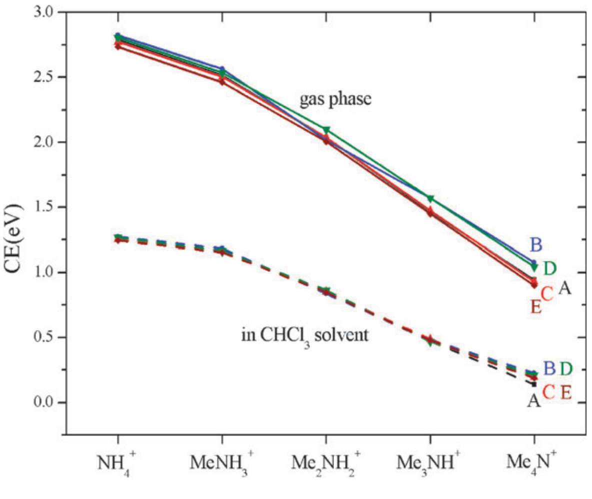


Fig. 9 Complexation energies corrected for BSSE (CE) of the lowest minima of the dibenzo-18-crown-6 ether of fulleroN-methyl pyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4.

The calculated lowest minima of dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4 are presented in Fig. 7 and 8 and Fig. 3S–6S of the ESI.† The most stable complexes are those of the **18B** isomer (Fig. 8), followed by **18D**, **18A**, **18C**, and **18E**. It might be noted that in the **18B** and **18D** isomers the direction of the crown ether is down with respect to fullero-N-methylpyrrolidine and the hydrogen atoms of the methyl groups of $(CH_3)_xNH^+_{4-x}$ interact with the fullerene, see Fig. 8 and Fig. 3S and 5S of the ESI.†

The geometries of the dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine with the $(CH_3)_xNH^+_{4-x}$, $x = 0$–4, in the gas phase and in $CHCl_3$ solvent are similar to the corresponding geometries of the corresponding complexes without the fullero-N-methylpyrrolidine. Similarly, the CE's values are comparable in both types of complexes, see Tables 2 and 3, showing that the presence of the fullero-N-methylpyrrolidine does not affect the formation of complexes of the crown ethers with ammonium cations.

The CE of the lowest calculated minima of the dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine with the $(CH_3)_xNH^+_{4-x}$, $x = 0$–4, in the gas phase and in $CHCl_3$ solvent as the number of the constituents H change are depicted in Fig. 9. The CE of the five lowest isomers of dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x = 0$–4, range from 2.82 to 1.08 eV in the gas phase, while in $CHCl_3$ solvent the values decrease and range from 1.27 to 0.23 eV. The presence of fullero-N-methylpyrrolidine attached to the crown ethers does not change the CE values, the corresponding CE values of the dibenzo-18-crown-6 ethers with the $(CH_3)_xNH^+_{4-x}$, $x = 0$–4, in the gas phase are 2.82–0.99 and in $CHCl_3$ solvent are 1.29–0.24, see Tables 2 and 3. Moreover, the presence of the solvent reduces the differences in CE of the complexes of different **18A**, **18B**, **18C**, **18D**, and **18E** minimum structures of the dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine.

To the best of our knowledge, there is no information in the literature for complexes of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine with $(CH_3)_xNH^+_{4-x}$, $x =$ 0–4 in the gas phase or in $CHCl_3$ solvent. However, there are data on complexation of 12-crown-4 and 18-crown-6 ethers with substituted ammonium cations, but there is no study for complexes of 24-crown-8 ether. Experimentally, the complexation enthalpy of the $(CH_3)_3NH^+$·12-crown-4 and $(CH_3)_3NH^+$·18-crown-6 complexes was determined as 1.55 and 1.8 ± 0.2 eV, respectively, from high pressure mass spectrometric measurements of proton-transfer reactions.[9a] These CE values are larger than our calculated values of 1.16 and 1.45 eV for the analogous $(CH_3)_3NH^+$·dibenzo-12-crown-4 and $(CH_3)_3NH^+$·dibenzo-18-crown-6 complexes. Moreover, in the case of $NH_4{}^+$·18-crown-6 complex, the CE was estimated at 3.1 ± 0.1 eV based on H_3O^+·18-crown-6 complex by high pressure mass spectrometry. Our analogous complex has a CE of 2.82 eV. The observed reduction in the stability with the introduction of an aromatic ring on crown ethers (or protonated amines) is known by relative intensity measurements in a series of complexes $RNH_3{}^+$·18-crown-6 and $RNH_3{}^+$·benzo-18-crown-6 by the use of quadrupole ion trap mass spectrometry.[37] The $(CH_3)_xNH^+_{4-x}$·18-crown-6 complexes in methanol were determined by titration calorimetry[11] and the tetramethylammonium complex was not detected. In our calculations for the analogous tetramethylammonium dibenzo-18-crown-6 complex we found a complexation energy of 0.99 eV in the gas phase, but only 0.24 eV in $CHCl_3$ solvent rather than methanol. Molecular mechanics calculations[11] yield vdW distances of 1.88 Å for $NH_4^+ \cdot$18-crown-6 complex in agreement with our 1.83 Å for the analogous dibenzo complex.

Conclusions

The electronic and geometric structures of dibenzo-12-crown-4, dibenzo-18-crown-6, dibenzo-24-crown-8 ethers, and dibenzo-18-crown-6 ether of fullero-N-methylpyrrolidine and their complexes with $(CH_3)_xNH_{4-x}^+$, x = 0–4 were studied by employing density functional theory (B3LYP, M05-2X, M06-2X, MPWBIK and B2PLYP-D) in conjunction with three basis sets. The work presented here is the first systematic theoretical study on above complexes of crown ethers which are currently of interest for the formation of technologically important supramolecular complexes.

About 200 minima were calculated in the gas phase and in $CHCl_3$ solvent. We calculated the complexation energies, the geometries, the harmonic frequencies and some thermochemical data. A summary of our main results follows.

1. The complexation energies (CE) of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with $(CH_3)_xNH_{4-x}^+$, x = 0–4, range from 3.29 to 0.73 eV in the gas phase and from 1.56 to 0.13 eV in the $CHCl_3$ solvent.

2. The lowest-energy complex of the dibenzo-12-crown-4, dibenzo-18-crown-6, and dibenzo-24-crown-8 ethers with NH_4^+ have 2, 3 and 4 N–H···O hydrogen bonds, with a CE of 1.00, 0.94 and 0.82 eV per H atom, respectively.

3. Various types of hydrogen interactions are observed in the complexes. Bonds are formed between the H of ammonium and/or the methyl group and the O of ethers. However, the interactions are not always 1 to 1 and in many cases one H atom interacts with two O atoms and in others two H atoms interact with the same O atom. In addition, in the case of the dibenzo-12-crown-4 ethers, hydrogen bonds are formed between the H of ammonium or methyl group and the π-system of the phenylene group. In the case of the dibenzo-18-crown-6 and dibenzo-24-crown-8 ether complexes, the last type of vdW bonds are observed only in higher energy lying complexes.

4. The dibenzo-24-crown-8 ethers present the largest CE, because they are folded around the ammonium cation maximizing the number of hydrogen bonds formed. In the case of complexation with NH_4^+ the crown ether is twisted the most, while as the H atoms of N are substituted with methyl groups, the crown ether becomes more relaxed.

5. Mulliken population analysis of our calculated complexes shows that a larger electron charge on N is observed in the complexes than on the free ammonium cation, by about 0.1 e^-.

6. CE of the five lowest isomers of dibenzo-18-crown-6 ethers of fullero-N-methylpyrrolidine with $(CH_3)_xNH_{4-x}^+$, x = 0–4, range from 2.82 to 1.08 eV in the gas phase and from 1.27 to 0.23 eV in the $CHCl_3$ solvent.

7. The presence of fullero-N-methylpyrrolidine in the crown ethers does not affect the formation of complexes with ammonium cations and does not change the CE values, whereas it changes only slightly the geometry.

8. CE decreases with solvation in $CHCl_3$, as expected, while the vdW distances are similar or elongated.

9. Finally, in a more technical aspect, even though the M05-2X, M06-2X, MPWBIK, and B2PLYP-D functionals are recommended for non-covalent interactions, for hydrogen bonding and weak interaction calculations, they require a larger basis set such as 6-311++G(2df,2p) for the complexes under study. Otherwise, their use with a smaller basis set than above leads to overestimation of the CE values. However, the use of such large basis sets is prohibitive for calculations on the CrE-fullero-N-methylpyrrolidine clusters. By performing test calculations on the most strongly and most weakly bond complexes of the three CrEs, we proved that the B3LYP/6-31G(d,p) is the best choice for the systems studied here.

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