

Chapter 31

A Theoretical Study of Complexes of Crown Ethers with Substituted Ammonium Cations

Demeter Tzeli, Ioannis D. Petsalakis, and Giannoula Theodorakopoulos

Abstract The electronic and geometric structures of the complexes of dibenzo-18-crown-6 ether and of dibenzo-18-crown-6 ether of fullerene-methylpyrrolidine with diphenylammonium cation, Ph_2NH_2^+ , and its derivative with π -extended tetrathiafulvalene, π -exTTF, were investigated by employing density functional theory. We calculate geometries, complexation energies and some absorption spectra of the lowest energetic minima of the above complexes in the gas phase as well as in CHCl_3 solvent. The complexation energies, corrected for basis set superposition error reach up to 2.2 eV in the gas phase and up to 1.3 eV in the CHCl_3 solvent, at the M06-2X/6-31G(d,p) level of theory. In the complexes, the cations and the crown ethers are deformed to maximize the number of the hydrogen bonds. The presence of fullerene-methylpyrrolidine, attached to the crown ethers, increases the complexation energies by up to 0.2 eV due to additional interactions. The complex of fullerene crown ethers with a π -exTTF derivative of Ph_2NH_2^+ presents charge transfer transitions in the absorption spectrum and may serve as candidate for organic photovoltaics.

31.1 Introduction

There is great interest in the study of crown ethers since their discovery [1, 2] because they are highly adaptable hosts for a large number of guests [3–5]. The complexation of crown ethers with many guests, both neutral [4] and cationic [3, 6] and their high degree of selectivity have been investigated both experimentally and theoretically [3, 4, 6, 7]. The conformations of the crown ethers, the size of the

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guest, the nature of the intermolecular interactions and in solution the solvating ability of the solvent with respect to the cation and the complex determine the strength of their binding with various species and its specificity. As a result they are used in many diverse fields such as in catalysis, in enantiomer resolution, in membrane separation of cationic species etc. [8].

Moreover, supra-molecular systems involving crown ethers, fullerene and π -extended systems have been achieved that can mimic the photosynthetic process [9–14]. The fullerene C_{60} has been used successfully as an electron acceptor in the construction of model photosynthetic systems [9], the π -extended systems, such as porphyrins [12], phthalocyanines [13], π -extended tetrathiafulvalene (π -exTTF) derivatives [9, 10], which are utilized as electron donors, while the crown ethers act as a bridge between the electron donor and acceptor. In the absorption spectrum of the complexes, the absorption maxima are associated experimentally and theoretically with the formation of charge-transfer states [14–16]. Consequently, these supramolecular systems have potential for applications in photonic, photocatalytic, and molecular optoelectronic gates and devices [9–14]. As a result, the study of the conformations and the complexation behavior of crown ethers and their derivatives are motivated both by scientific curiosity regarding the specificity of their binding and by potential technological applications.

The present work is a continuation of our previous studies on the electronic and geometric structures of four crown ethers and their complexes with $(CH_3)_xNH_{4-x}^+$, $x = 0 - 4$ in the gas phase and in $CHCl_3$ solvent [7] and on the complexes of the dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine with a π -exTTF derivative [16]. In the present work a theoretical study on the complexes of dibenzo-18-crown-6 ether and of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine with the diphenylammonium cation, $Ph_2NH_2^+$, were investigated by employing density functional theory. In what follows, we describe the computational approach in Sect. 31.2, we discuss our results in Sect. 31.3, and we summarize our findings in Sect. 31.4.

31.2 Computational Approach

We used the density functional theory, at the M06-2X/6-31G(d,p) level of theory, to study the electronic and geometric structures of the complexes of dibenzo-18-crown-6 ether and of dibenzo-18-crown-6 ether of fulleroN-methylpyrrolidine with diphenylammonium cation, $Ph_2NH_2^+$. M06-2X [17] is a hybrid meta exchange correlation functional, a highly-nonlocal functional with double the amount of nonlocal exchange and is recommended for the study of non-covalent interactions [18], such as the present interactions. The decision to employ this functional was based on the conclusions of our previous studies about the applicability of the B3LYP, M05-2X, M06-2X, MPWB1K and B2PLYP-D functionals in conjunction with three

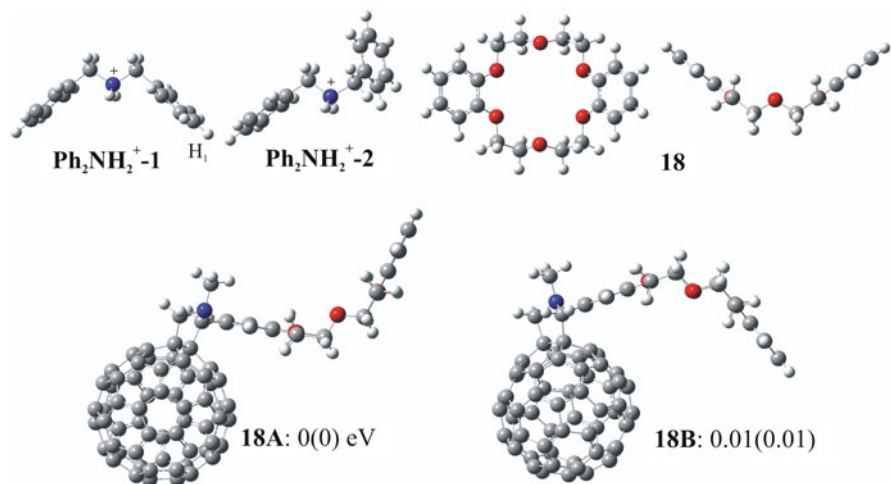


Fig. 31.1 Ph_2NH_2^+ : the lowest isomers of the diphenylammonium cation; **18**: dibenzo-18-crown-6 ether (*top and side view*); **18A** and **18B**: the lowest isomers of the dibenzo-18-crown-6 ether of fullereneN-methylpyrrolidine; BSSE corrected energy differences from the most stable structure are shown in the gas phase (in CHCl_3 solvent) at the M06-2X/6-31G(d,p) level of theory

basis sets on complexes of crown ethers with $(\text{CH}_3)_x\text{NH}_{4-x}^+$, $x = 0 - 4$ [7] and the applicability of the B3LYP, CAM-B3LYP, M06-HF and M06-2X on the benzene dimer and the fullerene-benzene system [16] and on complexes of fullerene crown ethers with a π -exTTF derivative [16]. We concluded that the M06-2X functional in conjunction with the 6-31G(d,p) basis set [19] is a good choice for complexes having both hydrogen bonds and very weak vdW interactions (dispersion forces between nonpolar species) such as interactions between phenyl groups or between phenyl group and C_{60} [16].

In the present study, we calculated two energetically degenerate minima of the diphenylammonium cation, i.e., $\text{Ph}_2\text{NH}_2^+ -1$ and $\text{Ph}_2\text{NH}_2^+ -2$, see Fig. 31.1. The lowest minimum of the dibenzo-18-crown-6 ether, **18**, is given in Fig. 31.1. while the second lowest minimum lies 0.16 eV above the global minimum [7]. The two lowest isomers, **18A** and **18B**, of the dibenzo-18-crown-6 ether of fullereneN-methylpyrrolidine are practically degenerate and differ in the direction of the crown ether, namely up (**A**) or down (**B**) with respect to fullereneN-methylpyrrolidine, [7] see Fig. 31.1.

Different isomers of the complexes of $\text{Ph}_2\text{NH}_2^+ -1$ and $\text{Ph}_2\text{NH}_2^+ -2$ with **18** and **18A** or **18B** were determined and optimized. The full optimization of these structures led to two and eight low-lying energy minima of the complexes of cations with the crown ether **18** and the fullerene crown ether **18A** or **18B** in the gas phase, respectively, see Figs. 31.2 and 31.3. A derivative of the $\text{Ph}_2\text{NH}_2^+ -1$ isomer was

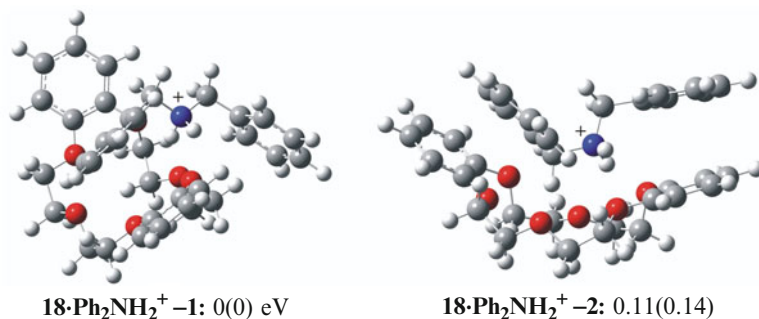


Fig. 31.2 The energetically lowest conformers of the $18 \cdot \text{Ph}_2\text{NH}_2^+$ complex, i.e., complex of dibenzo-18-crown-6 ether with diphenylammonium cation; BSSE corrected energy differences from the most stable structure are shown in the gas phase (in CHCl_3 solvent) at the M06-2X/6-31G(d,p) level of theory

obtained when the H_1 atom was substituted with a π -exTTF through a $\text{C} \equiv \text{C}$ group, see Fig. 31.4. The energetically lowest complexes of **T** with **18A** and **18B**, i.e., **18A** · **T** and **18B** · **T** are depicted in Fig. 31.4. For the calculation of their absorption spectra of the two calculated complexes, 50 singlet-spin excited electronic states have been calculated by Time Dependent DFT (TDDFT) calculations [20]. It was necessary to include a large number of excited states, about 50 excited states, in order to reach the **T** absorbing states because there are many fullerene excited states at lower excitation energies [16].

Single point calculations at the gas phase optimum geometry of all structures have been carried out in CHCl_3 solvent. As we showed in our previous study on the complexation of the present crown ethers and others with $(\text{CH}_3)_x\text{NH}_{4-x}^+$, $x = 0 - 4$ cations, full optimization in CHCl_3 solvent of the optimum gas phase geometry of the complexes results only in a slight change in geometry and an increase of the complexation energy by less than 0.02 eV [7]. Thus, we did not carry out full optimization in CHCl_3 solvent. The calculations in the solvent were carried out employing the polarizable continuum model [21]. This model is divided into a solute part lying inside a cavity, surrounded by the solvent part represented as a structureless material characterized by its macroscopic properties, i.e., dielectric constant and solvent radius. This method reproduces well solvent effects [22, 23].

For all minima determined, the complexation energy (CE_u) and the corrected values with respect to the basis set superposition error (CE) in the gas phase and in CHCl_3 solvent (CE_{sol}) were calculated. The basis set superposition error (BSSE) corrections were made using the counterpoise procedure [24] since such corrections are especially important for van der Waals (vdW) systems [25, 26] which is the case of the complexes calculated here.

All calculations were performed using the Gaussian 09 program package [27].

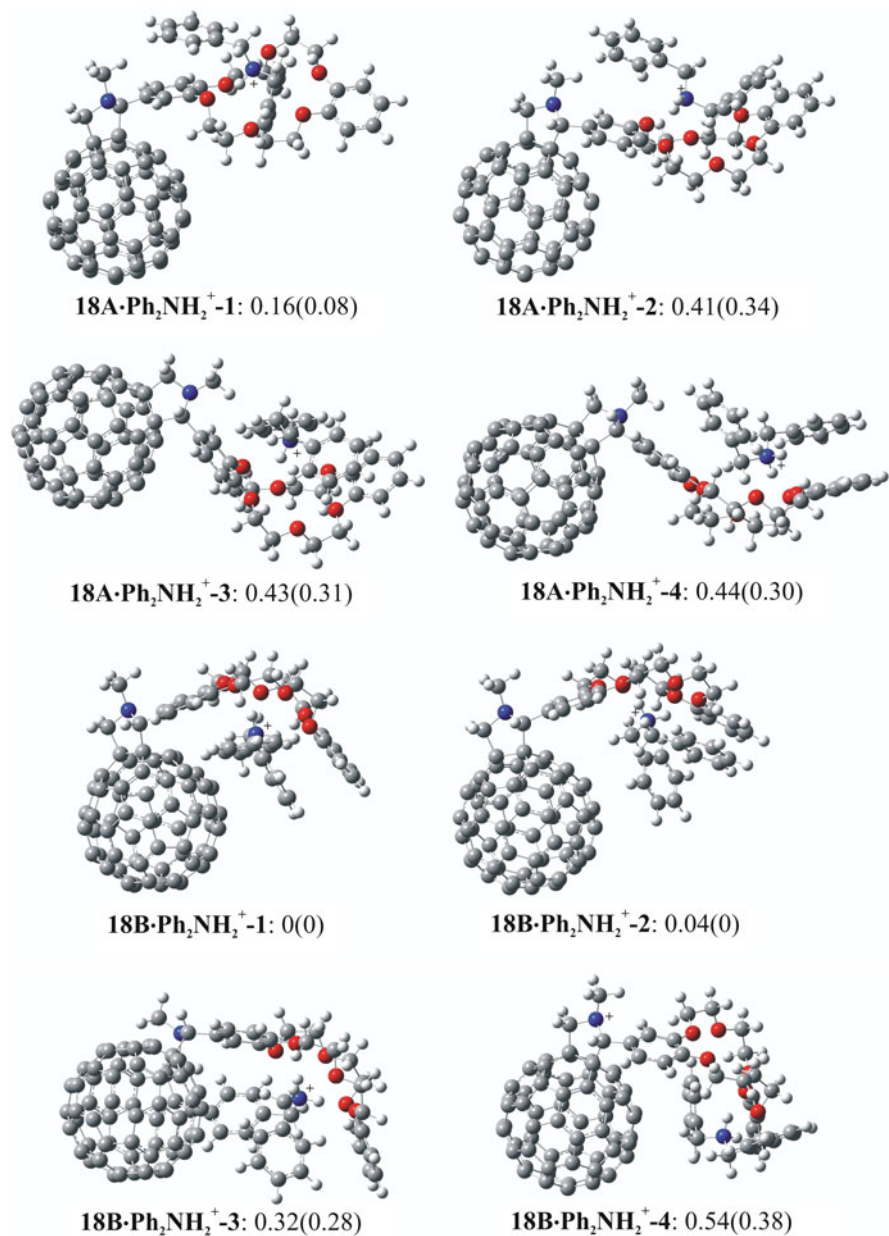


Fig. 31.3 The energetically lowest conformers of the 18A·Ph₂NH₂⁺ and 18B·Ph₂NH₂⁺ complexes. Gas phase (CHCl₃ solvent) BSSE corrected energy differences from the most stable structure are shown at the M06-2X/6-31G(d,p) level of theory

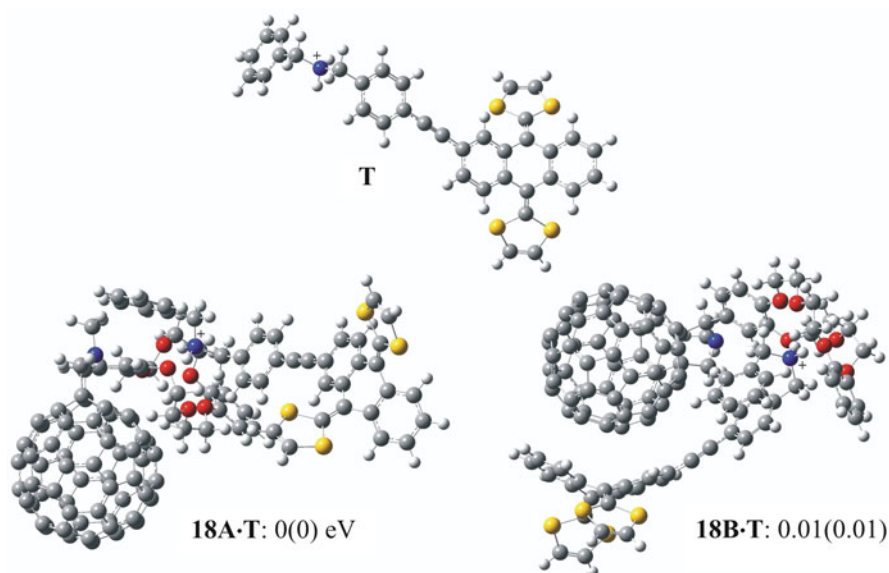


Fig. 31.4 Minimum structures of the **T** cation (π -exTTF derivative of diphenylammonium cation) and **18A**·**T** and **18B**·**T** complexes of **18A** and **18B** with **T**. BSSE corrected energy differences from the most stable structure are shown in the gas phase (in CHCl_3 solvent) at the M06-2X/6-31G(d,p) level of theory

31.3 Results and Discussion

Two energetically degenerate minima of the diphenylammonium cation, i.e., $\text{Ph}_2\text{NH}_2^+-1$ and $\text{Ph}_2\text{NH}_2^+-2$, have been identified, see Fig. 31.1. $\text{Ph}_2\text{NH}_2^+-2$ results from $\text{Ph}_2\text{NH}_2^+-1$ when the H of the CH_2 group and the phenyl group exchange positions. Calculating the frequencies, we find that both isomers are true minima.

In the present study 10 low energy supramolecular complexes have been identified; two minima of the complex of **18** with Ph_2NH_2^+ , i.e., **18**· $\text{Ph}_2\text{NH}_2^+-1$ and **18**· $\text{Ph}_2\text{NH}_2^+-2$, four minima of the complex of **18A** with Ph_2NH_2^+ , i.e., **18A**· $\text{Ph}_2\text{NH}_2^+-1$, **-2**, **-3**, and **-4**, and four minima of the complex of **18B** with Ph_2NH_2^+ , i.e., **18B**· $\text{Ph}_2\text{NH}_2^+-1$, **-2**, **-3**, and **-4**, see Figs. 31.2 and 31.3. The last number in the name of the complexes specifies the energy rank of the **18**· Ph_2NH_2^+ , **18A**· Ph_2NH_2^+ , and **18B**· Ph_2NH_2^+ species at the M06-2X/6-31G(d,p) level of theory after taking into account the BSSE correction. The vdW bond distances of the complexes are given in Table 31.1 and the complexation energies, CE, in Table 31.2.

Table 31.1 Van der Waals bond distances $R(\text{\AA})$ of the complexes of the **18**, **18A**, and **18B** crown ethers with ammonium cations at the M06-2X/6-31G(d,p) level of theory

Complex	$R_{\text{H}_N \dots \text{O}}$	$R_{\text{H}_C \dots \text{O}^a}$	$R_{\text{H}_C \dots \text{O}^b}$	$R_{\text{ph} \dots \text{ph}^c}$	$R_{\text{ph} \dots \text{F}^d}$	$R_{\text{H}_C \dots \text{ph}^e}$
18 · $\text{Ph}_2\text{NH}_2^+ - 1$	1.969, 1.917	2.473, 2.559	2.419, 2.403	3.710		2.468
18 · $\text{Ph}_2\text{NH}_2^+ - 2$	1.838, 2.242	2.153, 2.292/ 2.402 ^f	2.615	3.747		2.863, 2.899
18A · $\text{Ph}_2\text{NH}_2^+ - 1$	1.821, 1.845	2.316	2.330	3.569		
18A · $\text{Ph}_2\text{NH}_2^+ - 2$	1.754, 2.545	2.089, 2.175	2.592, 2.658			2.920
18A · $\text{Ph}_2\text{NH}_2^+ - 3$	1.944, 2.055/2.056 ^f	2.588	2.332, 2.673	3.695		2.415, 3.063
18A · $\text{Ph}_2\text{NH}_2^+ - 4$	1.759, 2.301	2.290, 2.109	2.496	3.712, 3.911		3.284
18B · $\text{Ph}_2\text{NH}_2^+ - 1$	1.853, 1.930/2.523 ^f	2.126	2.678	3.574	3.345	2.504, 2.941
18B · $\text{Ph}_2\text{NH}_2^+ - 2$	1.952, 2.079/2.366 ^f	2.188, 2.615	2.396			2.367, 2.396
18B · $\text{Ph}_2\text{NH}_2^+ - 3$	2.140/2.326 ^f 1.916/2.258 ^f	2.291, 2.403/ 2.418 ^f	2.444, 2.627			
18B · $\text{Ph}_2\text{NH}_2^+ - 4$	1.671, 1.713		2.040, 2.241, 2.543	3.728	3.123	2.250

^aH_C atoms of the CH₂ groups^bH_C atoms of phenyl groups^cDistance between the two centers of the phenyl groups^dDistance between the center of a phenyl group and the nearest C atoms of fullerene^eDistance between the H_C atoms of the CH₂ or phenyl groups and the center of phenyl group^fOne H atom interacts with two O atoms

31.3.1 18·Ph₂NH₂⁺ Complexes

The two lowest minima of the complex of **18** with Ph₂NH₂⁺ were obtained from the complexation of **18** with each of the energetically degenerate minima of the diphenylammonium cation, i.e., Ph₂NH₂⁺–1 and Ph₂NH₂⁺–2. However, the Ph₂NH₂⁺–1 cation interacts more strongly with the **18** crown ether than with the Ph₂NH₂⁺–2 species, by 0.1 eV both in the gas phase and in CHCl₃ solvent, showing some selectivity of the crown ether. The CE(CE_{sol}) of the **18**·Ph₂NH₂⁺–1 is 1.97 (1.17) eV, see Table 31.2.

Different types of van der Waals interactions are observed in the complexes. Hydrogen bonds formed between the ammonium H_N atoms and the crown ether O atoms. The strongest H_N⋯O bonds in complexes of dibenzo-18-crown-6 ether with ammonium cation have a CE of 0.9 eV per bond [7] and bond distances of 1.8 Å. The H atoms of the methylene and/or the phenyl group interact with the O atoms of ethers. The weakest interactions observed are between H atoms and phenyl groups as well as between two phenyl groups. In addition, the interactions are not always 1

Table 31.2 Complexation Energies CE(eV) in the gas phase and in CHCl₃ solvent, CE_{sol}, of the complexes of the **18**, **18A**, and **18B** crown ethers with ammonium cations at the M06-2X/6-31G(d,p) level of theory

Complex	CE _g ^a	CE ^b	CE _{sol} ^b
18 · Ph ₂ NH ₂ ⁺ –1	2.36	1.97	1.17
18 · Ph ₂ NH ₂ ⁺ –2	2.22	1.86	1.04
18A · Ph ₂ NH ₂ ⁺ –1	2.43	2.05	1.23
18A · Ph ₂ NH ₂ ⁺ –2	2.15	1.80	0.97
18A · Ph ₂ NH ₂ ⁺ –3	2.16	1.78	1.00
18A · Ph ₂ NH ₂ ⁺ –4	2.15	1.77	1.01
18B · Ph ₂ NH ₂ ⁺ –1	2.73	2.21	1.31
18B · Ph ₂ NH ₂ ⁺ –2	2.57	2.17	1.31
18B · Ph ₂ NH ₂ ⁺ –3	2.28	1.89	1.03
18B · Ph ₂ NH ₂ ⁺ –4	2.12	1.67	0.93
18A · T ^c	2.40	2.02	1.27
18B · T ^c	2.50	1.99	1.18

^aBSSE uncorrected values

^bBSSE corrected values

^cReference [16]

to 1 and in many cases one H atom interacts with two O atoms. All vdW distances are given in Table 31.1.

31.3.2 **18A** · Ph₂NH₂⁺ and **18B** · Ph₂NH₂⁺ Complexes

Eight low lying minima of the complex of dibenzo-18-crown-6 ether of fullereneN-methylpyrrolidine with the Ph₂NH₂⁺ cation, four with the **18A** isomer of crown ether and four with the **18B** isomer have been determined, see Fig. 31.3. The **18B** isomer forms the most stable structures, because the cation can be captured between fullerene and crown ether and additional vdW bonds formed can further stabilize the complex. The complexation energies of minima range from 2.21 to 1.67 eV in the gas phase and from 1.31 to 0.93 eV in CHCl₃ solvent at the M06-2X/6-31G(d,p) level of theory, see Table 31.2. It is worth noting that the BSSE corrections are up to 0.5 eV, however, the relative stability of the structures does not change.

In all eight minima, hydrogen bonds are formed between the H_N atoms, which are attached to the N atoms, and the O atoms of the crown ethers with bond distances ranging from 1.7 to 2.5 Å. Additional vdW bonds between the H_C atoms of the CH₂ or phenyl groups and the O atoms of the crown ether are formed, and the distances range from 2.0 to 2.7 Å. The above three types of interactions are not always 1 to 1 and one H atom can interact with two O atoms, see Table 31.2. Moreover, π-stacking interactions between phenyl groups are formed in all cases with the exception of **18B** · Ph₂NH₂⁺–2 and **18B** · Ph₂NH₂⁺–3, with distances of 3.6–3.9 Å, while interactions between C₆₀ and phenyl group appear only in **18B** · Ph₂NH₂⁺–1 and **18B** · Ph₂NH₂⁺–4, with distances of 3.3 and 3.1 Å, respectively. Finally, hydrogen vdW interactions between H atoms and phenyl groups are formed in all cases with the exception of **18A** · Ph₂NH₂⁺–1 and **18B** · Ph₂NH₂⁺–3.

The two lowest minima are the $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ isomers and they contain the $\mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ isomer of the cation, but it is deformed and twisted, respectively. These minima are further stabilized by the existence of the fullerene, see above. Without the fullerene, the structures are not stable minima. Further optimization of these structures lead to significant change of the complexation in both isomers and finally lead to the $\mathbf{18} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ complex. The CE values of $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ are $\text{CE}(\text{CE}_{\text{sol}}) = 2.21(1.31)$ and $2.17(1.31)$ eV, respectively. In CHCl_3 solvent, the minima are energetically indistinguishable.

The third lowest minimum is formed by the $\mathbf{18A}$ isomer, $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$. It consists of the $\mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ minimum and the crown ether is deformed with respect to the free $\mathbf{18}$ crown ether. However, even though the fullerene does not interact with the cation as in the above cases, without the fullerene this structure is not stable. The CE values are $\text{CE}(\text{CE}_{\text{sol}}) = 2.05(1.23)$ eV.

In the remaining five isomers, the $\mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ minimum is included in both $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 3$ and $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 4$, while in the last isomer the $\mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ cation is deformed. The $\mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ minimum is part of $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ and $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 4$. Finally, the $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 3$ isomer does not include any stable minimum of the $\mathbf{Ph}_2\mathbf{NH}_2^+$ cation.

The two lowest minima $\mathbf{18} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and $\mathbf{18} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$ of the complex of the $\mathbf{18}$ crown ether are part of the $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 3$ or $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 4$ and $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 4$, respectively and not of the two lowest minima of the complex of the fullerene crown ether, i.e., $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 2$. Comparing the CE values of the $\mathbf{18} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 3$, which differ only in the existence of the fullerene, the first one has a CE value larger by 0.2 eV than the second one. However, the existence of the fullerene causes another minimum to be the global one, as mentioned above, which is more stable by 0.2 eV than the global $\mathbf{18} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ minimum of the complex of the $\mathbf{18}$ crown ether.

31.3.3 $\mathbf{18A} \cdot \mathbf{T}$ and $\mathbf{18B} \cdot \mathbf{T}$ Complexes

Substituting the H_1 atom of the $\mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ isomer with a π -exTTF through a $\text{C} \equiv \text{C}$ group, the \mathbf{T} cation is obtained, see Fig. 31.4. The energetically lowest complexes of \mathbf{T} with $\mathbf{18A}$ and $\mathbf{18B}$, i.e., $\mathbf{18A} \cdot \mathbf{T}$ and $\mathbf{18B} \cdot \mathbf{T}$, [16] are depicted also in Fig. 31.4. These two minima correspond to $\mathbf{18A} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$ and to a slightly deformed $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 3$, respectively. Again, the lowest in energy $\mathbf{18B} \cdot \mathbf{T}$ does not correspond to the lowest minimum $\mathbf{18B} \cdot \mathbf{Ph}_2\mathbf{NH}_2^+ - 1$. Moreover, in $\mathbf{18B} \cdot \mathbf{T}$ additional interactions are formed between the fullerene and the π -exTTF of \mathbf{T} . The $\text{CE}(\text{CE}_{\text{sol}})$ values of $\mathbf{18A} \cdot \mathbf{T}$ and $\mathbf{18B} \cdot \mathbf{T}$ are $2.02(1.27)$ and $1.99(1.18)$ eV, respectively.

The $\mathbf{18A} \cdot \mathbf{T}$ and $\mathbf{18B} \cdot \mathbf{T}$ isomers form a dyad each consisting of an electron donor (fullerene), an electron acceptor (π -exTTF of \mathbf{T}) and a crown ether as a bridge between them. Their absorption spectra are given in Fig. 31.5. The spectrum

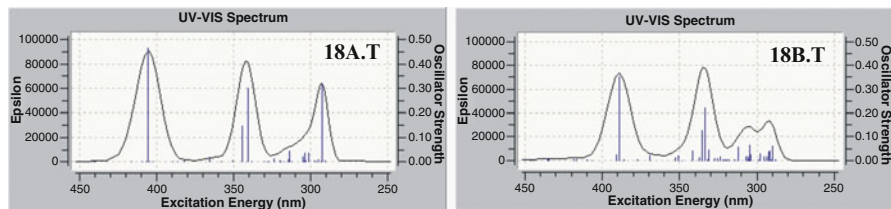


Fig. 31.5 Absorption spectrum of **18A·T** and **18B·T** at the M06-2X/6-31G(d,p) level of theory

of **18A·T** presents three major features at about 400, 340, and 290 nm which correspond to transitions from the **T** cation also to **T**. However, charge transfer transitions from **T** to the fullerene are observed very close to the **T** → **T** transitions. On the other hand, the absorption spectrum of **18B·T** presents also three major absorption peaks at about 390, 330, and a double peak around 300 nm with smaller oscillator strengths. The first and the second major peaks correspond to transition from **T** to **T**/fullerene, i.e., the excited orbital has electron density in both **T** and fullerene species. That happens because the fullerene interacts with the π -exTTF of **T**, see Fig. 31.5. We can label these transitions as charge transfer transitions. The last double peak corresponds to transitions from **T** to fullerene, namely charge transfer transitions. Moreover, the absorption spectra of five other isomers of **18A·T** and **18B·T** complexes are similar to spectrum of **18A·T** and the use of the CAM-B3LYP functional leads to similar major absorption peaks, transitions and conclusions [16]. Thus, the studied complex may serve as a candidate for molecular optoelectronics applications.

31.4 Remarks and Conclusions

The complexes of dibenzo-18-crown-6 ether and of dibenzo-18-crown-6 ether of fullereneN-methylpyrrolidine with the diphenylammonium cation, Ph_2NH_2^+ , and its derivative with π -extended tetrathiafulvalene, π -exTTF, were investigated by employing density functional theory. We calculated geometries, complexation energies and some absorption spectra of the lowest energetic minima of the above complexes in the gas phase as well as in CHCl_3 solvent. A summary of our main results follows:

1. The complexation energies, corrected for basis set superposition error, reach up to 2.2 eV in the gas phase and up to 1.3 eV in the CHCl_3 solvent, at the M06-2X/6-31G(d,p) level of theory.
2. The minima of the cations and of the crown ethers are deformed to maximize the number of the hydrogen bonds formed and present the largest complexation energies. Bonds are formed between the H atom of ammonium, of the methylene

- and/or the phenyl group and the O atoms of ethers. Moreover, π -stacking interactions arise between two phenyl groups or phenyl group with fullerene.
3. The presence of fulleroN-methylpyrrolidine, attached to the crown ether, results in minima, where the cation is captured between fullerene and crown ether. Additional interactions that can further stabilize the complex are formed.
 4. The attachment of the fulleroN-methylpyrrolidine to the dibenzo-18-crown-6 ether or the attachment of π -exTTF to Ph_2NH_2^+ cation changes the complexation of the global minimum. As a result, it is not safe to suppose that the attachment of a group even if it is away from the complexation area will not change the type of the global minimum complex.
 5. The complex of fullerene crown ethers with a π -exTTF derivative of Ph_2NH_2^+ presents charge transfer transitions in its absorption spectrum and may have potential for applications in organic photovoltaics and molecular electronic devices.

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