Investigation of the Ground-State Complex Formation Between Pyrene, Cyanopyrene and Amines by Semiempirical AM1 Method

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The aim of the present study is to investigate the intermolecular ground-state complex formation between pyrene (Py), cyanopyrene (CNPy) and amines. Seven different amines have been selected with different but related properties: aliphatic diamines N,N,N',N'-tetramethylethylenediamine (TMED), N,N,N',N'-tetramethyl-1,3-propanediamine (TMPD), N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD); aliphatic cyclic amines 1-azabicyclo-[2.2.2]-octane (ABCO), 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (diamine); dimethyl aniline (DMA) and diethyl aniline (DEA). The complex formation has been investigated by using the AM1 semiempirical method implemented in VAMP module of Accelrys Materials Studio. Heat of formation values, ionization potentials and dipole moments of the studied structures have been calculated for fully optimized structures. Our results have shown that pyrene cannot form amine complexes in the ground state whereas cyanopyrene may form ground-state complexes with the studied aromatic amines dimethyl aniline and diethylaniline. The results have been discussed further in terms of the stability of the investigated systems based on the computed data.

Key Words: Hydrocarbon, Amine, Intermolecular ground-state complex, Semiempirical method, AM1.

INTRODUCTION

Many aromatic hydrocarbons and their derivatives can form ground and/or excited-state donor-acceptor complexes with other molecules including proteins and DNA. The main reason of their carcionogenic activities is acting as an acceptor of π-electronic excitation energy. In general, the behaviour of a molecule in the electronically excited state differs considerably from that in the ground state. Its ionization potential is smaller and its electron affinity is larger in the excited state, so that the molecular interaction may be expected to bring about new interesting phenomena. The amines also resemble the N containing structures in many molecular systems and may form complexes with hydrocarbons. However, it is mostly claimed that no specific interactions exist between a ground state hydrocarbon and an amine as the absorption spectra of hydrocarbons with the amines do not show any significant change[1].

Pyrene, which is a polyaromatic hydrocarbon (PAH), is planar and contains four benzene rings displaying an aromatic character. It shows characteristic UV-absorption and fluorescence properties due to its π-electronic system. It is a very important compound in fluorescence spectroscopy because of its high quantum yield (0.65 in cyclohexane)[2] and long life-time. Pyrene and some of its derivatives form complexes with nitrogen containing molecules in the excited state called

exciplexes. The electronic and geometrical structures of the pyrene change upon exciplex formation[2].

The behaviour of pyrene is typical of several other poly-cyclic hydrocarbons and their derivatives which exhibit excimer fluorescence. Birks and coworkers had studied the time behaviour of the monomer and excimer fluorescence and they had described a kinetic scheme consistent with the experimental observations[3].

Although extensive studies have been dedicated to pyrene and its derivatives during the last few decades, photophysical properties of complex formation with different amines are not yet fully understood. Intramolecular systems formed by the bridging molecules between donors and acceptors have been investigated both experimentally and computationally[4]. The main purpose of these studies is to have a better understanding of the electron and energy transfer for developing a model based on the electron transfer process in photosynthetic reaction centers. However, there are only a few studies present in the literature about the nature of the intermolecular systems of hydrocarbon-amine systems[5,6]. Especially, the computational studies are very rare[7,8]. This study will focus on the ground-state intermolecular complex formation. Additionally, effects of geometry changes on the complex will be investigated by using different conformations.

We have recently reported a study on ground state-complex formation of the four dialkyl diamines[9]. In the present study, we extend our study where hydrocarbons pyrene (Py) and cyanopyrene (CNPy) are chosen as acceptors and aliphatic diamines N,N,N',N'- tetramethylethylenediamine (TMED), N,N,N',N'-tetramethyl-1,3-propanediamine (TMPD), N,N,N',N'-tetramethyl-1,3-butanediamine (TMBD); aliphatic cyclic amines 1-azabicyclo-[2.2.2]-octane (ABCO), 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (diamine); aromatic amines dimethyl aniline (DMA) and diethyl aniline (DEA) as donors. Quantum chemical model calculations were carried out to discuss properties of the compounds by using the semi-empirical AM1 method[10].

COMPUTATIONAL DETAILS

A detailed conformational analysis has been performed for the studied amines by using the systematic search module of the Spartan 08 for Windows[11] with MMFF force field[12].

The obtained conformers have been further optimized with AM1 semiempirical method as implemented in the VAMP[13] module of the Accelrys Materals Studio 4.1[14].

The complexes have been formed by using the most stable complexes of the amines and the hydrocarbons Py and CNPy. Various possible complex conformations have been studied to locate all the possible ground-state complexes for each system. This paper reports the most stable complexes.

The optimized structures have been verified as minimum with frequency calculations. The structures with all positive frequencies indicate a minimum whereas presence of imaginary frequencies indicate that the structure is not a minimum.

RESULTS AND DISCUSSION

Ground-state complex formation between pyrene (Py) and cyano pyrene (CNPy) and the aliphatic diamines N,N,N',N'-tetramethylethylenediamine (TMED), N,N,N',N'-tetramethyl-1,3-propanediamine (TMPD) and N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD); aliphatic cyclic amines 1-azabicyclo-[2.2.2]-octane (ABCO), 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (diamine); dimethyl aniline (DMA) and diethyl aniline (DEA) have been investigated by semiempirical AM1 method. Table-1 summarizes the heat of formation (ΔH_f, in kcal/mol) values, dipole moments (μ, in Debyes) and ionization potentials (IP, in eV) of the hydrocarbons and the amines. The most stable conformers optimized with AM1 are displayed in Fig. 1.

TABLE-1
CALCULATED VALUES FOR THE MOST STABLE
CONFORMERS AMONG AM1 OPTIMIZED STRUCTURES OF
PYRENE (Py), CYANO PYRENE (CNPy) AND THE AMINES
TMED, TMPD, TMBD, ABCO, DABCO, DMA AND DEA; HEAT
OF FORMATION (ΔH_f kcal/mol), DIPOLE MOMENTS (μ debyes)
AND IONIZATION POTENTIALS (IP eV)

Compound	ΔH_f	μ	IP
Py	67.41	0.01	8.13
CNPy	99.72	3.83	8.44
TMED	1.92	0.00	8.68
TMPD	-5.24	1.47	8.96
TMBD	-12.13	0.01	8.96
ABCO	-8.18	1.37	9.41
DABCO	20.91	0.00	9.00
DMA	31.14	1.49	8.28
DEA	19.82	1.51	8.23
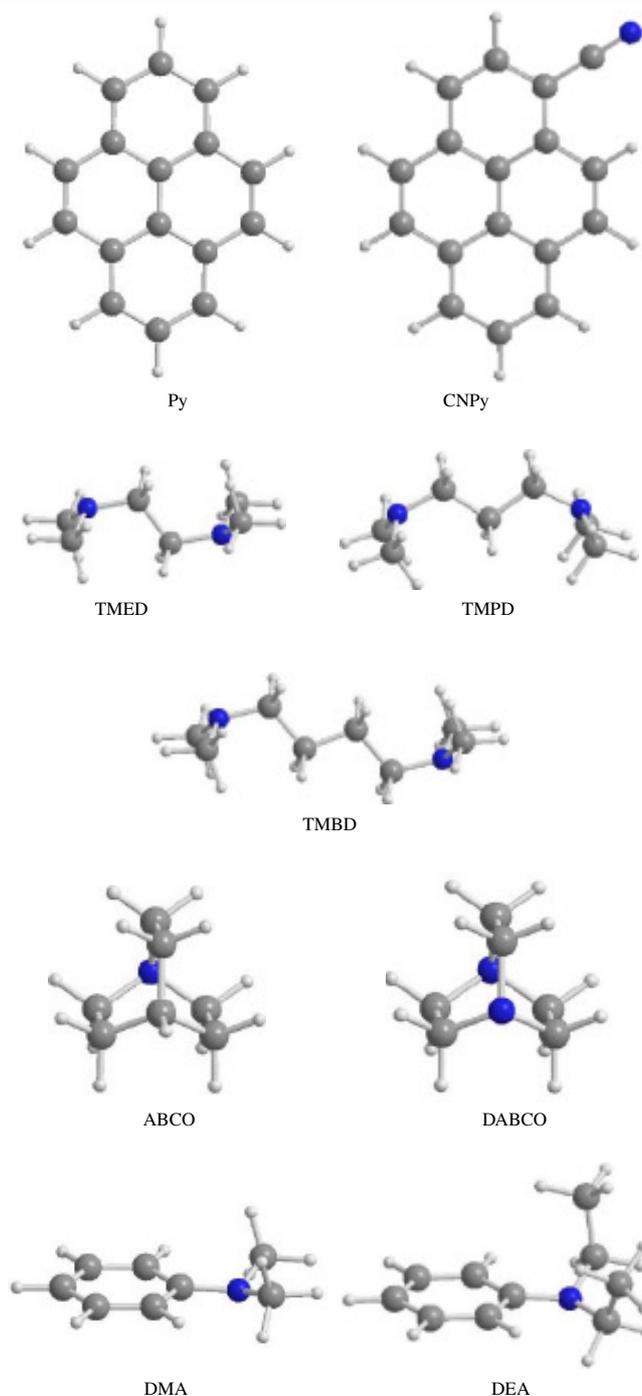
Fig. 1. AM1 optimized structures of Py, CNPy and the studied amines TMED, TMPD, TMBD, ABCO, DABCO, DMA and DEA

As seen from Table-1, CNPy has a higher heat of formation compared to Py indicating that the reactivity of CN group has a significant effect on the stability of the hydrocarbon. It is also observed that the diamine becomes more stable as the number of methylene groups between the two nitrogen increases. The cyano group also increases the dipole moment of the Py ring due to the presence of an electronegative heteroatom, N. The diamines prefer to have linear conformations and the dipole moment is neglicible due to the symmetric structure of this conformation. However, TMPD has a considerable dipole moment as the symmetry is lost because of the odd number of methylene groups. The ionization potential values show that

amines have higher IPs than the studied hydrocarbons except the aromatic amines DMA and DEA which have ionization potential values between those of Py and CNPy.

Py-Amine complexes: The computed values for the most stable Py-amine complexes are given in Table-2 and the AM1 optimized structures are shown in Fig. 2. In addition to the values given in Table-1, complexation energies (E_C, in kcal/mol) have been calculated for the complexes. This energy simply gives the difference between the energy of a complex and the sum of its separated components and formulated as:

$$E_S = \Delta H_f(Complex) - [\Delta H_f(Hydrocarbon) + \Delta H_f(Amine)]$$

TABLE-2
CALCULATED VALUES FOR THE MOST STABLE
CONFORMERS OF Py-AMINE COMPLEXES OPTIMIZED WITH
AM1; HEAT OF FORMATION (ΔH_f kcal/mol), DIPOLE MOMENTS
(μ debyes), IONIZATION POTENTIALS (IP eV) AND
COMPLEXATION ENERGIES (E_C kcal/mol)

Compound	ΔH_f	μ	IP	E_C
Py-TMED	68.78	0.17	8.11	-0.56
Py-TMPD	61.68	1.48	8.09	-0.49
Py-TMBD	55.06	0.06	8.15	-0.23
Py-ABCO	58.75	1.76	8.00	-0.48
Py-DABCO	87.90	0.47	8.05	-0.43
Py-DMA	98.27	1.75	8.03	-0.28
Py-DEA	86.36	1.54	8.12	-0.88

Py-TMED

Py-TMPD

Py-TMBD

Py-ABCO

Py-DABCO

Py-DMA

Py-DEA
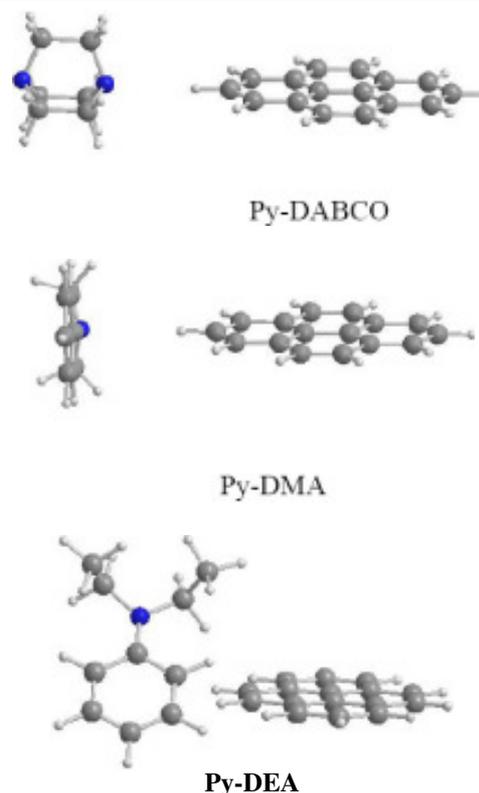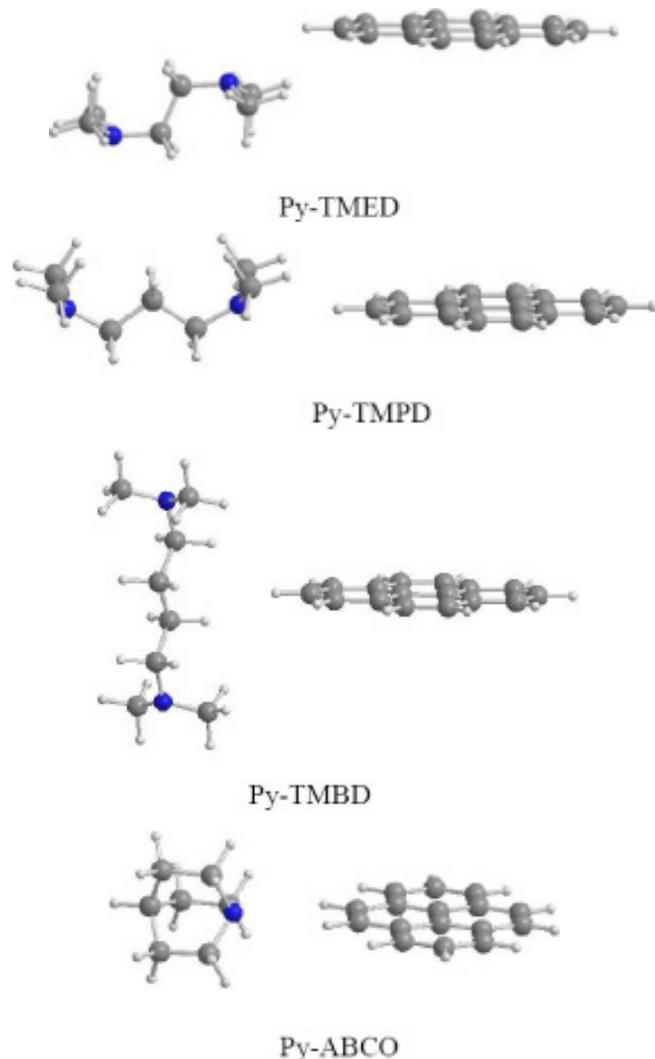
Fig. 2. AM1 optimized structures of Py-amine complexes

Although the systems include different number of atoms and computed heat of formation values can not be directly compared, one can comment on the general trends of the studied systems. The stability of the Py complexes resembles the stability of amines in the case of alkyl diamines. The stability increases with the increasing amine size (each additional -CH₂ group decreases ΔH_f by *ca.* 7 kcal/mol). On the contrary, complexation energy decreases. This is expected since a more stable compound will be less reactive and has a lower tendency to form a complex. Complexes of ABCO and DABCO show similar behaviour, but the pyrene-aromatic amine complexes completely display a different behaviour *i.e.*, stability is directly proportional to the complexation energy.

The dipole moments indicate that in Py-amine complexes, amines are the components in determining the dipole value. The ionization potentials of formed complexes are closer to the ionization potentials of Py. This may be an indication that the hydrocarbons are main components in complex formation and the contributions from the amines are limited.

We have also investigated the HOMO and LUMO of the studied compounds. From the shapes and location of these orbitals further insight can be gained about the complex formation. Fig. 3 diplays the orbitals of Py and Py-amine complexes. As seen from all these structures the HOMO and LUMO of the complexes are always located on Py and there is no contribution from the amines. The HOMO and LUMO of the complexes are also very similar to the HOMO and LUMO of the uncomplexed Py. By summing up all the data computed in this study, it may be concluded that the ground-state complexes of Py and amines are not charge and/or electron transfer complexes. They are formed as a result of strong electrostatic interactions either van der Waals or dispersive

HOMO   LUMO

Py

Py-TMED

Py-TMPD

Py-TMBD

Py-ABCO

Py-DABCO

Py-DMA

Py-DEA
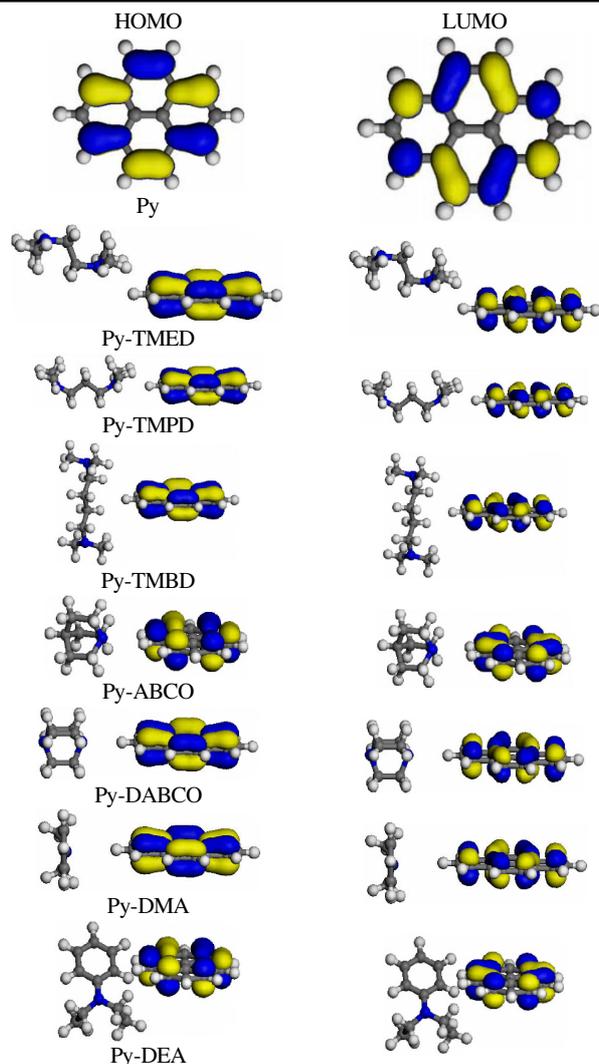
Fig. 3.   HOMO and LUMO of the AM1 optimized structures of Py and Py-amine complexes

CNPy-TMED

CNPy-TMPD

CNPy-TMBD

CNPy-ABCD   CNPy-DABCO

CNPy-DMA   CNPy-DEA

Fig. 4. AM1 optimized structures of CNPy-amine complexes

interactions. These complexes therefore may be referred as collisional complexes. It may also be concluded that the probability of complex forming reactions are higher in the excited state, supported by the high ionization potentials of the studied systems.

CNPy-Amine complexes: Table-3 displays the computed values for CNPy-amine complexes. The optimized geometries for the most stable complexes are given in Fig. 4. The stability of the CNPy complexes resembles the stability of amines as observed for the Py complexes for alkyl diamines. The stability

increases with the increasing amine size; on the contrary, complexation energy decreases. The other four amines display significantly different characteristics in CNPy complexes. Complexes of ABCO and DABCO have very high complexation energies. In fact, they are the highest among all optimized complex structures. Diethyl aniline complex is still more stable than the DMA complex but the difference between the complexation energies have decreased to one third of the value in Py complexes.

For CNPy it is observed that the position and/or orientation of the CN group significantly determine the value and direction of the dipole moment. The dipole moments indicate that in CNPy-amine complexes CNPy is the component in determining the dipole value in contrast to the observed behaviour for Py complexes. The IPs of formed complexes are closer to the IPs of CNPy. This may be an indication that the hydrocarbons are main components in complex formation and the contributions from the amines are limited. However, these conclusions are invalid for the CNPy complexes of aromatic amines DMA and DEA. Their dipole moments and IP values are not just close to the one of the components but rather form as a result of contribution from each component. The dipole moments seem to be the sum of CNPy and the amine because of the orientation of the molecules and the IP values of the complexes are somewhere in between the IP of the CNPy and the amines. This may indicate the first significant evidence for a ground-state electron and/or charge transfer complex formation between the studied hydrocarbons and amines.

Orbital analysis will give a better understanding and additional information about the nature of the CNPy complexes. Fig. 5 shows the orbitals for CNPy and CNPy-amine complexes. As it is seen in the figure all HOMO and LUMO of the complexes are located on CNPy except for the complexes of DMA and DEA. In these complexes, the HOMO are located on the amines whereas the LUMO are on CNPy. This

TABLE-3
CALCULATED VALUES FOR THE MOST STABLE
CONFORMERS OF CNPy-AMINE COMPLEXES OPTIMIZED
WITH AM1; HEAT OF FORMATION (ΔH_f kcal/mol), DIPOLE
MOMENTS (μ debyes), IONIZATION POTENTIALS (IP eV) AND
COMPLEXATION ENERGIES (E_C kcal/mol)

Compound	ΔH_f	μ	IP	E_C
CNPy-TMED	101.05	3.95	8.42	-0.58
CNPy-TMPD	93.89	3.70	8.40	-0.58
CNPy-TMBD	87.38	3.80	8.46	-0.21
CNPy-ABCO	90.67	2.57	8.33	-0.86
CNPy-DABCO	119.74	3.49	8.36	-0.88
CNPy-DMA	130.58	5.18	8.38	-0.27
CNPy-DEA	119.04	5.48	8.36	-0.50

HOMO   LUMO

Fig. 5.   HOMO and LUMO of the AM1 optimized structures of CNPy and CNPy-amine complexes

additional evidence indicates that CNPy and DMA and DEA may form an electron and/or charge transfer complex in the ground-state.

On the contrary to the Py complexes, aromatic amines may form ground-state electron and/or charge transfer complexes with CNPy. However, all other amine complexes may be referred as collisional complexes as mentioned earlier. It may also be concluded that the probability of complex forming reactions are even higher in the excited state for CNPy, supported by the high IPs of the studied systems.

It is noteworthy to emphasize that the hydrocarbon-amine complexes mostly have similar structures for both hydrocarbons except the aromatic amines which behave significantly different when reacting with Py and CNPy. Altough the CN group alters the reactivity, its position do not affect the complex geometry. This allowed us to compare all the computed results directly for the studied structures.

Conclusion

Pyrene and its derivative cyanopyrene can form complexes with many other compounds including amines. The results of this study have shown that Py and CNPy do not form charge and/or electron transfer complexes with the studied amines except CNPy-DMA and CNPy-DEA complexes which can form ground-state complexes as supported by the analysis of molecular orbitals. The optimized structures may result due to the strong interactions between the molecules that are located in the close proximity of other molecules. It is also suggested that excited state complex formation is more probable as indicated by the computed ionization potentials.

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