

ARTICLE

Hydrogen Bonding-Mediated Assembly of Perylene Dianhydride and Pyridine Derivatives

Shi Wu, Qi-wen Teng*

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

(Dated: Received on January 31, 2005; Accepted on April 28, 2005)

Semi-empirical AM1 method was used to study 1:1 and 1:2 hydrogen bond complexes formed with perylene dianhydride and pyridine derivatives. The weak interaction energy become bigger as the number of hydrogen bonds increases. The donor groups on the host and electron-withdrawing groups on the guest molecules favor hydrogen bonding interactions, and the formation of hydrogen bonding leads to electron density flow from the host to the guest molecules. Electronic spectra of these complexes were computed using INDO/SCI method. Blue-shift of the electronic absorption spectra for the complexes, comparing that of the host, takes place, and the first peaks for different complexes changed slightly. These are in agreement with the experimental results. The cause of blue-shift was discussed, and the electronic transitions were assigned based on theoretical calculations. The potential curve of double proton transfer in the complex was calculated, and the transition state and activated energy relative to the N-H bond were obtained.

Key words: Perylene dianhydride, Hydrogen bonding assembly, Electronic spectra, AM1

I. INTRODUCTION

Hydrogen bonds play important roles in physics, chemistry and biological science, and molecular assembly with supermolecular structure from organic compounds through hydrogen bonding interactions has been an active research subject in recent years [1–8]. Bonar-Law *et al.* investigated intermolecular hydrogen bonds between cholaphane and methyl β -D-glucoside, as well as its possible conformation [1]. Inouye *et al.* explored molecular recognition of polypyridine-macrocyclic with β -ribofuronosides via multipoint hydrogen bonding [2]. Jin *et al.* calculated hydrogen-bonding assemblies of bispyrimidine and bisbarbituric acid using the AM1 method [3]. We have studied the molecular recognition and switching of cyclo-bis(paraquat-p-phenylene) to neutral guests [4] and of calyx-4-arene to pyrimidine with AM1 method [5]. Based on the hydrogen-bond self-assembly experiment [6], we used AM1 method to optimize supermolecular structures of perylene dianhydride and pyridine derivatives. We tried to understand their abilities to assemble, and we computed their electronic spectra using the INDO/SCI method.

II. CALCULATIONAL METHOD

We define ΔE as the weak interaction energy between the host and guest, E_C as the energy of the complex, E_i as the energy of the single host or guest molecules, respectively. Then $\Delta E = E_C - \sum E_i$. Here we did not compute Basis Set Superposition Error (BSSE) owing to the constrain of our current calculating conditions. The structures of the 1:1 complexes are in Figure 1,

where we defined the center of symmetry of host 1 ($R_1, R_2=H$) as the original point and put the guest 1 ($R_3, R_4=H$) on the XY plane. The 1:2 host-guest complex 2 was formed by connecting two hydrogen atoms on the other guest 1 with the two oxygen atoms of the anhydride on host 1. The structure of the host, guest molecules, and complexes 1–11 were optimized using the AM1 method [3–5]. Configuration interaction was studied by the INDO/SCI method [9–11] without any adjustment of the parameters. There are 197 single electron transition states with the ground state through excitation of electrons from the highest 14 occupied orbitals to the lowest 14 virtual orbitals.

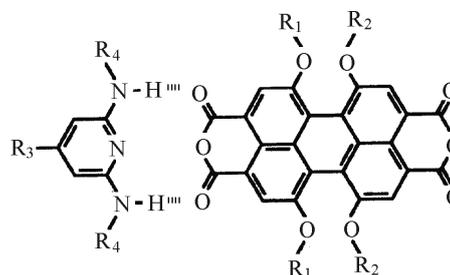


FIG. 1 Optimized geometries of the 1:1 host-guest complexes

- Complex 1: $R_1, R_2, R_3, R_4=H$;
- Complex 3: $R_1, R_2, R_4=H, R_3=Cl$;
- Complex 4: $R_1, R_2, R_4=H, R_3=F$;
- Complex 5: $R_1, R_2, R_4=H, R_3=NO_2$;
- Complex 6: $R_1, R_2, R_4=H, R_3=COOH$;
- Complex 7: $R_1, R_2, R_3=H, R_4=CH_3$;
- Complex 8: $R_1, R_2, R_3=H, R_4=CH_2Cl$;
- Complex 9: $R_2, R_3, R_4=H, R_1=CH_3$;
- Complex 10: $R_2, R_3, R_4=H, R_1=C_6H_5$;
- Complex 11: $R_3, R_4=H, R_1, R_2=CH_3$

*Author to whom correspondence should be addressed. E-mail: wuteng@mail.hz.zj.cn

TABLE I Weak interaction energy of complexes 1–11

Complexes	$\Delta E/\text{eV}$
1	-0.1322
2	-0.2122
3	-0.1455
4	-0.1431
5	-0.2009
6	-0.2209
7	-0.0951
8	-0.1526
9	-0.14136
10	-0.3324
11	-0.3499

III. RESULTS AND DISCUSSION

A. Stability of the complexes

ΔE of complex 2 is bigger than that of complex 1 (Table I) because two guests are associated with host 1, thus hydrogen bonding interaction becomes stronger. Complexes 3 and 4 possess larger ΔE than complex 1, resulted from the existence of groups $-\text{Cl}$ and $-\text{F}$ on the meta position of $-\text{NH}_2$ on the pyridine ring in guest 1. With $-\text{Cl}$ and $-\text{F}$ changed into $-\text{NO}_2$ and $-\text{COOH}$, ΔE for complexes 5 and 6 becomes much higher because stronger electron-withdrawing effect can increase the positive charge of hydrogen atoms on the $-\text{NH}_2$ groups, resulting in stronger hydrogen bonds. Similarly, the substitution of one hydrogen atom of $-\text{NH}_2$ by $-\text{CH}_3$ group leads to the increase of the negative charge for the other hydrogen atom. Thus the interaction decreases and complex 7 has less stability energy than complex 1; whereas the substitution of a hydrogen atom of $-\text{NH}_2$ by $-\text{CH}_2\text{Cl}$ group elevates ΔE of complex 8. The substitution of the hydrogen atom of $-\text{OH}$ on host 1 by $-\text{CH}_3$ and $-\text{C}_6\text{H}_5$ groups enhances the electron density on the benzene ring of host 1, strengthening hydrogen bonds for complexes 9 and 10, in comparison to complex 1. Increase of the number of $-\text{CH}_3$ groups on host 1 plays an important role in stabilizing complex 11. The length of the hydrogen bond in complex 1 is 0.2214 nm, while the lengths of the two hydrogen bond in complex 2 are 0.2067 and 0.3809 nm, respectively. This is why complex 2 is more stable than complex 1, but ΔE for complex 2 is not two times of that for the complex 1. The donor group on host 1 and the electron-withdrawing group on guest 1 are helpful to hydrogen bonding interactions.

B. Electronic structures

Complex 3 is a stable closed-shell super-molecule. Its HOMO(111) and LUMO(112) energies are -7.8527 and -2.6455 eV, respectively. Its LUMO-HOMO energy gap is 5.2072 eV (Fig.2), bigger than those of other complexes, leading to blue-shift of UV bands of complex 3. This is because substituting groups can change host-

guest interaction through hydrogen bonds, and they can change electronic properties, and energies of orbitals of the host and guest molecules. The net AM1 charge for guest 1 in complex 1 is -0.0035 , which means that electrons flow from the host to the guest via hydrogen bonds. Charges on two guests in complex 2 are -0.0036 and -0.0046 , thus the second guest does not affect net charge of the first and electrons flow to the two guests. The charge density of the guest for complex 6 is changed into -0.0060 because of $-\text{COOH}$ group, meanwhile two $-\text{C}_6\text{H}_5$ groups on the host lead to the increase in negative charges of the guest (-0.0052) compared with complex 1. Hereby the donor group on the host and the electron-withdrawing group on the guest are beneficial to the flow of electrons from the host to the guest, thus increasing the stability energy of the complex.

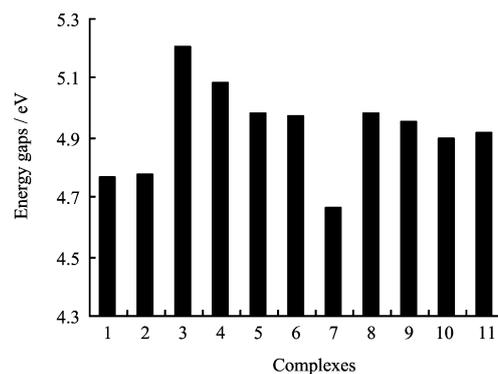


FIG. 2 LUMO-HOMO energy gaps of complexes 1–11

C. Electronic absorption spectra

Main absorption peaks in the electronic spectrum for host 1 was computed to be at 277.4, 286.4, 365.3, 369.1 and 454.5 nm. The first absorption peak for complex 1 appears at 451.6 nm (Table II), arisen from electronic transition of $a_1(102) \rightarrow a_1(104)$ according to contribution coefficient of transition. The first peak for complex 2 is at 451.3 nm, resulted from electronic transition of $a_g(122) \rightarrow b_{2u}(125)$. The blue-shift of first absorptions in electronic spectra for complexes 1 and 2 relative to that of host 1 occurs, in agreement with Jin's calculation [3]. The first peaks of complexes 1 and 2 are basically the same in wavelengths but a little different in oscillation strength, which agrees with Liu's experiment [6].

The change of substituting groups on the guest has some influence on spectra of complexes 4 and 5. The maximum absorptions for complex 4 and 5 are also the first absorption transition at 450.4 and 452.0 nm, respectively. They were produced by the electronic transitions of $a'(110) \rightarrow a'(112)$ and $a_1(105) \rightarrow a_1(107)$. The blue-shift of UV peaks for complexes 4 and 5 compared with that of host 1 is because electron-deficient groups on guest 1 improve charge interaction between host 1 and guest 1 by hydrogen bonding. The first absorption peaks for complexes 8 and 11 appeared at 451.5 and 454.8 nm, which were the electronic transitions of $a_1(114) \rightarrow a_1(116)$ and $b_2(130) \rightarrow a_1(132)$. The first peak

TABLE II Electronic spectra of complexes 1, 2, 4, 5, 8 and 11

λ/nm	f	Trans nature and coeff.	λ/nm	f	Trans nature and coeff.
Complex 1			Complex 2		
451.6	1.0759	$a_1(102) \rightarrow a_1(104)$, 0.9827	451.3	1.0717	$a_g(122) \rightarrow b_2u(125)$, -0.9783
364.3	0.0800	$b_2(100) \rightarrow a_1(104)$, -0.6794	374.4	0.0025	$a_g(123) \rightarrow b_2u(125)$, -0.9429
360.9	0.0103	$b_2(99) \rightarrow a_1(104)$, -0.5236	363.8	0.0786	$b_{1g}(120) \rightarrow b_2u(125)$, -0.6943
337.7	0.0015	$a_1(102) \rightarrow b_2(106)$, 0.7322	360.3	0.0110	$a_g(122) \rightarrow b_{1g}(128)$, -0.4967
336.4	0.0027	$b_2(93) \rightarrow a_1(104)$, 0.5109	337.3	0.0033	$a_g(122) \rightarrow b_{1g}(127)$, 0.8068
332.6	0.0013	$b_2(94) \rightarrow a_1(104)$, 0.5165	327.1	0.0057	$a_g(122) \rightarrow a_g(126)$, -0.9551
Complex 4			Complex 5		
450.4	1.0938	$a'(110) \rightarrow a'(112)$, -0.9835	452.0	1.0969	$a_1(105) \rightarrow a_1(107)$, -0.9833
363.6	0.0057	$a''(111) \rightarrow a'(112)$, -0.8976	364.2	0.0761	$b_2(103) \rightarrow a_1(107)$, -0.6444
363.3	0.0728	$a'(108) \rightarrow a'(112)$, 0.6361	361.2	0.0124	$b_2(102) \rightarrow a_1(107)$, -0.4908
360.4	0.0113	$a'(107) \rightarrow a'(112)$, 0.5134	342.0	0.0026	$a_1(105) \rightarrow b_2(109)$, -0.7845
338.2	0.0013	$a''(100) \rightarrow a'(112)$, -0.5523	331.0	0.0010	$b_2(97) \rightarrow a_1(107)$, -0.5186
336.8	0.0021	$a'(110) \rightarrow a''(114)$, -0.8079	329.4	0.0069	$a_1(105) \rightarrow b_2(108)$, 0.9241
Complex 8			Complex 11		
451.5	1.0832	$a_1(114) \rightarrow a_1(116)$, 0.9843	454.8	1.0926	$b_2(130) \rightarrow a_1(132)$, -0.9824
363.8	0.0816	$a_1(114) \rightarrow b_1(118)$, 0.7013	369.5	0.1003	$a_1(129) \rightarrow a_1(132)$, -0.6809
360.5	0.0099	$b_2(111) \rightarrow a_1(116)$, 0.5462	356.5	0.0312	$b_2(126) \rightarrow a_1(132)$, -0.6612
337.1	0.0028	$a_1(114) \rightarrow b_1(118)$, -0.4879	327.7	0.0010	$b_2(130) \rightarrow b_1(133)$, 0.9601
330.6	0.0015	$b_2(106) \rightarrow a_1(116)$, 0.5139	305.1	0.0935	$b_2(121) \rightarrow a_1(132)$, -0.5983
328.4	0.0043	$a_1(114) \rightarrow a_1(117)$, -0.9324	293.8	0.1420	$b_2(121) \rightarrow a_1(132)$, -0.5056

More than one long-waved absorption peaks were chosen where oscillation strength was bigger than 0.0010.

of complex 11 is almost the same as that of host 1, and there is only little difference of the first bands between host 1 and complexes 1–11 although slight blue-shift of the UV peaks for some complexes compared with that of host 1 takes place, consistent with experimental results by Liu *et al.* [6]. The first peak of complex 11 is red-shifted relative to those of other complexes owing to the less LUMO-HOMO energy gap.

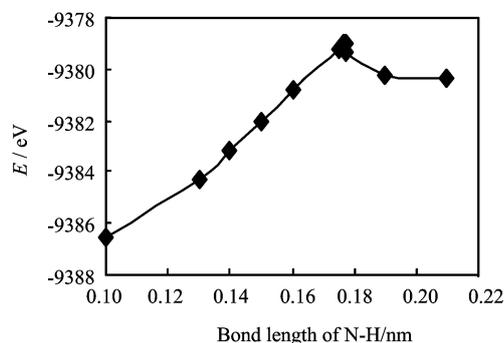


FIG. 3 Potential curve for H^+ transfer

D. Potential curve for the transfer of hydrogen ions

The potential curves for H^+ transfer were obtained by AM1 method (fig. 3). In order to find out the transition state, we restricted the N–H bond lengths on the guest at 0.1000, 0.1300, 0.1400 nm and so on, and optimized other parameters to get the minima of total energy for these complexes. With gradual departure of H^+ from

N to O, total energy of the complexes increased until the N–H bond length attains 0.1770 nm, which is the transition state where the O–H bond length is 0.1891 nm, then decreased to form the isomer of complex 11. In the process of proton transfer on N–H bond, forward and backward activated energies are 7.5200, 1.3364 eV, respectively.

- [1] R. P. Bonar-Law, A. P. Davis and B. A. Murray, *Angew. Chem. Int. Ed. Engl.* **29**, 1407 (1990).
- [2] M. Inouye, T. Miyake, M. Furusyo and H. Nakazumi, *J. Am. Chem. Soc.* **117**, 12416 (1995).
- [3] H. Jin, J. Feng, A. Ren, Z. Li, Z. Wang and X. Zhang, *Acta Chimica Sinica.* **2**, 194 (2000).
- [4] Q. Teng, S. Wu, S. Chen, Y. Zhang and X. Zheng, *Chem. J. Chin. Univ.* **23**, 1331 (2002).
- [5] S. Wu, Q. Teng, X. Chen and R. Zhou, *Chem. J. Chin. Univ.* **24**, 1271 (2003).
- [6] Y. Liu, S. Xiao, H. Li, Y. Li, H. Liu, F. Lu, J. Zhuang and D. Zhu, *J. Phys. Chem. B* **108**, 6256 (2004).
- [7] T. Moriuchi, T. Tamura and T. Hirao, *J. Am. Chem. Soc.* **124**, 9356 (2002).
- [8] J. A. Theobald, N. S. Oxtoby, M. A. Philips, N. R. Champness and P. H. Beton, *Nature* **424**, 1029 (2003).
- [9] Q. Teng, S. Wu and Z. Zhu, *Int. J. Quantum Chem.* **91**, 39 (2003).
- [10] Q. Teng and S. Wu, *J. Mol. Stru. (Theochem)* **719**, 47 (2005).
- [11] Y. Zhu, Q. Yin, L. Cao, Y. Yang, Y. Kan and Z. Su, *Chin. J. Chem. Phys.* **17**, 126 (2004).