

***Ab initio* studies on complexes formed by melamine and cyclotrione**

LIANGIANG ZHU, QIWEN TENG and SHI WU*

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China
(e-mail: wushi@zju.edu.cn)

(Received 8 March, revised 15 June 2006)

Abstract: *Ab initio* methods were used to study the binding energies of non-bonded complexes formed by melamine and cyclotrione, with the STO-3G, 3-21G and 6-31G (d) basis sets. The electronic spectra were computed using the INDO/CIS method, and the IR spectra, Raman and NMR spectra with the RHF/6-31G (d) method. It was demonstrated that the complexes could be formed because of the negative binding energies, which were changed with the change in the electronic properties of the monomers. A red-shift of the first absorptions in the electronic spectra and the vibrational frequencies of the N–H bonds in the IR and Raman spectra of the complexes, compared with those of the monomers, occurred; simultaneously, the ^1H and ^{13}C chemical shifts were altered, due to the non-bonded interaction.

Keywords: melamine, cyclotrione, non-bonded interaction, RHF/6-31G (d)

INTRODUCTION

Self-assembly is of great significance in the synthesis of polymers. As an important way of self-assembly, weak molecular interactions have attracted a great deal of the attention of scientists. The melamine system, due to its widespread application, has been and active topic in this field. Non-bonded interactions between the six reactive hydrogen atoms on melamine and the electron-drawing groups in another molecule can exist. Melamine has several isomers, but the isomer with C_s symmetry is the most stable one.¹ As the starting material, melamine can be used to synthesize polycyclic compounds such as melem.² As a proton donor, melamine can be coordinated with metals or other molecules to form miscellaneous non-bonded complexes.^{3–5} Especially, there are very many reports on the complexes formed by melamine and cyanuric acid due to the weak interaction between the hydrogen atoms and the nitrogen atoms in the two monomers.^{6,9} Also, the effect of non-bonded steric interaction between two large substituents on melamine on the arrangement of the complex formed with cyanuric acid was discussed.^{7,8} Still, just a few reports have focused on

* Corresponding author.

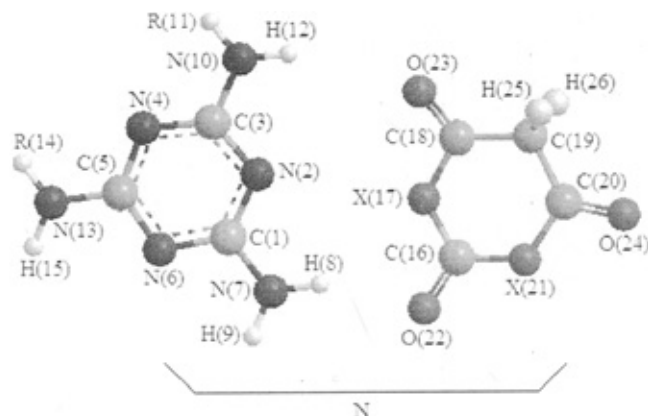


Fig. 1. The optimized geometries of complexes 1–4 at the RHF/6-31G (d) level.

Complex 1: X=O, R=H, N=1; Complex 2: X=CH₂, R=H, N=1; Complex 3: X=S, R=H, N=1;
Complex 4: X=O, R=H, N=2.

non-bonded complexes formed by melamine and other molecules. Cyclotriene is such a suitable monomer which can be associated with melamine to form non-bonded complexes. In this theoretical study the non-bonded dimers formed by melamine and cyclotriene with different substituents located on the molecular skeleton were investigated. First the geometries of the complexes were optimized using several basis sets of RHF and B3LYP. Then their spectra were computed. The effect of the substituents on the binding energies and spectra are also discussed in this paper.

CALCULATIONAL METHODS

The 1:1 complex formed by cyanuric acid and melamine is arranged in a linear form when the substituents on the melamine are small.^{7,8} Based on this, the linear non-bonded complex **1** composed of melamine and cyclotriene was built. Then complexes **2**, **3** and **4** were constituted by replacing the X atoms in the cyclotriene with other groups, and changing the degree of polymerization *N*, as shown in Fig. 1. In order to simplify the computation, the AM1 method and several basis sets of B3LYP and RHF in the GUASSIAN 03 program were used, step by step, to optimize the structures of the non-bonded dimers (complexes **1**, **2** and **3**) and tetramer (complex **4**) to achieve binding energies and relative enthalpies of formation. In view of the overestimation of the hydrogen bonding and an inadequate Hamiltonian for nitrogen atoms at distances that are common for intermolecular interaction using AM1 method,^{10–12} the AM1 optimized results are not shown here. The basis set superposition error (BSSE) rectification was performed using the RHF and B3LYP methods with different basis sets.

On the basis of the optimized geometries, the configuration interactions for the complexes were studied by the INDO/CIS method as in the ZINDO program using the original parameters. 197 single electronic transition states including the ground state, generated by exciting electrons from the 14 highest occupied molecular orbitals to the 14 lowest unoccupied molecular orbitals, were produced in this calculation. The IR, Raman and NMR spectra of the dimers were computed at the RHF/6-31G (d) level based on the RHF/6-31G (d) optimized geometries.

RESULTS AND DISCUSSION

Structures and stability of the complexes

The bond lengths of the C–N bonds in melamine, calculated by RHF/6-31G (d) and B3LYP/6-31G (d), were within the range 0.1327–0.1341 and 0.1343–0.1364 nm, which

are in good agreement with X-ray experimental results of 0.1333–0.1357 nm.¹ As can be seen in Table I, the ΔE values of the complexes **1–4** after revision of BSSE using the counterpoise method are very close to the uncorrected calculation. The values of BSSE were less than 0.0369, 0.0581 and 0.0560 eV at B3LYP/STO-3G, B3LYP/3-21G and B3LYP/6-31G (d) levels; whereas they were not greater than 0.0860, 0.0133 and 0.0054 eV at the RHF/STO-3G, RHF/3-21G and RHF/6-31G (d) levels, respectively. These errors are less than the value of 0.1037 eV, given in the literature.¹³ The distance between H(8) and O(22) at the RHF/6-31G (d) level was 0.2320 nm and that of H(12) and O(23) was 0.3160 nm in complex **1**. These values are consistent with the distance of H and O in other melamine complexes determined by Goodgame *et al.*³ using the XRD technique and computed by Zhou *et al.*¹⁴ Hence it can be concluded that the complex could be formed by the two monomers *via* non-bonded interaction.

TABLE I. Binding energies ΔE /eV of complexes **1–4**

	B3LYP/STO-3G		B3LYP/3-21G		B3LYP/6-31G (d)	
	Calculation	Revision	Calculation	Revision	Calculation	Revision
Complex 1	-0.5638	-0.5822	-0.7835	-0.7823	-0.4336	-0.4385
Complex 2	-0.8937	-1.0207	-0.9542	-1.0123	-0.4493	-0.5052
Complex 3	-0.4378	-0.4380	-0.4740	-0.4728	-0.2079	-0.2202
Complex 4	-1.7838	-1.8207	-2.4487	-2.4472	-1.3011	-1.3100
	RHF/STO-3G		RHF/3-21G		RHF/6-31G (d)	
	Calculation	Revision	Calculation	Revision	Calculation	Revision
Complex 1	-0.2695	-0.2924	-0.6177	-0.6177	-0.4118	-0.4064
Complex 2	-0.2795	-0.3655	-0.7461	-0.7594	-0.3687	-0.3640
Complex 3	-0.1749	-0.1749	-0.3197	-0.3197	-0.2873	-0.2819
Complex 4	–	–	–	–	–	–

The values of ΔE and $\Delta \Delta H_f$ (see Table II) of complex **4** were apparently larger than those of complex **1**, indicating that the non-bonded interaction became stronger with the extension of the system. Other factors affecting the non-bonded interaction include electronic properties and deformability of the atoms. The carbon atom on the methylene group in cyclotrione in complex **2** has an electron-donating effect, which retained the high electron density on the carbonyl groups at the neighboring sites. Thus, the non-bonded interaction between the oxygen atoms of the carbonyl groups on cyclotrione and the hydrogen atoms on melamine was strengthened. Therefore, the values of ΔE and $\Delta \Delta H_f$ for complex **2** were basically bigger than those of complexes **1** and **3**. The sulfur atom possessed the larger radius, greater deformability and lower electronegativity than the oxygen atom, leading to complex **3** being less stable than complex **1**.

The dipole moment of complex **1** optimized at the RHF/6-31G (d) level was 3.4610 while those of melamine and cyclotrione were 0.0003 and 3.2347, respectively. The charges on melamine and cyclotrione in complex **1** were -0.0083 and 0.0083, showing that the electrons were totally transferred from cyclotrione to melamine with the forma-

tion of the complex. The Mulliken charges for H(8) and H(12) were 0.4402 and 0.3956, respectively, while those of O(22) and O(23) were -0.5272 and -0.4886 respectively. It was indicated that strong electrostatic interactions within a certain distance exist between the hydrogen atoms on melamine and the oxygen atoms on cyclotriene.

TABLE II. Relative enthalpies of formation $\Delta \Delta H_f^0/\text{eV}$ complexes 1–4

	B3LYP/STO-3G	B3LYP/3-21G	B3LYP/6-31G (d)
Complex 1	-0.4879	-0.7105	-0.3699
Complex 2	-0.8143	-0.8798	-0.3907
Complex 3	-0.3641	-0.4011	-0.1450
Complex 4	-0.9564	-2.2226	–
	RHF/STO-3G	RHF/3-21G	RHF/6-31G (d)
Complex 1	-0.2051	-0.5371	-0.2562
Complex 2	-0.2028	-0.7332	-0.1955
Complex 3	-0.1062	-0.3030	-0.1647
Complex 4	–	–	–

Electronic absorption spectra

The strongest absorption peak of melamine computed by the INDO/CIS^{15–21}

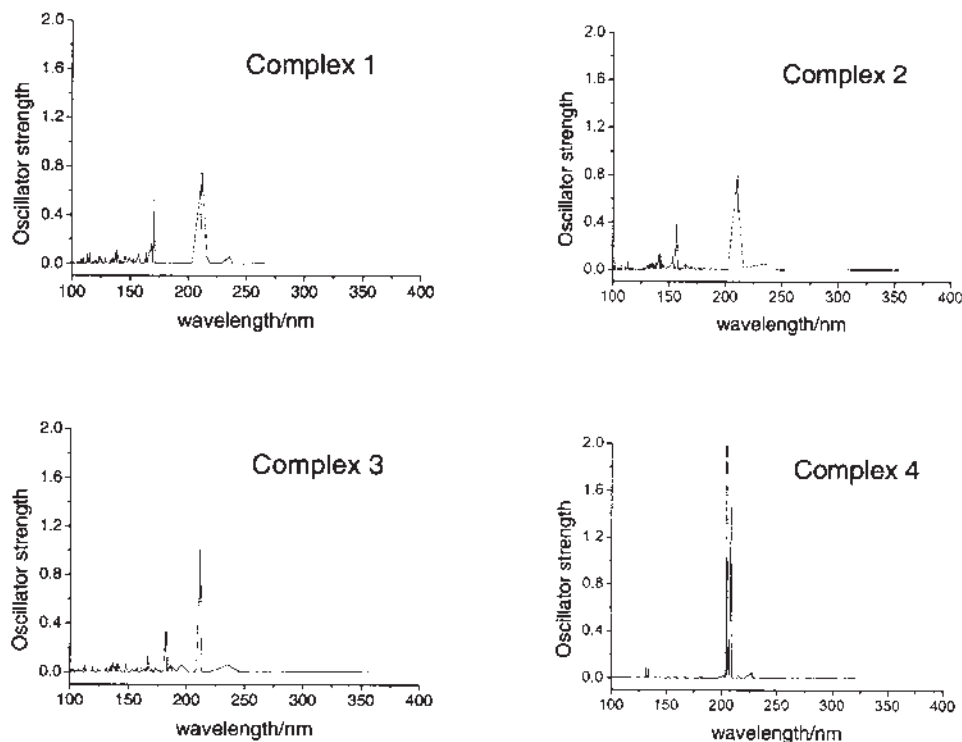


Fig. 2. The electronic spectra of complexes 1–4 calculated by the INDO/CIS method.

method was 216.4 nm, which is in agreement with the experimental data.⁵ The first absorption at 328.2 nm of complex **1** in Fig. 2 resulted from the electronic transition from (43) to (50). This transition is symmetry-allowed and the contribution coefficient of 0.6534 was the biggest of all the configurations. This absorption was red-shifted compared with those (264.3 and 178.3 nm) of the monomers A and B because LUMO–HOMO energy gap of complex **1** (13.04 eV) was less than those of the monomers A and B (14.77 and 15.74 eV), optimized by the RHF/6-31G (d) level. Meanwhile, the absorptions in the electronic spectrum of complex **4** were split in contrast to those of complex **1**, owing to the extension of the system *via* non-bonded interaction. The first absorptions of complexes **2** and **3** appearing at 382.0 and 374.8 nm, respectively, were red-shifted compared

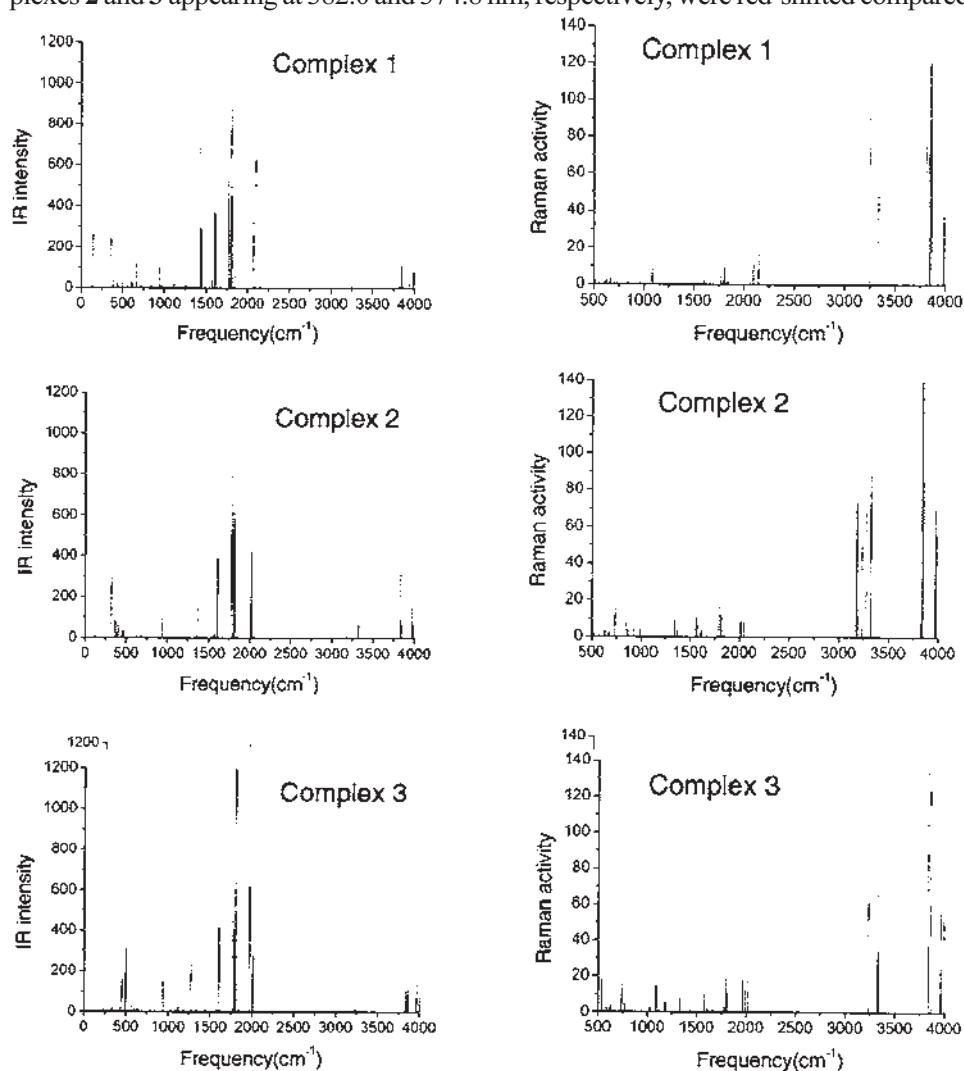


Fig. 3. The IR (left) and Raman (right) spectra of the complexes 1–3 at the RHF/6-31G (d) level.

to that of complex **1**, also resulting from their lower LUMO–HOMO energy gaps (12.25 and 12.11 eV, respectively) compared to that of complex **1**.

IR and Raman spectra

The IR and Raman spectra for melamine, computed with RHF/6-31G (d), were compatible with the experimental ones.²² The IR absorptions for complexes, **1**, **2** and **3** in Fig. 3 can be divided into three regions. The first region ranged from 2500 to 4000 cm^{-1} , mainly corresponding to the stretching vibrations of N–H bonds. The second region extended from 1000 to 2000 cm^{-1} , generally caused by stretching vibrations of C=C, C=N and C=O bonds. The last region below 1000 cm^{-1} was formed by a few

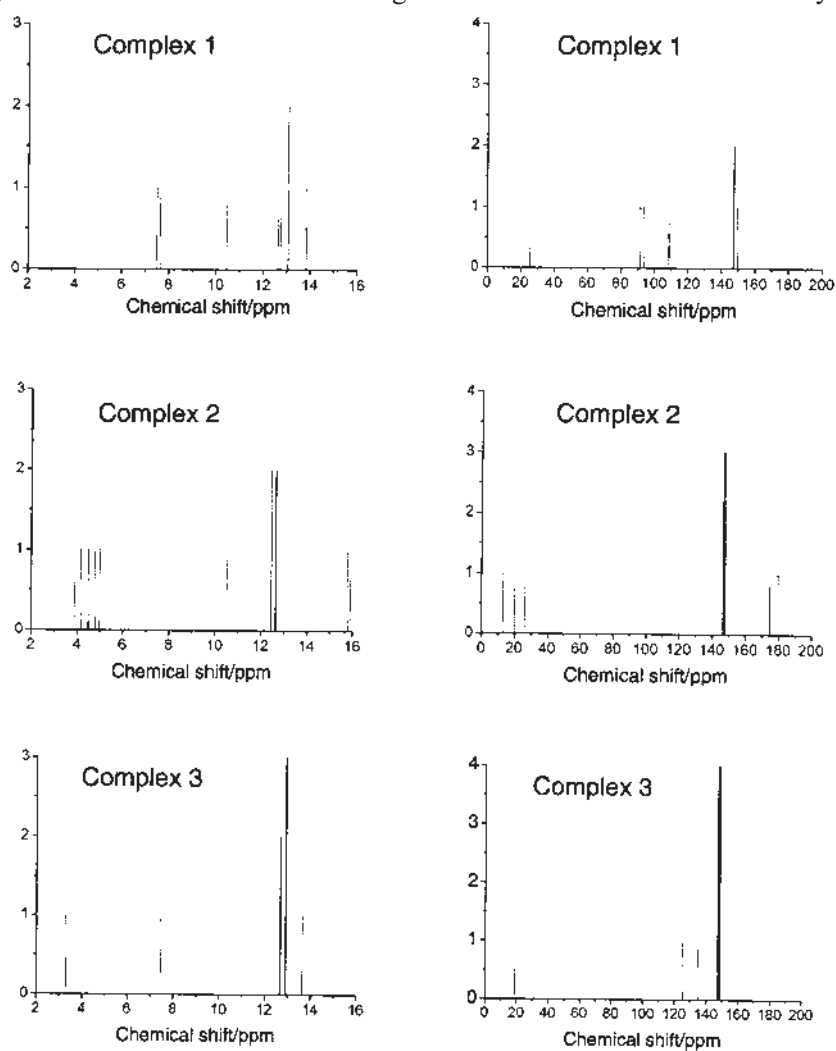


Fig. 4. The ^1H NMR (left) and ^{13}C NMR (right) spectra of complexes **1**–**3** at the RHF/6-31G (d) level.

flexural vibrations and ring-puckering vibrations. There were several characteristic peaks with high intensity in the area of 1500–2000 cm^{-1} , nearly stationary with the formation of the complexes. The stretching vibration of the N–H bond with the highest frequency in complexes **3**, **1** and **2** were located at 3996, 3993 and 3981 cm^{-1} , respectively, showing that the vibrational frequencies of the N–H bonds were gradually red-shifted and these vibrational bands were simultaneously broadened with the strengthening of the non-bonded interaction and the weakening of the N–H bonds. There was a similarity of the absorption peaks, ranging from 3500 to 4000 cm^{-1} , between the Raman spectra and IR spectra of complexes **3**, **1** and **2** in Fig. 3.

NMR Spectra

The NMR spectra of complexes **1**, **2** and **3**, computed by the GIAO method at the RHF/6-31G (d) level in the GAUSSIAN 03 program,²³ are illustrated in Fig. 4. It can be seen that the chemical shift δ of protons in the ^1H -NMR of the melamine was 10.3 ppm, agreeing with the experimental values between 5 and 10 ppm reported by Damodaran.²⁴ As the non-bonded interaction is affected by many factors, the δ values of the protons on the $-\text{NH}_2$ groups would change widely. Compared with those of melamine, the δ values of H(8) and H(12) in complex **1** were increased by 3.2 and 1.2 ppm, respectively. The reason is that the proton shield was decreased due to the strengthening of the non-bonded interaction. The δ value of the proton with the largest chemical shift in complex **2** was larger than that of the proton in complex **1**, while that of the proton in complex **3** was less.

The δ values of the ^{13}C atoms in complex **2** were diminished compared with those of complexes **1** and **3**. The δ values of C(16) and C(18) in complex **1** were both high field shifted by about 11 ppm. This is due to the influence of the non-bonded interaction on the electronic properties of O(22) and O(23). In this situation, the deshielding effect of the electrons on neighboring atoms was decreed and the resonance absorptions of these ^{13}C atoms were high field shifted.

CONCLUSION

The calculation results for the monomers using different theoretical methods were in good agreement with the experimental data. The binding energies were increased with extension of the system. The electronic properties of the atoms and substituents had a great influence on the stabilities of the complexes. The LUMO–HOMO energy gaps of the complexes were decreased and a red-shift of the absorptions in the electronic spectra of the complexes relative to those of the monomers resulted. The vibration frequencies of the N–H bonds and the chemical shifts of the protons were changed due to the non-bonded interaction.

ИЗВОД

Ab initio ПРОУЧАВАЊА КОМПЛЕКСА МЕЛАМИНА И ЦИКЛОТРИОНА

LIANGLIANG ZHU, QIWEN TENG и SHI WU

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

Ab initio методе су коришћене за проучавање енергија везивања у невезивним комплексима које грде меламин и циклотрион, са скуповима базних функција STO-3G, 3-21G и 6-31G (d). Електронски спектри су рачунати коришћењем INDO/CIS методе, а IR, рамански и NMR спектри RHF/6-31G (d) методом. Показано је да би комоплекси могли настати, услед негативних енергија везивања, које се мењају са променом електронских својстава мономера. Појавио се црвени помак првих апсорпција у IR и Раманским спектрима комплекса у односу на мономере; истовремено, променили су се и ^1H и ^{13}C хемијска померања услед невезивних интеракција.

(Примљено 8. марта, ревидирано 15. јуна 2006)

REFERENCES

1. Y. L. Wang, A. M. Mebel, C. J. Wu, Y. T. Chen, C. E. Lin, J. C. Jiang, *J. Chem. Soc. Faraday Trans.* **93** (1997) 3445
2. B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, *J. Am. Chem. Soc.* **125** (2003) 10288
3. D. M. L. Goodgame, I. Hussain, A. J. P. White, D. J. Williams, *J. Chem. Soc. Dalton Trans.* (1999) 2899
4. R. Venkatraman, P. C. Ray, C. S. Choi, *Int. J. Quantum Chem.* **100** (2004) 758
5. F. Würthner, S. Yao, *J. Org. Chem.* **68** (2003) 8943
6. M. Arduini, C. C. Mercedes, P. Timmerman, *J. Org. Chem.* **68** (2003) 1097
7. J. A. Zerkowski, C. T. Seto, D. A. Wierda, *J. Am. Chem. Soc.* **112** (1990) 9025
8. J. A. Zderkowski, C. T. Seto, G. M. Whitesides, *J. Am. Chem. Soc.* **114** (1992) 5473
9. M. G. J. ten Cate, D. N. Reinhoudt, M. Crego-Calama, *J. Org. Chem.* **70** (2005) 8443
10. L. Grierson, M. J. Perkins, H. S. Rzepa, *J. Chem. Soc. Chem. Commun.* (1987) 1779
11. H. Rzepa, *J. Chem. Res.* (1988) 224
12. I. Juranic, H. S. Rzepa, M-Y. Yi, *J. Chem. Soc. Perkin Trans.* (1990) 877
13. X. M. Zhou, Z. Y. Zhou, H. Fu, Y. Shi, H. Zhang, *J. Mol. Struct. (THEOCHEM)* **47** (2005) 714
14. Y. X. Zhou, X. Zhao, Z. T. Li, G. J. Chen, R. Z. Liu, *Acta. Chim. Sinica* **61** (2003) 963
15. J. Ridly, M. C. Zerner, *Theor. Chim. Acta. Berl.* **32** (1973) 111
16. J. D. Head, M. C. Zerner, *Chem. Phys. Lett.* **131** (1986) 359
17. Q. Teng, S. Wu, *Chem. J. Chinese Universities* **22** (2001) 1019
18. S. Wu, Q. Teng, *Chem. J. Chinese Universities* **23** (2002) 132
19. Q. Teng, S. Wu, *J. Mol. Struct. (THEOCHEM)* **47** (2005) 719
20. Q. Teng, S. Wu, *Int. J. Quantum Chem.* **104** (2005) 279
21. Q. Teng, S. Wu, *Int. J. Quantum Chem.* **104** (2005) 279
22. M. B. Sayed, *Ind. Eng. Chem. Res.* **43** (2004) 4822
23. M. J. Frish, et al., *Gaussian 03, Revision B.01*, Gaussian Inc., Pittsburgh, PA, 2003
24. K. Damodaran, G. J. Sanjayan, P. R. Rajamohanam, S. Ganapathy, K. N. Ganesh, *Org. Lett.* **3** (2001) 1921.