



ELECTRONIC STRUCTURES AND SPECTRA OF 1,3-DITHIOLANRADIALENE

Zhouyang LUO,^{a,c} Zhangqin Ni,^a Longyi ZHU^b and Qiwen TENG^{a,*}

^aDepartment of Chemistry, Zhejiang University, Hangzhou 310027, China

^bDepartment of Material Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China

^cCollege of Chemistry and Molecule Engineering, Beijing University, Beijing 100871, China

Received July 8, 2009

The electronic structures of the luminescent 1,3-dithiolanradialene derivatives were investigated using density function theory at B3LYP/6-31G(d) level. The energy gaps of the derivatives are reduced in the presence of the electron-attracting substituents on the 1,3-dithiol rings. The first absorptions in the electronic spectra of the derivatives, calculated with INDO/CIS method, are red-shifted compared with that in the electronic spectrum of the parent compound. The C-S and C-H stretching vibrations in the IR spectra of the derivatives with the electron-attracting substituents on 1,3-dithiol rings, calculated with AM1 method, are blue-shifted relative to those in the IR spectrum of the parent compound. The 1,3-dithiolan ring behaves as a better electron-donor at the triply excited state than ground state, which leads to the excellent cross-conjugation effect between the 1,3-dithiolan ring and macrocyclic skeleton.

INTRODUCTION

Macrocyclic molecules with complex structures possess luminescent and conductive properties, which stimulates an intensive interest of scientists.¹⁻¹⁰ A macrocyclic hexagon formed by the spontaneous polymerization of diethynylbenzene exhibits optoelectronic properties.¹ The aromatic rings and thiophene in heterocyclic annulenes act as fluorescent chromophores.² On one hand, the conjugation macrocycle based on the diphenylalkyne skeleton can bind metal ions, which leads to the formation of the soluble fluorescent complex.³ On the other hand, a newly synthesized macrocycle formed by dialkyne and thiafulvalene segments becomes a molecular wire in the solution since the charge is transferred through the π - π stacking between the dimers of the macrocycle.⁴ An ethynylene macrocycle has been utilized to fabricate the one-dimensional nano-structure.⁵ The extended polyenyne radialene substituted by the aromatic rings possesses the inner cavity, which can

incorporate a silver cation.⁶ The neutral cyano-substituted radialene with the strong electron-accepting ability becomes an excellent candidate for polyanions and efficient organic conductor.⁷ The near infrared absorptions of the extended radialenes with thioxanthene have been produced due to the narrow energy gaps.⁸ Zhao et al. have synthesized 1,3-dithiolanradialene. They found that the alkylthiolated radialene shows strong intramolecular push-pull interaction and macrocyclic cross-conjugation.⁹

There are few reports on the electronic structures and spectroscopic characters of the radialenes. Herein a series of radialene derivatives are designed. 1,3-dithiolanradialene is considered as compound **1**, which has been synthesized by Zhao et al., and compounds **2-10** are theoretical models designed by changing the substituents on compound **1** (Fig. 1). The effects of the substituents on the electronic structures and spectroscopy of the radialenes are explored.

* Corresponding author: wushi@zju.edu.cn

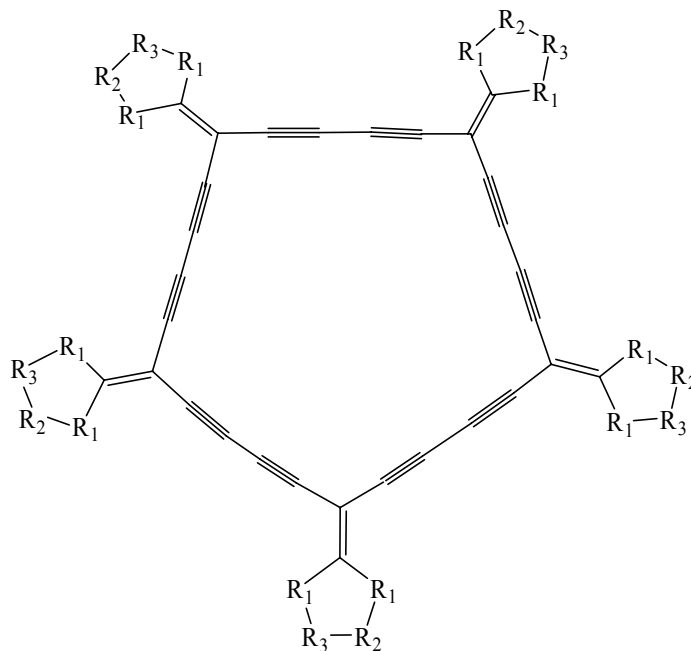


Fig. 1 – The structural schemes of compounds 1-10.

Compound 1: $R_1 = S, R_2 = R_3 = CH_2$; Compound 2: $R_1 = O, R_2 = R_3 = CH_2$;
 Compound 3: $R_1 = PH, R_2 = R_3 = CH_2$; Compound 4: $R_1 = S, R_2 = R_3 = CH$;
 Compound 5: $R_1 = N, R_2 = R_3 = CH$; Compound 6: $R_1 = S, R_2 = CH_2, R_3 = CHCH_3$;
 Compound 7: $R_1 = S, R_2 = R_3 = CHCH_3$; Compound 8: $R_1 = S, R_2 = R_3 = CHOH$;
 Compound 9: $R_1 = S, R_2 = CH, R_3 = CNO_2$; Compound 10: $R_1 = S, R_2 = R_3 = COH$.

RESULTS AND DISCUSSION

LUMO-HOMO energy gaps

The energy gaps of the compounds are affected by the heteroatoms and substituents. The energy gaps of compounds 2, 1 and 3 are decreased (Table 1). The conjugation effects between the heteroatoms and double bonds in compounds 2, 1 and 3 are increased with the increase in the electron-donating abilities of O, S and P. The energy gaps of compounds 4 and 10 are narrower than that of compound 1, since the

conjugation systems are extended in the presence of the C=C bonds on the 1,3-dithiol rings. The narrow energy gap of compound 5 with respect to that of compound 4 arises from the formation of the C=N bonds upon the substitution of the nitrogen atoms. The energy gap of compound 9 in comparison with that of compound 4 is decreased in the presence of NO_2 on the 1,3-dithiol rings. The energy gaps of compounds 6, 7 and 8 are wider than that of compound 1, which results from the presence of the electron-donating groups on the 1,3-dithiolan rings.

Table 1

The Energy Gaps of Compounds 1-10 at B3LYP/6-31G(d) Level

Compound	1	2	3	4	5
Energy gap (eV)	2.861	3.430	2.820	2.720	2.158
Compound	6	7	8	9	10
Energy gap (eV)	2.891	2.887	2.956	2.121	2.627

Electronic spectra

The calculation absorptions in the electronic spectrum of compound 1 are compared with the experimental results. The first peak in the electronic spectrum of compound 1 is calculated to

be at 323.9 nm (Fig. 2), and other main peaks are located at 256.0, 249.0 and 198.2 nm. The experimental UV absorptions of compound 1 are determined to be at 443, 403, 390 and 288 nm in the literature.⁹ These experimental values are also demonstrated in Fig. 2 for the comparison. From

Fig. 2, we can see that the calculated absorptions of compound **1** are basically consistent with the experimental results after multiplying by a factor of 1.37. There is a systematic deviation of the calculation using INDO method. In addition, the experiment is often done in the solvent.

The first absorption, of compound **3**, at 335.5 nm relative to that of compound **1** is predicted to be red-shifted, which is ascribed as the decrease in the energy gap. The main absorptions at 409.5 and 296.8 nm for compound **5** in contrast to 323.9 and 256.0 nm for compound **1** are also red-shifted,

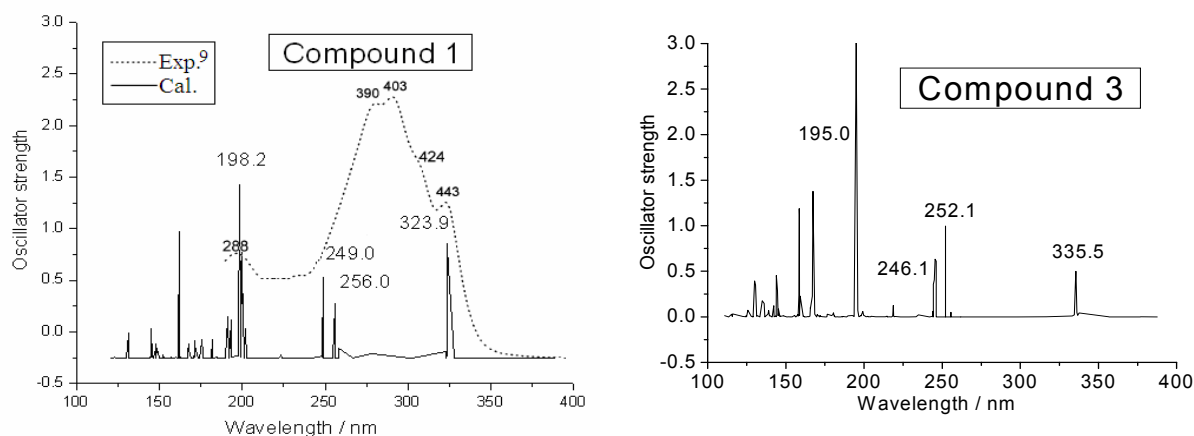


Fig. 2 – The electronic spectra of compounds 1 and 3 using INDO/CIS method.

IR spectra

The presence of substituents leads to the change in the intensification of bonds. The main absorptions in the IR spectrum of compound **1** are computed to be at 1254, 1569, 1753 and 2327 cm^{-1} (Fig. 3). These absorptions are assigned to the stretching vibrations of the C-S, C-C, C=C and C \equiv C bonds, respectively. The experimental IR frequencies of compound **1** are measured to be at 1280, 1492, 1631 and 2122 cm^{-1} ,⁹ which are also shown in Fig. 3. The computation IR absorptions of compound **1** are in agreement with the experimental results. Other main absorptions at 818 and 3270 cm^{-1} of compound **1** are ascribed to the bending and stretching vibrations of the C-H bonds.

The IR absorptions at 1259, 1253, 1252, 1253, 1261 and 1236 cm^{-1} of compounds **4**, **6**, **7**, **8**, **9** and **10** are attributed to the stretching vibrations of the C-S bonds. The C-S frequencies of compounds **6**, **7**, **8** and **10** compared with 1254 cm^{-1} of compound **1** are red-shifted. The electron density on the 1,3-dithiolan rings in compounds **6**, **7** and **8** or 1,3-dithiol rings in compound **10** is decreased with the increase of the electron density on the macrocyclic

which results from the extended conjugation system. The main peaks of compound **9** at 316.7, 274.1 and 200.0 nm compared with 232.0, 214.0 and 197.9 nm for compound **4** are red-shifted in the presence of the electron-attracting groups NO_2 . The absorptions of compound **8** compared with those of compound **1** split because of the decrease in the symmetry. The electronic spectrum for compound **8** is similar to that of compound **1**. The change of the substituents on 1,3-dithiolan rings has little effect on the electronic spectrum.

skeleton in the presence of electron-donating methyl or hydroxyl groups. On the contrary, the C-S frequencies of compounds **4** and **9** compared with that of compound **1** are blue-shifted in the presence of C=C and NO_2 on the 1,3-dithiol rings.

The acute and strong peaks at 1739, 1751, 1749, 1757, 1751 and 1741 cm^{-1} for compounds **4**, **6**, **7**, **8**, **9** and **10** are produced by the stretching vibrations of the C=C bonds between the skeleton and 1,3-dithiolan or 1,3-dithiol rings. The absorptions at 1780 and 1879 cm^{-1} of compounds **4** and **5** are caused by the stretching vibrations of the C=C and C=N bonds on 1,3-dithiol rings. The C-H stretching vibrations at 3308, 3327 and 3305 cm^{-1} of compounds **4**, **5** and **9** compared with that of compound **1** are blue-shifted owing to the presence of the carbon atoms with sp^2 hybridization on 1,3-dithiol rings.

The absorptions within the region of 1600-1800 cm^{-1} in the IR spectra of compounds **6**, **7** and **8** are similar to those of compound **1**. Thus, the stretching vibrations of the C=C bonds are little affected by the methyl and hydroxyl groups on 1,3-dithiolan rings.

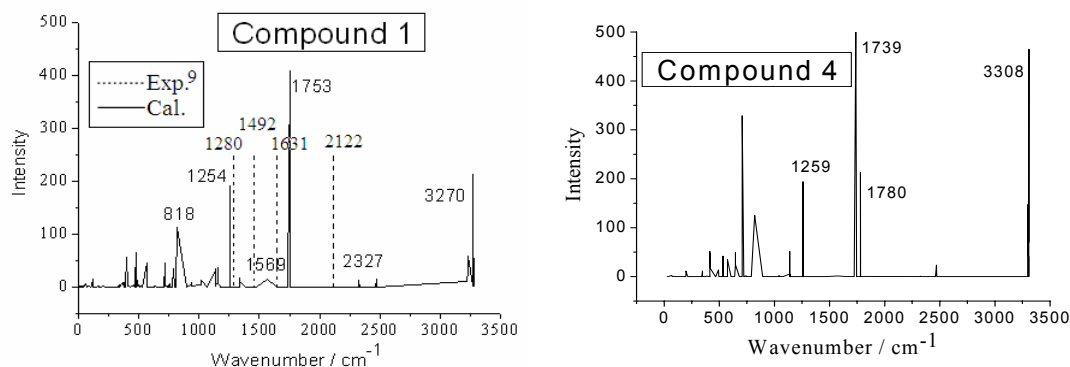


Fig. 3 – The IR spectra of compounds 1 and 4 with the AM1 method.

The geometries at the triply excited state

The fluorescence of radialenes is related to the formation of excited molecules. The triplet excited states for compounds **1-5** have been calculated at B3LYP/6-31G(d) level. At the ground state, the lengths of the C≡C and C-C bonds on the macrocyclic skeleton in compound **1** with D_{5h} symmetry are 0.1220 and 0.1419 nm. The lengths of the above two kinds of bonds are determined via the X-ray diffraction to vary within the ranges of 0.1203-0.1212 and 0.1397-0.1449 nm, since the molecular symmetry is decreased upon the inclusion of a DMSO molecule inside the cavity of compound **1**.⁹ Our calculated bond lengths are basically compatible with the experimental results. At the excited state, the lengths of the C≡C and C-C bonds on the macrocyclic skeleton in compound **1** are within the ranges of 0.1220-0.1236 and 0.1382-0.1419 nm. The lengths of the C≡C bonds on the macrocyclic skeleton at the excited state compared with those at the ground state are increased, whereas those of the C-C bonds are decreased. Therefore, the bond lengths on the macrocyclic skeleton in the excited state are averaged and the conjugation effect is improved.

In the ground state, the lengths of the S-C (sp^2 -C) and S-C (sp^3 -C) bonds on the 1,3-dithiolan rings of compound **1** are 0.1806 and 0.1914 nm. The experimental lengths of the S-C (sp^2 -C) and S-C (sp^3 -C) bonds are within the ranges of 0.1723-0.1738 and 0.1737-0.1896 nm.⁹ The lengths of the C-C bonds on the 1,3-dithiolan rings of compound **1** are 0.1543 nm. At the excited state, the lengths of S-C (sp^2 -C), S-C (sp^3 -C) and C-C bonds on the 1,3-dithiolan rings of compound **1** are located within the range of 0.1801-0.1807, 0.1913-0.1916 and 0.1544-0.1545 nm, respectively. The lengths of the S-C (sp^3 -C) and C-C bonds on the 1,3-

dithiolan rings at the excited state compared with those at the ground state are generally increased, whereas those of the S-C (sp^2 -C) bonds are decreased. Thus, the electron density is transferred from sp^3 -C to sp^2 -C on the 1,3-dithiolan rings, which leads to the increase in the electron density on the macrocyclic skeleton. In this way, the cross-conjugation effect is created in the excited state.

In the ground state, the length of one side for the pentagon formed by the macrocyclic skeleton in compound **1** is 0.6617 nm. The corresponding experimental length is within the range of 0.6551-0.6638 nm.⁹ In the excited state, the lengths of the sides for this pentagon are within 0.6571-0.6617 nm. Thus this pentagon is compressed at the excited state owing to the cross-conjugation effect. Furthermore, the mulliken charges of the 1,3-dithiolan ring at the ground state and excited state are 0.0529 and 0.0597, respectively. Thus the electron-donating ability of the 1,3-dithiolan ring is elevated at the excited state, which is favorable to the cross-conjugation effect between the 1,3-dithiolan rings and macrocyclic skeleton.

The C≡C and C-C bond lengths in compound **2** are 0.1219 and 0.1417 nm at the ground state, whereas those are within the ranges of 0.1219-0.1232 and 0.1380-0.1418 nm at the excited state. Therefore, the bond lengths on the skeleton in compound **2** tend to be average and the conjugation effect is intensified at the excited state. The mulliken charges of the 1,3-dithiol rings in compound **4** in the ground state and excited states are 0.0594 and 0.0659, consequently, the electron-donating effect of the 1,3-dithiol rings is enhanced at the excited state. Similarly, the mulliken charges of the 1,3-diazoheterocyclic rings in compound **5** in the ground state and excited states are 0.0060 and 0.0270, and the electron-donating ability of the 1,3-diazoheterocyclic rings is also elevated at the

excited state. Thereby, the cross-conjugation effect at the excited state compared with that at the ground state is improved.

THEORETICAL

Full geometric optimization without any symmetric restriction of compounds **1-10** was performed with the semiempirical AM1 method and B3LYP method in DFT using 3-21G basis set in GAUSSIAN 03 program.¹⁰ These methods have been used to elucidate the electronic structures of the supramolecular complexes,¹¹⁻¹⁴ conductive polymers,¹⁵ fluorescent materials,^{16,17} fullerene derivatives,¹⁸ and other compounds.¹⁹ The equilibrium geometries with the minimum energies of compounds **1-10** were obtained. Then the energies of these compounds were computed at the single point on B3LYP/6-31G(d) level.

On the basis of the optimized geometries of compounds **1-10** at B3LYP/3-21G level, the configuration interaction was investigated using INDO/CIS method.²⁰ This method was used to elucidate the electronic spectra of the organic compounds.²¹⁻²⁹ One hundred and ninety-seven configurations including the ground state were generated by exciting electrons from 14 HOMOs into 14 LUMOs. The IR spectra of compounds **1-10** were computed using AM1 method.

CONCLUSION

As stated above, the energy gaps of 1,3-dithiolanradialene derivatives are decreased in the presence of the electron-donating heteroatoms and electron-attracting substituents. The first absorption peaks in the electronic spectra of these derivatives compared with that of the parent compound are red-shifted. The C-S stretching vibrations of the derivatives in the presence of the electron-attracting substituents on the 1,3-dithiolan rings relative to those of the parent compound are blue-shifted. The cross-conjugation effect between the 1,3-dithiolan ring and macrocyclic skeleton in the excited state with respect to that in the ground state is improved due to the growing electron-donating ability of 1,3-dithiolan rings. This cross-conjugation effect is not only beneficial to the fluorescence, but also binding affinity to electron-deficient guest molecules.

REFERENCES

1. A. Nomoto, M. Sonoda, Y. Yamaguchi, T. Ichikawa, K. Hirose and Y. Tobe, *J. Org. Chem.*, **2006**, *71*, 401–404.
2. P. N. W. Baxter and R. Dali-Youcef, *J. Org. Chem.*, **2005**, *70*, 4951–4953.
3. C. Ma, A. Lo, A. Abdolmaleki and M. J. MacLachlan, *Org. Lett.*, **2004**, *6*, 3841–3844.
4. H. Enozawa, M. Hasegawa, D. Takamatsu, K. Fukui and M. Iyoda, *Org. Lett.*, **2006**, *8*, 1917–1920.
5. K. Balakrishnan, A. Datar, W. Zhang, X. Yang, T. Naddo, J. Huang, J. Zuo, M. Yen, J. S. Moore and L. Zang, *J. Amer. Chem. Soc.*, **2006**, *128*, 6576–6577.
6. M. Iyoda, Y. Kuwatani, S. Yamagata, N. Nakamura, M. Todaka and G. Yamamoto, *Org. Lett.*, **2004**, *6*, 4667–4670.
7. I. Despotović and Z. B. Maksić, *J. Mol. Struct. (Theochem)*, **2007**, *811*, 313–322.
8. Y. Kuwatani, G. Yamamoto and M. Iyoda, *Org. Lett.*, **2003**, *5*, 3371–3374.
9. Y. Zhao, Q. Liu, J. Zhang and Z. Liu, *J. Org. Chem.*, **2005**, *70*, 6913–6917.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 03, Revision B 01, Gaussian Inc, Pittsburgh, PA*, **2003**.
11. (a) Q. Teng, S. Wu, S. Chen, Y. Zhang and X. Zheng, *Chem. J. Chin. Univ.*, **2002**, *23*, 1331–1334; (b) S. Wu, Q. Teng, X. Chen and R. Zhou, *Chem. J. Chin. Univ.*, **2003**, *24*, 1271–1273; (c) L. Qi, Q. Teng, S. Wu and Z. Liu, *Chem. J. Chin. Univ.*, **2005**, *26*, 1909–1912; (d) C. Yan and S. Wu, *Acta Chim. Slov.*, **2007**, *54*, 755–760; (e) X. Ren, Y. Miao, N. Li and S. Wu, *Indian J. Chem. Sec. A*, **2009**, *48*, 623–630.
12. O. L. Radu, S. Armand, F. Lenouvel, H. Driguez and A. Cimpean, *Rev. Roum. Chim.*, **2006**, *51*, 147–153.
13. C. Hamciuc, E. Hamciuc and T. Vlad-Bubulac, *Rev. Roum. Chim.*, **2006**, *51*, 53–60.
14. (a) D. Visinescu, J. P. Sutter, H. W. Roesky, J. Magull and M. Andruh, *Rev. Roum. Chim.*, **2005**, *50*, 737–745; (b) L. Zhu, Q. Teng and S. Wu, *Chem. J. Chin. Univ.*, **2006**, *27*, 680–683; (c) X. Chen, Q. Teng, S. Wu and L. Xu, *Indian J. Chem. Sec. A*, **2007**, *46*, 391–395.
15. Z. Zhu, S. Wu and Y. Zhang, *Russ. J. Phys. Chem. A*, **2008**, *82*, 2293–2298.
16. L. Ding, Y. Ding, Q. Teng and K. Wang, *J. Chin. Chem. Soc.*, **2007**, *54*, 853–860.
17. (a) A. Ozdemir, H. Aksoy, E. Dinc, D. Băleanu and S. Dermis, *Rev. Roum. Chim.*, **2006**, *51*, 117–123; (b) L. Xu, Q. Teng and Y. Ding, *Rev. Roum. Chim.*, **2010**, in press.
18. (a) Q. Teng and S. Wu, *Chem. J. Chin. Univ.*, **2001**, *22*, 1019–1021; (b) S. Wu and Q. Teng, *Chem. J. Chin. Univ.*, **2002**, *23*, 132–134; (c) Q. Teng, S. Wu and Z. Zhu, *Int. J. Quantum Chem.*, **2003**, *91*, 39–45; (d) Q. Teng and S. Wu, *Chem. J. Chin. Univ.*, **2004**, *25*, 2345–2348; (e) Q.

- Teng and S. Wu, *J. Mol. Struct. (Theochem)*, **2005**, *719*, 47–51; (f) Q. Teng and S. Wu, *J. Mol. Struct. (Theochem)*, **2005**, *756*, 103–107; (g) S. Wu, Q. Teng and S. Chen, *Chin. J. Chem.*, **2007**, *25*, 149–153.
19. (a) A. C. Radutiu, I. Baci, M. T. Căproiu, C. Drăghici, A. Nicolae, T. Constantinescu and A. T. Balaban, *Rev. Roum. Chim.*, **2006**, *51*, 653–661; (b) R. D. Bărătioiu, A. E. Barbu, L. Mutihac, M. T. Căproiu, C. Drăghici, R. Socoteanu and T. Constantinescu, *Rev. Roum. Chim.*, **2006**, *51*, 261–267; (c) G. Zbancioc, M. Căproiu, C. Moldoveanu and I. I. Mangalagiu, *Rev. Roum. Chim.*, **2005**, *50*, 353–358; (d) M. Bem, M. T. Caproiu, M. Vasilescu, M. Tudose, R. Socoteanu, A. Nicolae, T. Constantinescu and M. D. Banciu, *Rev. Roum. Chim.*, **2003**, *48*, 709–715; (e) M. Mracec, L. Juchel and M. Mracec, *Rev. Roum. Chim.*, **2006**, *51*, 287–292.
20. M. A. Thompson and M. C. Zerner, *J. Amer. Chem. Soc.*, **1991**, *113*, 8210–8212.
21. N. Su, Q. Guo and S. Wu, *Indian J. Chem. Sec. A*, **2008**, *47*, 1473–1479.
22. S. Wu and Q. Teng, *Int. J. Quantum Chem.*, **2006**, *106*, 526–532.
23. Q. Teng and S. Wu, *Int. J. Quantum Chem.*, **2005**, *104*, 279–285.
24. X. Wen, X. Ren and S. Wu, *Acta Chim. Slov.*, **2008**, *55*, 419–424.
25. W. Zhang, S. Wu and X. Wen, *Indian J. Chem. Sec. A*, **2007**, *46*, 1911–1916.
26. Z. Wang and S. Wu, *Chem. Pap.*, **2007**, *61*, 313–320.
27. C. Yan, N. Su and S. Wu, *Russ. J. Phys. Chem. A*, **2007**, *81*, 1980–1985.
28. Y. Ding, P. Gao, L. Qin and Q. Teng, *Int. J. Quantum Chem.*, **2009**, *109*, 693–700.
29. H. Sun, S. Wu and X. Ren, *J. Mol. Struct. (Theochem)*, **2008**, *855*, 6–12.