Ab Initio and Experimental Studies on Dibenzothiazyl-Disulfide

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Ab initio calculations of the structure, atomic charges and natural bond orbital (NBO) have been performed at HF/6-311G** and B3LYP/6-311G** levels for the title compound of dibenzothiazyl-disulfide. The calculated results show that the two nitrogen atoms have the biggest negative charges and they are the potential sites to react with the metallic ions, which make the title compound become a di-dentate ligand. Vibrational frequencies of the title compound have been obtained and compared with the experimental value and the comparison indicates that B3LYP/6-311G** level is better than HF/6-311G** level to predict the vibrational frequencies for the system studied here. For the title compound, electronic absorption spectra calculated by time–dependent density functional theory (TD-DFT) are more accurate than Hartree-Fock single-excitation CI (CI-Singles) method. NBO analyses show that the electronic transitions are mainly derived from the contribution of bands $\pi \to \pi^*$. Thermodynamic calculated results show that the formation of the title compound from 2-mercaptobenzothiazole is a spontaneous process at room temperature with the change of free Gibbs being negative value.

Key Words : *Ab initio* calculation, Vibrational frequency, Electronic spectroscopy, Thermodynamic calculation

Introduction

The study of heterocyclic molecules with aromatic rings and their absorption on metals is of considerable important from both a theoretical and a technological point of view. These molecules are interesting because of their applications as corrosion inhibitors and flotation collectors and for their ability to form self-assembly layers.[1] 2-mercaptobenzothia-zole ($C_7H_5NS_2$) is an important heterocyclic molecule, which can be used as corrosion inhibitors[2] and can be vaporized in a vacuum onto a metal surface to form absorbed layers.[1] It also can be used as organic ligand to coordinate to metal ions.[3] Using 2-mercaptobenzothiazole and its derivatives as ligands, we have obtained several new metal complexes. However, during our experiments, we found that the 2-mercaptobenzothiazole is very easy to turn to be the title compound of dibenzothiazyl-disulfide at room temperature in air, which attracted our attentions and promoted us to make a further study. As we know, aromatic disulfides are useful synthetic intermediates. They play essential roles in a variety of chemical transformation[4] and exhibit some biologic activities[5] and industrial application values.[6] However, for the title compound of dibenzothiazyl-disulfide, apart from its crystal structure being reported by Zingarao *et al.* in 1980,[7] there are no theoretical studies available till now. Therefore, using classical *ab initio* methods based on self-consistent field molecular orbital Hartree-Fock theory and density functional theory (DFT) with the 6-311G** basis set, we investigate the optimized structure, atomic charges distribution, electronic transition and natural population analysis on dibenzothiazyl-disulfide and made comparisons between the calculated results and the experiments. In addition, we calculated the change of free Gibbs (ΔG) in the process of 2-mercaptobenzothiazole to dibenzothiazyl-disulfide at room temperature in air, which indicate that the process can take place spontaneously. Herein, we report the calculational and experimental results for the title compound of dibenzothiazyl-disulfide.

Experimental and Computational Methods

Physical Measurements. The IR spectra were recorded in the 4000-400 cm^{-1} region using KBr pellets on a Nicolet 170SX spectrophotometer. Electronic absorption spectra were measured on a Shimadzu UV3100 spectrophotometer in EtOH.

Computational Methods. Initial molecular geometry was optimized using MM+ molecular modeling and semi-empirical AM1 methods[8] (HYPERCHEM 6.0, Hypercube, Ont., Canada). In the next step, the DFT calculations with a hybrid Functional B3LYP at 6-311G** basis set and the Hatree-Fock calculations at 6-311G** basis set by the Berny method[9,10] were performed with the Gaussian 03 software package.[11] Vibrational frequencies calculated ascertain the structure was stable (no imaginary frequencies). Natural Bond Orbital (NBO) analyses,[12-14] the time–dependent density functional theory (TD-DFT)[15,16] and single-excitation CI (CI-Singles)[17] calculations of electronic absorption spectra were performed on the optimized structure. According to the statistic thermodynamic and based on the optimized structure, thermodynamic functions of the title compound were also obtained.

All calculations were performed on Pentium IV computer and DELL PC 2850 server using the default convergence criteria.
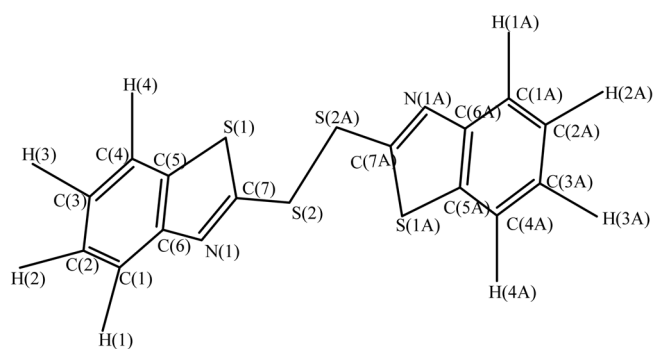
Figure 1. Molecular structure with the atomic numbering scheme.

Results and Discussion

Optimized Geometry. Figure 1 shows the molecular structure of the title compound with atomic numbering scheme. The selected optimized geometric parameters are listed in Table 1 along with the experimental data.

Although the crystal structure of dibenzothiazyl-disulfide has been reported by Zingarao *et al.* in 1980,[7] the available information about it, such as FTIR spectra and bond lengths and bond angles of the crystal structure, is not complete. So, in the following discussion, we use our own crystal data of the title compound, where the bond lengths and bond angles are almost the same as those reported earlier. (see supporting information)

Seen from Table 1, most of the calculated geometric

Table 1. Selected geometric parameter by X-ray single crystal diffraction and calculations at B3LYP/6-311G** and HF/6-311G** levels for the title compound

Bond lengths (Å)	Exp.	B3LYP/ 6-311G**	HF/ 6-311G**
S(1)-C(5)	1.743(4)	1.7581	1.7478
S(1)-C(7)	1.749(4)	1.7765	1.7546
S(2)-C(7)	1.768(4)	1.7849	1.7754
S(2)-S(2A)	2.027(2)	2.084	2.054
N(1)-C(7)	1.276(5)	1.2832	1.2603
N(1)-C(6)	1.381(5)	1.3862	1.3871
C(1)-C(2)	1.371(6)	1.3871	1.3762
C(2)-C(3)	1.382(6)	1.4029	1.3977
C(5)-C(6)	1.400(6)	1.4125	1.3893
Bond angles (°)			
C(5)-S(1)-C(7)	87.48(19)	87.406	87.687
C(7)-S(2)-S(2A)	102.26(15)	103.719	104.283
C(7)-N(1)-C(6)	109.5(3)	110.995	111.059
C(2)-C(1)-C(6)	118.7(4)	118.872	118.635
C(2)-C(3)-C(4)	121.1(4)	121.050	120.913
C(4)-C(5)-C(6)	122.0(4)	121.498	121.550
C(6)-C(5)-S(1)	109.3(3)	109.753	109.398
N(1)-C(6)-C(5)	115.6(4)	114.906	114.885
N(1)-C(7)-S(1)	118.0(3)	116.939	116.969
N(1)-C(7)-S(2)	118.8(3)	118.274	117.867
S(1)-C(7)-S(2)	123.1(2)	124.765	125.136

parameters are larger than those of experiments, due to that the theoretical values belong to isolated molecules in the gas-phase and the experimental results belong to the molecules in solid state. In view of the bond length, HF/6-311G** level can better reproduce the crystal structure than B3LYP/6-311G** level of theory. With regard to the differences of the bond angle between the calculated values and the experimental ones, B3LYP/6-311G** level is superior to HF/6-311G** level of theory. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as atomic charge, the vibrational frequencies, NBO analysis, electronic absorption spectra, as we described below. Based on B3LYP/6-311G** and HF/6-311G** optimized geometry, the total energy of the title compound has been calculated by MP2 method, which are −2236.7382525 and −2236.7326631 a.u., respectively.

Atomic Charges. Table 2 gives the Mulliken atomic charges of dibenzothiazyl-disulfide calculated at B3LYP/6-311G** and HF/6-311G** levels, respectively. In view of the symmetry of the molecule, only half of the atoms have been listed in the Table 2. The atom N(1) has the biggest negative charges, which makes it the most likely site of protonation as well as the potential coordination site with metallic ions. On the other hand, although the C(2), C(5) and C(7) atoms also have bigger negative charges, the sterically hindered effect prevents them from continuing to react with other atoms. Namely, the title compound can be used as a didentate ligand to react with metallic ions. The another feature of the atomic charges distribution is that the two benzothiazyl-groups have net negative charges, while two sulfur atoms of S(2) and S(2A) have net positive charges. The dipole moment of the title compound obtained by B3LYP/6-311G** and HF/6-311G** are 2.6280 and 3.0275 Debye, respectively.

Vibrational Frequencies. Some calculated harmonic frequencies and infrared intensities are shown in Table 3 and compared with the experimental data. Predicted vibrational

Table 2. Mulliken atomic charges (*e*) of the title compound

Atom	B3LYP/6-311G**	HF/6-311G**
S(2)	0.126735	0.107496
S(1)	0.310577	0.312121
N(1)	−0.299732	−0.416477
C(7)	−0.135682	−0.063245
C(1)	−0.030928	−0.046625
C(2)	−0.104269	−0.103737
C(3)	−0.083034	−0.079030
C(4)	−0.071943	−0.100566
C(5)	−0.263134	−0.254021
C(6)	0.142972	0.215261
H(1)	0.105485	0.112567
H(2)	0.100733	0.105352
H(3)	0.101342	0.105948
H(4)	0.100877	0.104956

Table 3. Selected vibrational frequencies[a]

Experimental	B3LYP/6-311G**	HF/6-311G**	Description
3077-3040	3072-3044	2992-2961	C-H str. in phenyl ring
1594	1569-1535	1590-1558	phenyl ring skeleton str.
1496	1468	1522	N(1)-C(7) and N(1A)-S(2A) str.
1426	1428-1404	1431-1422	ip phenyl ring C-H def.
1283	1288		phenyl ring skeleton str.
1245	1249	1249	ip phenyl ring C-H def.
1153-1072	1137-1097	1189	ip phenyl ring C-H def.
1034	1040	1050	N(1)-C(6) and N(1A)-C(6A) str.
937	954	999	C(7)-S(2) and C(7A)-S(2A) str.
751	744	759	oop phenyl ring C-H def.
501	480	510	S(2)-S(2A) str.

[a]Frequencies in cm^{-1}. Atomic numbering as shown in Figure 1. str.: stretch; ip: in-plane; oop: out-of-plane; def.: deformation

frequencies were scaled by 0.96 for B3LYP method and 0.89 for HF method, respectively, which are typical scale factors for these two methods. The descriptions concerning the assignment have also been indicated in this Table 3. Gauss-view program[18] was used to assign the calculated harmonic frequencies. Seen from Table 3, using B3LYP/6-311G** level, most of the predicted vibrational frequencies are well corresponding to the experimental values except the S(2)-S(2A) stretch vibration frequency. While using HF/6-311G** method, the phenyl ring skeleton stretch vibration at 1283 cm^{-1} can not be predicted and the predicted values for C-H stretch vibrations in phenyl ring (2992-2961 cm^{-1}) are much smaller than those of experimental values (3077-3040 cm^{-1}). In addition, above 1100 cm^{-1}, all of the HF calculational values are larger than those of experimental values. On the whole, for the title compound, B3LYP/6-311G** level is better than HF/6-311G** level to predict the vibrational frequencies.

Electronic Absorption Spectra. The electronic absorption spectra of the title compound in a solution of EtOH exhibit three intense bands near 217, 264 and 325 nm, respectively. For the title compound, based on the B3LYP/6-311G** level optimized structure, thirty singlet excited states have been calculated by time–dependent density functional theory (TD-DFT) method. Based on HF/6-311G** level optimized geometry, fifteen singlet excited states have also been calculated by Hartree-Fock single-excitation CI (CI-Singles) method. The calculated results are listed in Table 4. Seen from Table 4, for HF-CIS calculations, neither the numbers of the band nor the wave lengths are corresponding to the experimental results, which indicate that the HF-CIS method is not suitable to be used here to predict the electronic absorption spectra. For TD-DFT calculations, three broad electronic transition bands are at 213.49-215.68 nm, 222.54-227.11 nm and 261.76-268.21 nm, respectively. In other words, TD-DFT method predicts the numbers of the bands rightly, but the predicted wave lengths are different from the experimental values. The reason may be that the TD-DFT calculations do not evaluate the spin-orbit splitting and only singlet-singlet transitions are considered in the quasi-relativistic calculations. In addition,

Table 4. Electronic spectra values calculated by TD-DFT method and HF-CIS method

TD-DFT (B3LYP/6-311G**)		HF-CIS (HF/6-311G**)	
wave length (nm)	oscillator strength	wave length (nm)	oscillator strength
268.21	0.0616	221.21	0.0285
266.47	0.2726	214.79	0.3750
261.76	0.2865	212.37	0.0792
227.11	0.0520		
223.40	0.0210		
222.54	0.0239		
215.68	0.5190		
214.88	0.0396		
213.49	0.1228		

the role of the solvent effect of EtOH solution is not included in the theoretical calculations. Natural population analyses indicate that, for the B3LYP/6-311G** calculations, the frontier molecular orbitals are mainly composed of *p* atomic orbitals, so electronic transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) are mainly derived from the contribution of bands $\pi \rightarrow \pi^*$. [detailed calculational results, see Supporting Information]. Figure 2 shows the surfaces the HOMO and LUMO. Seen from Figure 2, in the HOMO, electron cloud is delocalized on all the atoms except two sulfur atoms of two thiazole rings, while in the LUMO, electron cloud is delocalized on all of the atoms except two phenyl rings. Namely, the *p* electrons transfer from carbon atoms in phenyl rings into sulfur atoms in thiazole rings and
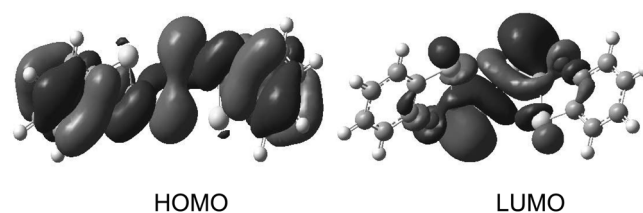

HOMO   LUMO

Figure 2. HOMO and LUMO of the title compound.

Table 5. The thermodynamic properties of the title compound at different temperatures at B3LYP/6-311G** level

T (K)	$C^0_{p,m}$ (J·mol^{-1}·K^{-1})	S^0_m (J·mol^{-1}·K^{-1})	H^0_m (kJ·mol^{-1})
200.0	203.06	495.10	23.89
298.1	286.28	591.94	47.97
300.0	287.76	593.71	48.50
400.0	360.09	686.76	81.02
500.0	417.11	773.51	120.00
600.0	461.00	853.61	164.00
700.0	495.08	927.34	211.88
800.0	522.03	995.27	262.78

sulfur atoms in the middle of the molecule, which are corresponding to the electron transitions of $\pi \rightarrow \pi^*$.
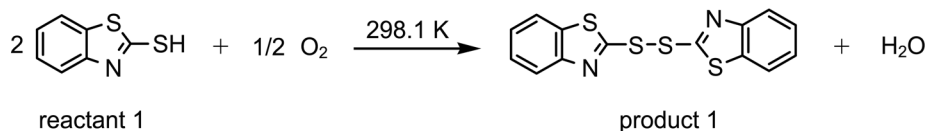
Thermodynamic Properties. Based on the vibrational analysis at B3LYP/6-311G** level and statistical thermodynamics, the standard thermodynamic functions-heat capaciy ($C^0_{p,m}$), entropy (S^0_m) and enthalpy (H^0_m)- were obtained and listed in Table 5. The scale factor for frequencies is also 0.96.

As observed from Table 4, the standard heat capacities, entropies and enthalpies increase at any temperature from 200.00 K to 800.00 K, due to that the intensities of molecular vibration increase while the temperature increases. The correlation equations between these thermodynamic properties and temperature T are as follows:

$$C^0_{p,m} = 3.0477 + 1.1282\,T - 6.0265 \times 10^{-4}\,T^2,$$
$$S^0_m = 343.6754 + 0.8340\,T,\ H^0_m = -71.2801 + 0.4029\,T$$

In addition, in order to explain why 2-mercaptobenzothiazole ($C_7H_5NS_2$) can easily turn to become the title compound at room temperature in air, we calculated the change of Gibbs free energy for the reaction shown in Scheme 1. The calculated results are listed in Table 6. The thermodynamic functions of oxygen (O_2), water (H_2O) and 2-mercaptobenzothiazole ($C_7H_5NS_2$) at 298.1 K were obtained based on their respective optimized geometries

calculated at B3LYP/6-311G** level.

In the course of 2-mercaptobenzothiazole to the title compound, both the changes of entropy and enthalpy are negative values ($\Delta S_T < 0$, $\Delta H_T < 0$), indicating that the reaction is an exothermic process accompanied by the decrease of confusion degree. From equation $\Delta G_T = \Delta H_T - T\Delta S_T$, the change of Gibbs free energies (ΔG_T) in the process is also negative, implying the spontaneous process of formation the title compound. At 298.1 K, on the calculation model of ideal-gas, the calculated equilibrium constant, based on the equation $\Delta G_T = -RT\ln K_p$, is 7.823×10^{31}. It reveals that the title compound is the main component at room temperature. That is to say, at room temperature in air, 2-mercaptobenzothiazole is very easy to turn to be the title compound.

Conclusion

Ab initio calculations for the title compound of dibenzothiazyl-disulfide have been performed at HF/6-311G** and B3LYP/6-311G** levels, respectively. By comparing the theoretical results with the experimental values, it can be concluded that, for the title compound, B3LYP/6-311G** level is better than HF/6-311G** level to predict the vibrtaional frequencies and electronic absorption spectra. Atomic charge distributions analyses show that the title compound can use its two nitrogen atoms to react with metallic ions. The change of Gibbs free energy is negative, indicating the process of formation the title compound from 2-mercaptobenzothiazole at room temperature in air is spontaneous.

Scheme 1

Table 6. Thermodynamic properties, total energy (E) and zero-point energy (ZPE) of the reactants and the products in Scheme 1 at 298.1 K[a]

	E (kJ/mol)	ZPE (kJ/mol)	S^0_m (J·mol^{-1}·K^{-1})	H^0_m (kJ·mol^{-1})	ΔS_T (J·mol^{-1}·K^{-1})	ΔH_T (kJ·mol^{-1})	ΔG_T (kJ·mol^{-1})
reactant 1	−2943231.5998	265.5162	381.05	24.83			
O_2	−394619.4960	9.7276	308.00	9.93			
H_2O	−200712.7747	55.9383	194.39	9.93			
product 1	−5883294.6444	490.4629	591.94	47.97	−129.77	−220.69	−182.01

[a]$\Delta S_T = (S^0_m)_{product\ 1} + (S^0_m)_{H_2O} - 2*(S^0_m)_{react\ 1} - 1/2*(S^0_m)_{O_2}$; $\Delta H_T = (H^0_m + E + ZPE)_{product\ 1} + (H^0_m + E + ZPE)_{H_2O} - 2*(H^0_m + E + ZPE)_{reactant\ 1} - 1/2 * (H^0_m + E + ZPE)_{O_2}$; $\Delta G_T = \Delta H_T - T\Delta S_T$ and the scale factor for all frequencies is 0.96.

References

1. Contini, G.; Carravetta, V.; Di Castro, V.; Stranges, S.; Richter, R.; Alagia, M. *J. Phys. Chem. A* **2001**, *105*, 7308.
2. Ohsawa, M.; Suetaka, W. *Corrosion Science* **1979**, *19*, 709.
3. Zhang, L. X.; Xie, M. H.; Ma, H. L. *Hechenghuaxue.* **2001**, *9*, 156.
4. Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609.
5. Parry, R. J. *Tetrahedron* **1983**, *39*, 1215.
6. Karchmer, J. H. *The Analytical Chemistry of Sulfur and Its Compounds*; Wiley: New York, 1972; p 103.
7. Zingaro, R. A.; Meyers, E. A. *Cryst. Struct. Commun.* **1980**, *9*, 1167.
8. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
9. Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 163.
10. Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **1996**, *17*, 49.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.
12. Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem)* **1988**, *169*, 41.
13. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
14. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.
15. Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.
16. Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.
17. Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.
18. Frish, A.; Nielsen, A. B.; Holder, A. J. *Gaussview Users Manual*; Gaussian Inc: Pittsburg, 2000.