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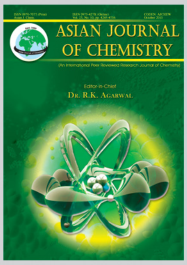

DFT Study on the 1:2 Hydrogen-Bonded Complexes of Dimethyl Sulfoxide with Water

GUO-DONG LIU[1,2] and TAO LIU[1,*]

[1]Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, Shandong Province, P.R. China
[2]School of Chemistry and Chemical Engineering, Shandong University, Jinan 250010, Shandong Province, P.R. China

*Corresponding author: E-mail: liutao3569@gmail.com; chem-tiger@126.com

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We study the hydrogen-bonded complexes formed between dimethyl sulfoxide molecule and water molecules (1:2 ratio) using density functional theory at varied basis set levels from 6-31g to 6-311++g (2d,2p). Four reasonable geometries are considered. The optimized geometric parameters and interaction energies for various isomers at different levels are estimated. The infrared spectrum frequencies, IR intensities and the vibrational frequency shifts of monomers and 1:1 DMSO-H_2O complexes at B3LYP/6-311++g(d,p) level are also reported.

Key Words: Density functional theory, Hydrogen bond, Dimethyl sulfoxide.

INTRODUCTION

Aqueous solution of dimethyl sulfoxide (DMSO) is used in a wide variety of biological and medical applications[1]. Because DMSO can dissolve both polar molecules and electrolytes, it is used as a transporter for salts, organics and polymers. The antiinflammatory properties of DMSO have led to its uses in the treatment of arthritis.

Recently, the behaviour of aqueous DMSO has attracted the interest of many researchers because of the large ideal mixing found in several physicochemical properties[2,3]. The prevailing view is the most of these effects are associated with DMSO's strong hydrophilic nature, which leads to formation of well-defined DMSO-H_2O aggregates, with the concomitant formation of a hydrogen bond network and pronounced structural microheterogeneities[4,5].

We have discussed the structures and hydrogen bond interaction energies of the 1:1 DMSO-H_2O complex between DMSO and H_2O as obtained by high level *ab initio* calculations[6]. In this paper, we will study the infrared spectrum frequencies, IR intensities and the vibrational frequency shifts of monomers and 1:1 complexes further. In the second part, as compared with 1:1 DMSO-H_2O complex, we will discuss the structures and hydrogen bond interaction energies of the 1:2 DMSO-H_2O complex.

EXPERIMENTAL

For hydrogen bond, it is expected that both diffuse and polarization functions may be necessary in the basis sets, we thus analyze the separate influence of the diffuse and polarization of the DMSO-H_2O has been carried out using B3LYP correlation methods with the 6-31g, 6-31g (d), 6-31+g (d), 6-311++g (d,p) and 6-311++g (2d,2p) basis set along with analytic vibrational frequency calculations.

After obtaining these optimized structures, the calculated binding energies obtained with all the above theoretical procedures are then corrected for the basis set superposition error (BSSE) and zero-point vibrational energy (ZPE). This is done using the counterpoise method. All calculations are performed using the Gaussian03 program[7].

RESULTS AND DISCUSSION

Vibrational spectroscopy is one of the most useful experimental tools for study of the H-bonded clusters, so the information on calculated harmonic vibrational frequencies can be useful. In Table-1, we give the values for both vibrational frequencies and IR intensities of the monomers and the corresponding values of the two 1:1 DMSO-H_2O complexes (DW1 and DW2 as shown in Fig.1) at B3LYP/6-311++g(d,p) level (we did not give the six vibrational models in the two complexes unrelated with the values in the monomers). Since the frequency shifts are relatively stable with respect to theoretical methods, one can estimate the IR spectrum for the complex by combining the observed fundamental vibrational frequency of its moieties and the frequency shift in Table-1.

Just as vibrational model $\nu 12$, the S=O stretching frequencies is red shift 28 cm^{-1} for DW1, since there is a hydrogen bond

TABLE-1
FREQUENCIES AND IR INTENSITIES OF MONOMERS AND COMPLEXES AT B3LYP/6-311++g(d,p) LEVEL (VIBRATIONAL FREQUENCIES (ν) IN cm^{-1}, IR INTENSITIES (I) IN km/mol) IN GAS PHASE AND IN SOLUTIONS

	DMSO			DW1			DW2		
	V (I)			V (I)			V (I)		
	Gas	ε = 46.7	ε = 78.39	Gas	ε = 46.7	ε = 78.39	Gas	ε = 46.7	ε = 78.39
ν1	177(0)	172(0)	169(0)	200(0)	189(1)	188(1)	199(51)	233(1)	233(1)
ν2	222(0)	217(0)	216(0)	244(1)	242(0)	215(7)	242(2)	275(8)	275(8)
ν3	278(0)	277(1)	277(1)	284(9)	284(8)	284(8)	283(1)	300(3)	300(3)
ν4	305(9)	305(9)	306(9)	309(6)	308(6)	308(6)	306(11)	313(64)	313(64)
ν5	356(9)	355(9)	355(9)	383(33)	382(34)	382(34)	366(9)	366(8)	366(8)
ν6	623(9)	626(9)	629(8)	632(5)	635(5)	635(5)	630(9)	638(8)	638(8)
ν7	653(19)	655(18)	660(18)	662(3)	665(5)	665(5)	661(17)	671(16)	671(16)
ν8	895(1)	895(1)	896(1)	918(5)	917(5)	917(5)	904(1)	909(1)	909(1)
ν9	930(6)	927(6)	927(6)	954(4)	951(5)	951(5)	948(7)	957(7)	957(7)
ν10	953(24)	950(29)	943(41)	954(62)	945(73)	945(73)	966(34)	1026(62)	1026(62)
ν11	1024(15)	1025(14)	1026(9)	1049(15)	1047(13)	1047(13)	1032(9)	1042(37)	1042(36)
ν12	1052(137)	1043(131)	1029(121)	1024(113)	1024(104)	1024(104)	1055(146)	941(86)	941(86)
ν13	1319(2)	1319(2)	1320(2)	1331(2)	1332(2)	1332(2)	1319(3)	1328(2)	1328(2)
ν14	1341(9)	1341(8)	1342(8)	1355(8)	1356(8)	1356(8)	1342(8)	1353(6)	1353(6)
ν15	1440(11)	1440(11)	1441(11)	1444(8)	1444(9)	1444(9)	1448(8)	1456(0)	1456(0)
ν16	1454(5)	1454(5)	1454(0)	1459(6)	1458(6)	1458(6)	1460(2)	1460(11)	1460(11)
ν17	1455(0)	1455(0)	1454(5)	1464(1)	1461(1)	1461(1)	1463(4)	1473(8)	1473(8)
ν18	1471(25)	1470(25)	1469(26)	1480(21)	1477(22)	1477(22)	1477(21)	1476(16)	1476(16)
ν19	3038(5)	3039(5)	3040(5)	3039(5)	3040(4)	3040(4)	3041(8)	3035(10)	3035(10)
ν20	3040(9)	3041(9)	3043(9)	3041(13)	3043(11)	3043(11)	3042(7)	3036(6)	3036(6)
ν21	3135(0)	3136(6)	3137(0)	3149(1)	3150(1)	3150(1)	3150(1)	3146(3)	3146(3)
ν22	3139(10)	3140(11)	3141(11)	3150(1)	3151(1)	3151(1)	3153(0)	3147(3)	3147(3)
ν23	3147(1)	3147(1)	3150(1)	3139(1)	3140(0)	3140(0)	3141(1)	3133(0)	3133(0)
ν24	3148(3)	3148(3)	3150(4)	3143(4)	3143(4)	3143(4)	3142(8)	3137(10)	3137(10)
	H_2O			DW1			DW2		
ν25	1603(67)	1615(64)	1615(64)	1636(98)	1646(87)	1646(87)	1617(102)	1637(70)	1637(70)
ν26	3818(9)	3808(9)	3808(9)	3497(485)	3467(583)	3466(584)	3809(12)	3796(18)	3796(18)
ν27	3923(57)	3907(54)	3907(54)	3892(60)	3898(60)	3898(60)	3912(69)	3888(72)	3888(72)

between the O of DMSO and H of water in DW1. The C-H stretching frequency also shows a slight change in its value on hydrogen bonding, in structure DW1 and DW2. For ν23, there is a weak interaction between the O of water and H of CH_3 group, the shift is 8 and 6 cm^{-1}, this is in consistent with the bond distance change discussed above. For the modes of water in the complex, the stretching frequency associated with the hydrogen bond undergoes a shift to a lower frequency compared to the free monomer. This occurs also because formation of the hydrogen bond weakens the O-H bond. For instance, the H_2O symmetrical stretching (ν26) of DW1 is founded to be red-shifted as much as 321 cm^{-1}, which corresponds to the stronger interaction.

With respect to IR intensities, they are all IR-active and most of them have large intensities, these predicted IR spectral characteristics might be of much interest in the analysis of the experimental spectral features. It is considered to be more difficult to predict accurate changes in absorption intensities, which is unfortunate. For this system, there is an extremely large increase in the intensity of the stretching vibration of the hydrogen donor. From the results presented in Table-1, it can be seen that the O-H stretching intensities of the water involved in the hydrogen bonds are enhanced largely in DW1, the O-H stretching mode intensities of the water varied from 9 to 485 km/mol, *ca.* 54 times larger than that of the mode in the monomer. For the other bending modes, most of them are slightly enhanced. In a word, owing to the formation of hydrogen bond, the force constants involved in the hydrogen bonding is reduced and the related stretching frequencies are red-shifted. Moreover, the increase of the change of the vibrational dipole moments leads to the enhancement of the IR intensities.

At all the DFT (B3LYP) levels employed here, four structures for the 1:2 DMSO-H_2O complexes in the gas phase were optimized. The structures optimized at B3LYP/6-311++g(d,p) level of all the complexes are shown in Fig. 2 and the most interesting geometrical parameters are listed in Table-2. All of these structures have no imaginary frequencies and this indicates that they are true local minima.

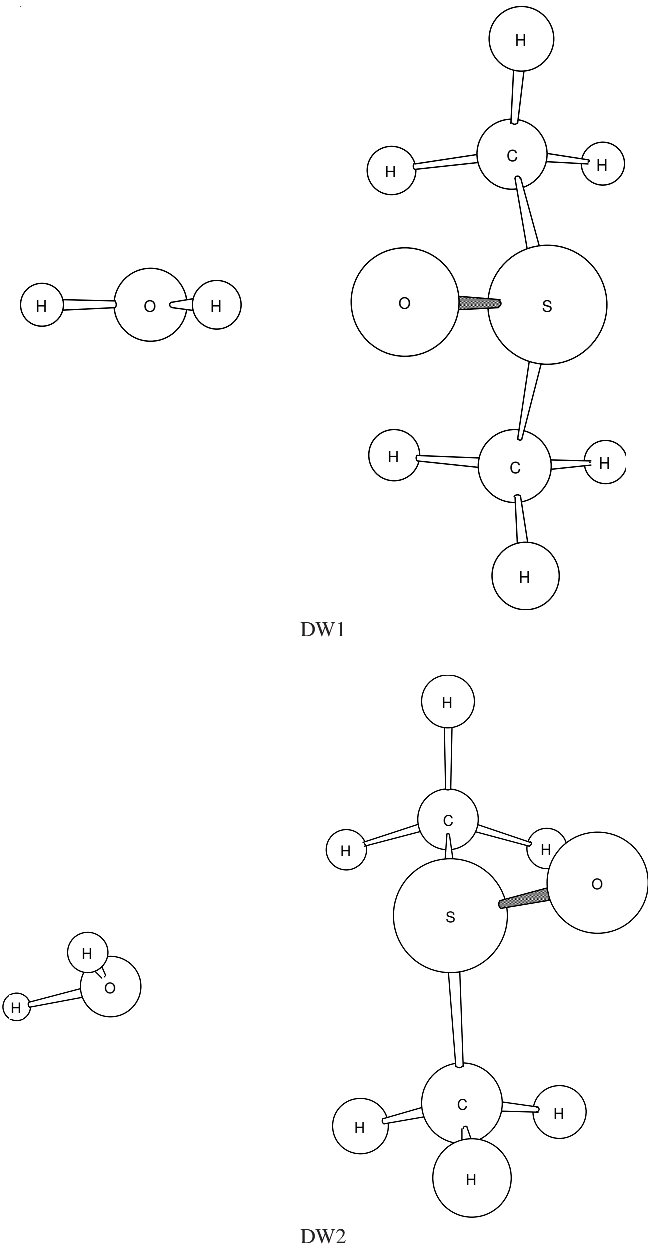
As shown in Fig. 2, for the structure of DW21-1, the two water molecules form hydrogen bonds to the sulfoxide oxygen, respectively and one water molecule to form hydrogen bond with another water molecule. ROW-HD (the hydrogen bond distance between the oxygen of water and hydrogen of DMSO) are 1.851 and 1.990 Å, respectively and the ROW1-HW2 (the hydrogen bond distance between the oxygen of water molecule and hydrogen of another water molecule) is 2.420 Å at the B3LYP/6-311++g(d,p) level.

For DW21-2, two water molecules form hydrogen bonds with DMSO, respectively. The hydrogen bond distances

TABLE-2
OPTIMIZED GEOMETRIC PARAMETERS OF 1:2 HYDROGEN-BONDED COMPLEXES OF DIMETHYL SULFOXIDE WITH WATER AT THE B3LYP/6-311++g(d,p) LEVEL (DISTANCES IN Å, ANGLES IN DEGREE)[a]

	$R_{OD\text{-}HW}$	$R_{OW\text{-}HD}$	$R_{OW1\text{-}HW2}$	α	$\beta 1$	$\beta 2$
DW21-1	1.851; 1.990	–	2.420	161.2; 152.1	–	122.9
DW21-2	1.853; 1.866	–	–	154.3; 158.8	–	–
DW21-3	1.724	2.252	1.790	171.9	158.0	162.4
DW21-4	1.830	2.558; 2.880	–	164.1	135.2; 118.5	–

*OD-HW means O of DMSO hydrogen-bonded to H of water, OW-HD means O of water hydrogen-bonded to H of DMSO, $R_{OW1\text{-}HW2}$ means O of one water molecule hydrogen-bonded to H of another water molecule. α is O_DHO, $\beta 1$ is CHO_W, and $\beta 2$ is $O_WH_WO_W$.



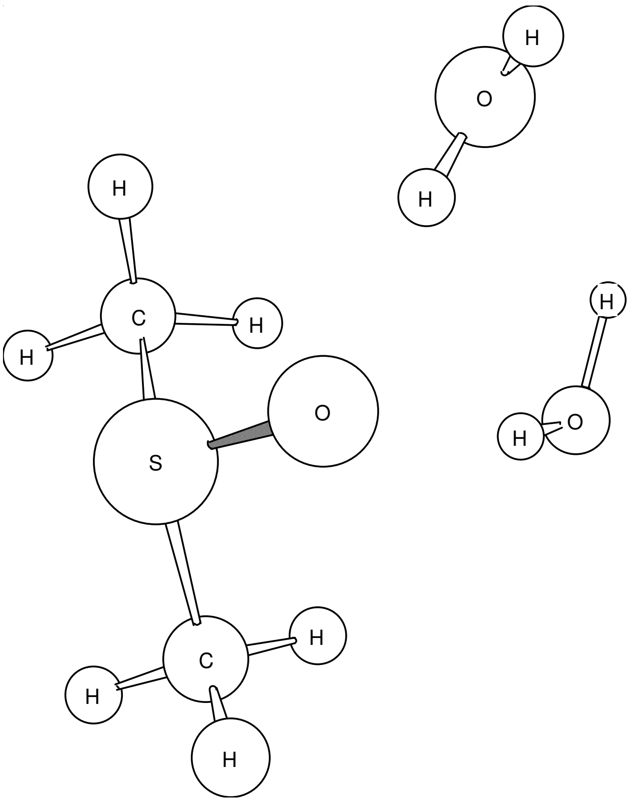
DW1

DW2

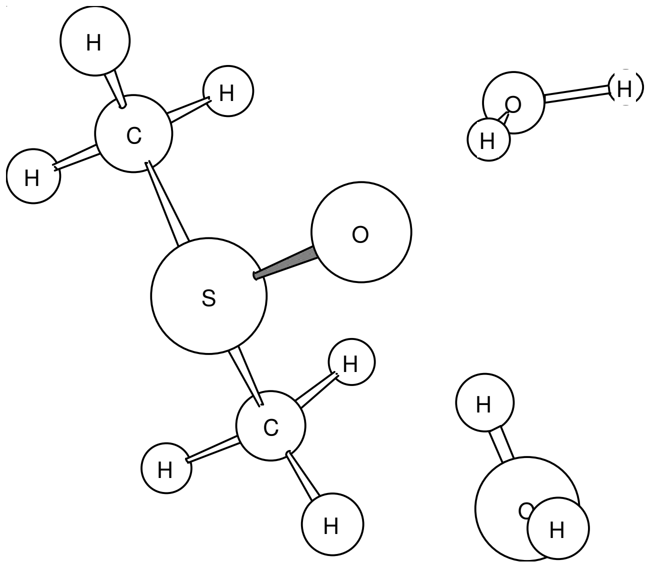
Fig. 1. Optimized 1:1 DMSO-water complexes in gas phase at the B3LYP/6-311++g(d,p) level

$R_{OW\text{-}HD}$ are 1.853 and 1.886 Å and the corresponding hydrogen bond angles $\angle O_DHO$ are 154.3° and 158.8°, respectively, at the B3LYP/6-311++g(d,p) level.

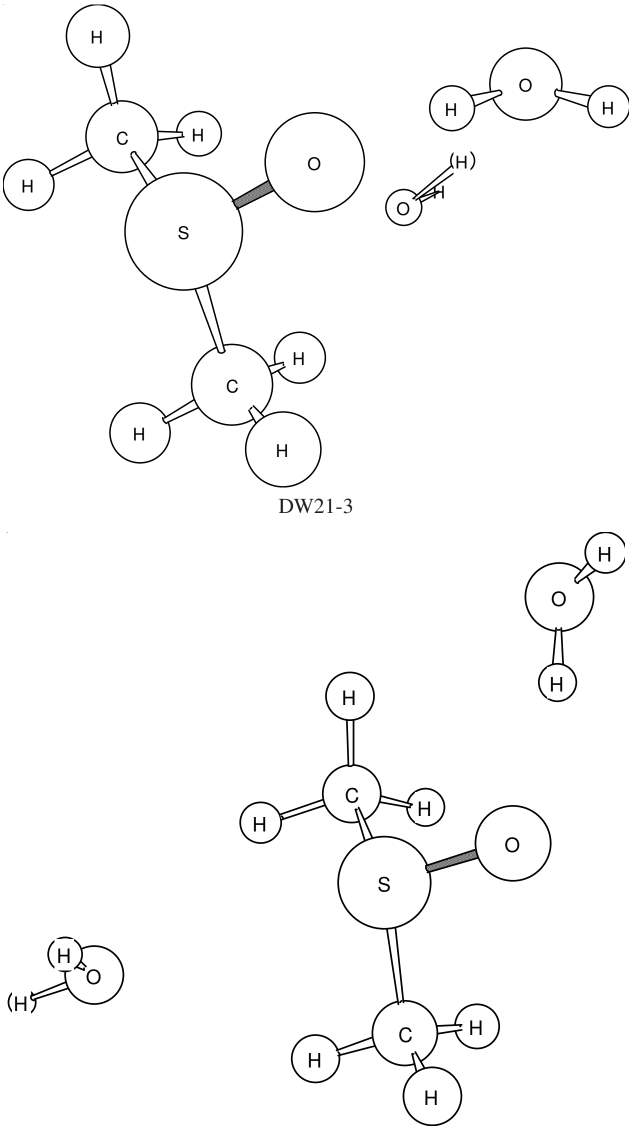
In the cyclic structure of DW21-3, water forms a hydrogen bond to the sulfoxide oxygen and receives a hydrogen bond from a methyl hydrogen of each of the two methyl and one



DW21-1



DW21-2



DW21-3

DW21-4

Fig. 2. Optimized 1:2 DMSO-water complexes in gas phase at the B3LYP/6-311++g(d,p) level

water molecule to form hydrogen bond with another water molecule, resulting in three relatively strong hydrogen bonds. The three hydrogen bonds R_{OW-HD}, R_{OD-HW} and $R_{OW1-HW2}$ are 1.724, 2.252 and 1.790 Å, respectively. For the three hydrogen bonds, interaction energy of this structure will be larger than those of DW21-1 and DW21-2, which is in accordance with the data (Table-3).

One water molecule forms a hydrogen bond to the sulfoxide oxygen and another water molecule receives a hydrogen bond from a methyl hydrogen of each of the two methyl in the structure of DW21-4. The three hydrogen bonds of 1.830, 2.558 and 2.880 Å are longer than the corresponding values in DW21-3, which shows that the interaction energy of DW21-4 is smaller than that of DW21-3.

Interaction energies are calculated for 1:2 DMSO-water complexes by taking the energy difference between the fragments and the complex.

$$E_{int} = E_{(DMSO)} + E_{(H_2O)} + E_{(H_2O)} - E_{(DMSO...H_2O...H_2O)} \quad (1)$$

where $E_{(DMSO)}$, $E_{(H_2O)}$ and $E_{(DMSO...H_2O...H_2O)}$ are the electronic energies of DMSO, H_2O and complex system, respectively. To correct the basis set superposition error (BSSE), the counterpoise (CP) method is employed. In this case, the corrected E_{int} is given by Valiron and Mayer[8], which is

$$\begin{aligned} E_{int(cp)} = {} & E_{ABC} - E_{AB}(ABC) + E_{AB}(AB) - E_{AC}(ABC) + E_{AC}(AC) \\ & - E_{BC}(ABC) + E_{BC}(BC) - E_A(AB) - E_A(AC) + E_A(ABC) \\ & - E_B(AB) - E_B(BC) + E_B(ABC) - E_C(AC) - E_C(BC) \\ & + E_C(ABC) \end{aligned} \quad (2)$$

where A, B, C stands for DMSO, H_2O and H_2O, respectively.

The inclusion of zero-point energy (ZPE) correction is also given by

$$\begin{aligned} E_{int(ZPVE)} = {} & E_{(DMSO)ZPE} + E_{(H_2O)ZPE} + E_{(H_2O)ZPE} \\ & - E_{(DMSO...H_2O...H_2O)ZPE} \end{aligned} \quad (3)$$

The interaction energies of complex between DMSO and 2 H_2O molecules are given in Table-3. The numbers shown in the first parentheses are corrected for BSSE using the counterpoise method of Boys and Bernadi. Values in the second parenthesis are results with correction for ZPE.

From Table-3, it can be seen that DW21-3 is the highest stable structure of the complexes between DMSO and 2 H_2O molecules and there is an overall strengthening of all the hydrogen bonds in this structure. As expected, basis set sensitivity exists. The magnitude of BSSE and ZPE correction decrease with the basis set enlarged, when the diffusion and polarization functions are considered, especially for the B3LYP/6-311++g (d,p) and B3LYP/6-311++g (2d,2p).

Conclusion

The 1:2 DMSO-H_2O complexes have been investigated using DFT at varied basis set levels from 6-31g to 6-311++g (2d,2p). The optimized geometric parameters and interaction energies for various isomers at different levels are estimated. In this paper, we also report the infrared spectrum frequencies, IR intensities and the vibrational frequency shifts of monomers and 1:1 DMSO-H_2O complexes at B3LYP/6-311++g(d,p) level.

TABLE-3
INTERACTION ENERGIES OF COMPLEXES BETWEEN ONE DMSO MOLECULE AND TWO WATER MOLECULES (KJ/mol) (VALUES IN THE FIRST PARENTHESIS ARE RESULTS WITH CORRECTION FOR BASIS SET SUPERPOSITION ERROR. VALUES IN THE SECOND PARENTHESIS ARE RESULTS WITH CORRECTION FOR ZPE)

Method	DW21-1	DW21-2	DW21-3	DW21-4
B3LYP/6-31g	141.1(116.6) (100.2)	141.4(120.3)(110.4)	158.6(139.5) (135.9)	93.7(71.3)(70.4)
B3LYP/6-31g(d)	102.4(80.3)(66.4)	95.6(75.9) (65.3)	111.5(91.0)(86.8)	66.1(52.2)(43.9)
B3LYP/6-31+g(d)	74.1(68.0)(55.2)	74.9(70.9)(57.4)	89.1(81.9)(69.0)	51.4(47.3)(38.6)
B3LYP/6-311++g(d,p)	73.2(67.4)(54.8)	74.3(70.7)(57.3)	87.5(81.4)(68.0)	52.6(46.5)(39.4)
B3LYP/6-311++g(2d,2p)	61.5(61.1)(48.6)	62.9(62.3)(51.0)	73.9(72.8)(59.9)	42.5(42.2)(34.9)

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