

Regulating Function of Methyl Group on the Strength of Dihydrogen Bond in HBeH-HCCH and HMgH-HCCH Complexes

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The regulating function of methyl group on the strength of dihydrogen bond was investigated in HBeH-HCCH and HMgH-HCCH complexes at the MP2/6-311++G(3df,2p) level. The bond lengths, infrared spectra, interaction energies, and charge transfers were analyzed. The presence of methyl group in the proton acceptor enhances the strength of dihydrogen bond, whereas its presence in the proton donor weakens the strength of dihydrogen bond. The charge analyses indicate that the methyl group in the proton donor and acceptor is electron-donating, thus the methyl group in the proton donor plays a negative role, whereas in the proton acceptor it plays a positive role in the formation of dihydrogen bond.

Keywords: Methyl group, Regulating function, Dihydrogen bond, HBeH-HCCH, HMgH-HCCH

INTRODUCTION

In recent years, more and more researchers have devoted their attention to the study of dihydrogen bonds. The dihydrogen bonding is an interaction with the form of A-H...H-D, where A-H acts as a proton acceptor and H-D as a proton donor [1,2]. It has been shown that metal hydrides are often taken as a proton acceptor in the formation of dihydrogen bonds. The dihydrogen bond is enhanced when the reactivity of metal hydrides is increased [3,4]. The usual proton donors in dihydrogen bonds are FH, OH, and NH groups [5-7], like those in conventional hydrogen bonds, although the dihydrogen bonds with CH and SH groups acting as a proton donor have also been reported [8-12]. The binding distances between the two interacting hydrogen atoms are typically 1.7-2.2 Å [13], significantly less than the sum of the van der Waals radii for the two hydrogen atoms (2.4 Å). It has

been demonstrated that dihydrogen bonds can influence structure, reactivity, and selectivity in solution and solid state [1,14,15], thus having potential utility in catalysis [16,17], crystal engineering and materials chemistry [18].

It is known that the properties of hydrogen bonds are not only determined by the properties of elements directly participating in formation of hydrogen bond but are related with the properties of substitution groups adjoined with these elements as well. Although the elements directly participating in the formation of hydrogen bond play a main role in the formation of a hydrogen bond, the substituted methyl groups also have a non-negligible influence on the properties and structures of hydrogen-bonded complexes [19-25]. For example, the strength of hydrogen bond between pterin and nucleobases was enhanced as pterin was joined with two methyl groups [19]. We also investigated the role of methyl group in the formation of OH...O hydrogen bond with methanol-dimethyl sulfoxide (DMSO) system as an example [22]. The results showed that the methyl group in the proton

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donor (methanol) is electron-withdrawing, whereas that in the proton acceptor (DMSO) is electron-donating, both making a positive contribution to the formation of OH \cdots O hydrogen bond. Similar results are also found in the C \cdots HO single-electron hydrogen bond in CH₃-H₂O complex [25].

Most studies on the dihydrogen bonds have mainly focused on the following three questions [10,26,27]. What molecule can form a dihydrogen bond? What is the nature of dihydrogen bond? Is there a difference between dihydrogen bonds and conventional H-bonds? It is found that there is no fundamental difference between the properties and nature of dihydrogen bonds and those of conventional hydrogen bonds. For example, the strength of dihydrogen bond has a positive relation with the proton acidity of the proton donors as does conventional hydrogen bond [9,28]. However, no study on the effect of methyl group on the properties of dihydrogen bonds has been reported. Thus, the aim in this work is to unveil the role of methyl group in the formation of dihydrogen bond with quantum chemical calculations, and to compare it with its role in conventional hydrogen bond. To understand the role of methyl group in the formation of dihydrogen bond, the charge analyses are also performed.

CALCULATION METHODS

In the previous paper on HXH \cdots HC \equiv CH (X = Be, Mg and Ca) complexes [29], the properties of dihydrogen bonds in these complexes have been described successfully with MP2/6-311++G(3df,2p) method. Thus, the same method was applied in this paper to study the role of methyl group in regulating the strength of dihydrogen bond in HBeH-HCCH and HMgH-HCCH complexes. First, their structures were optimized at this level. Then, the free H atom of the proton donor and acceptor in the two complexes was substituted with an F atom and methyl group, respectively, followed by another cycle of geometry optimization at the same level. Finally, frequency calculations of these complexes were also carried out at the same level to confirm that these structures are local minima on the energy surfaces. The interaction energies (ΔE) for these complexes have been computed as the difference between the total energy of the complex and the energies of the isolated monomers. The ΔE was corrected with basis set superposition error (BSSE). The BSSE was estimated with the

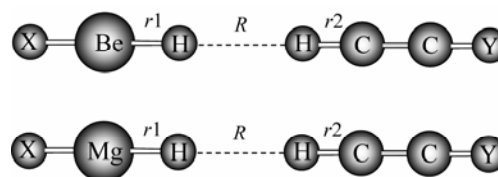


Fig. 1. Sketch map of the XBeH-HCCY and XMgH-HCCY complexes. X, Y = H, CH₃, F

counterpoise method of Boys and Bernardi [30]. All calculations were carried out using Gaussian 03 program [31].

RESULTS AND DISCUSSION

Geometrics

Based on the structures of HBeH-HCCH and HMgH-HCCH complexes [29], CH₃BeH-HCCH, FBeH-HCCH, HBeH-HCCCH₃, HBeH-HCCF, CH₃MgH-HCCH, FMgH-HCCH, HMgH-HCCCH₃ and HMgH-HCCF complexes are constructed. Figure 1 shows the sketch map of XBeH-HCCY and XMgH-HCCY complexes (X, Y = H, CH₃, F). The equilibrium structures of all complexes have C_{∞v} symmetry with a linear M-H \cdots H-C (M = Be and Mg) dihydrogen bond. Three bond lengths (R , r_1 , and r_2) are marked explicitly in Fig. 1: R is the binding distance of H \cdots H, r_1 the bond length of Be-H and Mg-H bonds, and r_2 the bond length of C-H bond. Their data are summarized in Table 1.

The binding distances (R) in all complexes are shorter than the normal H \cdots H of 2.4 Å, suggesting that these complexes are stable. These optimized binding distances are consistent with the common dihydrogen-bond length that has been observed experimentally in dihydrogen complexes [2]. The R in HBeH-HCCH and HMgH-HCCH clusters is 2.2088 Å and 2.1170 Å, respectively. Clearly, the R in HMgH-HCCH cluster is smaller. The result indicates that the dihydrogen bond in HMgH-HCCH cluster is stronger according to the correlation between the H \cdots H distance and dihydrogen bond strength [4,12]. The R in FBeH-HCCH and FMgH-HCCH clusters is 2.2323 Å and 2.1668 Å, respectively, larger than the corresponding one in HBeH-HCCH and HMgH-HCCH clusters. F is electron-withdrawing in the complexes. It is thus concluded that the presence of an F atom in the proton

Table 1. Selected Geometrical Parameters and their Complexation-Induced Changes (in Parentheses) in the Complexes

	R (Å)	$r1$ (Å)	$r2$ (Å)
HBeH-HCCH	2.2088	1.3291(-0.0002)	1.0647(0.0022)
CH ₃ BeH-HCCH	2.1864	1.3329(0.0036)	1.0650(0.0025)
FBeH-HCCH	2.2323	1.3236(-0.0057)	1.0640(0.0015)
HBeH-HCCCH ₃	2.2484	1.3288(-0.0005)	1.0639(0.0016)
HBeH-HCCF	2.1870	1.3292(0.0001)	1.0626(0.0024)
HMgH-HCCH	2.1170	1.7063(0.0003)	1.0671(0.0046)
CH ₃ MgH-HCCH	2.1099	1.7113(0)	1.0675(0.0050)
FMgH-HCCH	2.1668	1.6920(0)	1.0660(0.0035)
HMgH-HCCCH ₃	2.1626	1.7056(-0.0004)	1.0662(0.0039)
HMgH-HCCF	2.0922	1.7069(0.0009)	1.0653(0.0051)

acceptor weakens the strength of dihydrogen bond. In CH₃BeH-HCCH and CH₃MgH-HCCH clusters, however, the R decreases relative to the corresponding one in HBeH-HCCH and HMgH-HCCH clusters. That is to say, the presence of a methyl group in the proton acceptor enhances the strength of dihydrogen bond. A further analysis shows that the decrease of R due to the presence of methyl group in the proton acceptor of CH₃BeH-HCCH cluster (0.0224 Å) is larger than that in CH₃MgH-HCCH cluster (0.0071 Å). The result indicates that the contribution of methyl group is related to the dihydrogen bond strength. When an F atom is present in the proton donor (HBeH-HCCF and HMgH-HCCF clusters), the R decreases relative to the corresponding one in HBeH-HCCH and HMgH-HCCH clusters. The result indicates that the presence of an F atom in the proton donor enhances the strength of dihydrogen bond. However, the R increases in HBeH-HCCCH₃ and HMgH-HCCCH₃ clusters in comparison to the corresponding one in HBeH-HCCH and HMgH-HCCH clusters. The increase of R in HBeH-HCCCH₃ cluster is 0.0396 Å, smaller than that in HMgH-HCCCH₃ cluster (0.0456 Å). The result demonstrates that the presence of a methyl group in the proton donor weakens the strength of dihydrogen bond.

Upon the formation of a dihydrogen bond, the $r1$ changes a little in most clusters, and there are not any rules to follow. The results show that the change of the Be-H and Mg-H bond lengths in the proton acceptor is not adequate to evaluate the dihydrogen bond strength. For the conventional H-bonds, the elongation of the proton donating bond is often taken as an evidence for the hydrogen bond interaction. For the dihydrogen bonds in all complexes here, the C-H bonds ($r2$) of the proton donating bond are also elongated. The largest elongation of about 0.0050 Å is found in CH₃MgH-HCCH complex, whereas the smallest elongation of about 0.0015 Å is seen in FBeH-HCCH complex. The elongation of $r2$ in the complex of Be series is smaller than that in the complex of Mg series. In comparison to that in HBeH-HCCH complex, the elongation of $r2$ increases in CH₃BeH-HCCH and HBeH-HCCF complexes, whereas it decreases in FBeH-HCCH and HBeH-HCCCH₃ complexes. Similar results are found if the C-H bond lengths in the complex of Mg series are analyzed. The change of $r2$ is consistent with the change of R , both reflecting the change of dihydrogen-bonding strength.

Infrared Spectra

Table 2 shows the harmonic vibrational frequencies of the

Table 2. Selected Harmonic Vibrational Frequency Shifts ($\Delta\nu$, cm^{-1}) and Ratios of Intensities (I) in the Complexes

	Proton acceptor			Proton donor		
		$\Delta\nu$	I		$\Delta\nu$	I
HBeH-HCCH	$\nu_{\text{as}}(\text{Be-H})$	9	1.3	$\nu_{\text{as}}(\text{C-H})$	-17	1.8
CH ₃ BeH-HCCH	$\nu_{\text{as}}(\text{Be-H})$	10	1.5	$\nu_{\text{as}}(\text{C-H})$	-19	2.0
FBeH-HCCH	$\nu_{\text{as}}(\text{Be-H})$	0	1.4	$\nu_{\text{as}}(\text{C-H})$	-10	1.6
HBeH-HCCCH ₃	$\nu_{\text{as}}(\text{Be-H})$	8	1.3	$\nu_{\text{as}}(\text{C-H})$	-21	2.3
HBeH-HCCF	$\nu_{\text{as}}(\text{Be-H})$	9	1.3	$\nu_{\text{as}}(\text{C-H})$	-30	2.1
HMgH-HCCH	$\nu_{\text{as}}(\text{Mg-H})$	16	1.3	$\nu_{\text{as}}(\text{C-H})$	-43	2.7
CH ₃ MgH-HCCH	$\nu_{\text{as}}(\text{Mg-H})$	11	1.5	$\nu_{\text{as}}(\text{C-H})$	-47	2.9
FMgH-HCCH	$\nu_{\text{as}}(\text{Mg-H})$	16	1.6	$\nu_{\text{as}}(\text{C-H})$	-29	2.3
HMgH-HCCCH ₃	$\nu_{\text{as}}(\text{Mg-H})$	15	1.2	$\nu_{\text{as}}(\text{C-H})$	-53	3.8
HMgH-HCCF	$\nu_{\text{as}}(\text{Mg-H})$	17	1.3	$\nu_{\text{as}}(\text{C-H})$	-71	3.4

ten H \cdots H complexes calculated at the MP2/6-311++G(3df,2p) level. No scaling was applied for these frequencies. The selected stretching frequencies are from Be-H, Mg-H and C-H bonds. Evidently, the Be-H and Mg-H asymmetrical stretching frequencies ($\nu_{\text{as}}(\text{Be-H})$ and $\nu_{\text{as}}(\text{Mg-H})$) have a blue shift upon formation of a dihydrogen bond, whereas the C-H asymmetrical stretching frequency ($\nu_{\text{as}}(\text{C-H})$) has a red shift. In conventional hydrogen bond, such as O \cdots HO H-bond in DMSO-water complex [32], however, the S=O stretching vibration in the proton acceptor moves to low frequency. The blue shift of $\nu_{\text{as}}(\text{Be-H})$ and $\nu_{\text{as}}(\text{Mg-H})$ does not correlate with the change of the Be-H and Mg-H bond lengths. For example, the Be-H bond is lengthened in CH₃BeH-HCCH complex, whereas the $\nu_{\text{as}}(\text{Be-H})$ shifts to high frequency in this complex. Although the blue shifts of $\nu_{\text{as}}(\text{Be-H})$ and $\nu_{\text{as}}(\text{Mg-H})$ are found in these complexes, few rules are observed, thus it is not used to evaluate the strength of dihydrogen bond in these complexes.

The red shift of $\nu_{\text{as}}(\text{C-H})$ is consistent with the elongation of C-H bond. The red shift is not very large in comparison to that in conventional hydrogen bonds. The red shift of $\nu_{\text{as}}(\text{C-H})$

is -17 and -43 cm^{-1} for HBeH-HCCH and HMgH-HCCH complexes, respectively. The red shift increases about 2-4 cm^{-1} in CH₃BeH-HCCH and CH₃MgH-HCCH complexes. However, the red shift decreases about 7-14 cm^{-1} in FBeH-HCCH and FMgH-HCCH complexes. A red shift increase is also seen in HBeH-HCCF and HMgH-HCCF complexes. An interesting larger red shift is present in HBeH-HCCCH₃ and HMgH-HCCCH₃ complexes, whereas the elongation of the corresponding bond lengths is smaller.

The ratios of intensities (complex/monomer) of these stretches are also given in Table 2. Whether the M-H (M = Be and Mg) stretches or the C-H stretch, the ratios are larger than 1. However, no rule is found for the stretches. Thus, we think that the X-H stretching vibration in the proton donor of dihydrogen bond is not a good measure for evaluating the strength of dihydrogen bond in the complexes here as it is in conventional hydrogen bond.

Interaction Energies

Like other types of hydrogen bond, the interaction energy is one of the most powerful measurements for evaluating the

strength of dihydrogen bond. The interaction energies, corrected with BSSE, in the dihydrogen-bonded complexes were calculated at the MP2/6-311++G(3df,2p) level. The results are given in Table 3. The corrected interaction energies, ΔE_{corr} , in HBeH-HCCH and HMgH-HCCH complexes are calculated to be -4.34 and -8.01 kJ mol⁻¹, respectively, which are in good agreement with the reported results in Refs. [12] and [29]. Evidently, the strength of dihydrogen bond is stronger in the HMgH-HCCH complex, supporting the greater reaction of HMgH. Similar results are also found in other corresponding molecular clusters. The ΔE_{corr} in the two complexes are larger than that in C \cdots HC single-electron hydrogen bond of CH₃-HCCH complex (-3.065 kJ mol⁻¹) [33] and smaller than that in O \cdots HC hydrogen bond of H₂O-HCCH complex (-8.9 kJ mol⁻¹) [28]. In the three types of hydrogen bonds, the proton donor [$\sigma^*(\text{CH})$] is the same, whereas the proton acceptor is σ -bond electron, methyl radical, and lone electron pair, respectively. Clearly, the donating-electron ability is largest for the lone electron pair and smallest for the radical.

The ΔE_{corr} is -5.08 and -8.59 kJ mol⁻¹ for CH₃BeH-HCCH and CH₃MgH-HCCH complexes, respectively. The presence of a methyl group in the proton acceptor results in an energy increase of about 17% and 7% in magnitude for CH₃BeH-HCCH and CH₃MgH-HCCH complexes, respectively. It is also found that the methyl group in the proton acceptor is of more importance for the weaker dihydrogen bond. When the free H atom in the proton acceptor of HBeH-HCCH and HMgH-HCCH complexes is replaced with an electronegative F atom, the ΔE_{corr} is decreased by about 27% and 21%, respectively. The negative contribution of an F atom in the proton acceptor is larger for the stronger dihydrogen bond. These results show that the presence of the methyl group in the proton acceptor enhances the strength of the dihydrogen bond, whereas the presence of an electron-withdrawing group (F) weakens the strength of the dihydrogen bond. Such substitution effect is similar to that in other types of hydrogen bonds [22-25,34,35].

When the free H atom in the proton donor of HBeH-HCCH and HMgH-HCCH complexes is substituted with a methyl group, the ΔE_{corr} decreases by about 18% and 20%, respectively. The result indicates that the methyl group in the proton donor plays a negative role in the formation of

Table 3. Interaction Energies in the Complexes

	ΔE (kJ mol ⁻¹)	BSSE	ΔE_{corr} (kJ mol ⁻¹)
HBeH-HCCH	-5.15	0.81	-4.34
CH ₃ BeH-HCCH	-5.85	0.77	-5.08
FBeH-HCCH	-4.11	0.96	-3.15
HBeH-HCCCH ₃	-4.32	0.77	-3.55
HBeH-HCCF	-5.48	0.92	-4.56
HMgH-HCCH	-9.10	1.09	-8.01
CH ₃ MgH-HCCH	-9.56	0.97	-8.59
FMgH-HCCH	-7.16	0.85	-6.31
HMgH-HCCCH ₃	-7.48	1.08	-6.40
HMgH-HCCF	-9.74	1.27	-8.47

dihydrogen bond, which is different from that in O \cdots HO hydrogen bond [22]. Clearly, a big negative contribution of methyl group in the proton donor is found in HMgH-HCCCH₃ complex, where the dihydrogen bond is stronger than that in the HBeH-HCCCH₃ complex. It is also found that the negative contribution of the methyl group in the proton donor is larger than the positive contribution of the methyl group in the proton acceptor. The ΔE_{corr} is -4.56 and -8.47 kJ mol⁻¹ for HBeH-HCCF and HMgH-HCCF complexes, respectively. The presence of an electronegative F atom in the proton donor leads to an energy increase of about 5% in magnitude for HBeH-HCCF and HMgH-HCCF complexes. The positive contribution of an F atom in the proton donor is far smaller than the negative contribution of methyl group in the proton donor. These results indicate that the presence of methyl group in the proton donor weakens the strength of the dihydrogen bond, whereas the presence of an electron-withdrawing group (F) in the proton donor has an enhancing effect on the strength of the dihydrogen bond.

The methyl group in the proton donor and acceptor plays the same role (a positive contribution) in the formation of O \cdots HO hydrogen bond [22], whereas it plays a different role (a negative contribution in the proton donor and a positive

contribution in the proton acceptor) in the formation of dihydrogen bond. We thus deduce that there are also some differences between dihydrogen bond and conventional hydrogen bond although there is no fundamental difference in their nature.

Charge Analyses

To understand the influence of the methyl group on the strength of dihydrogen bond from the angle of charge transfer, the Mulliken charge of methyl group in the complex and the charge change relative to that in the monomer were calculated with the MP2/6-311++G(3df,2p) method. The results are presented in Table 4. It is seen from the table that a negative Mulliken charge is found for the methyl group in the complexes and their monomers. Upon the complexation, the negative Mulliken charge of the methyl group in the proton acceptor and donor decreases. The positive Mulliken Δq values in Table 4 indicate a decrease in electron density of the methyl groups. The less negative Mulliken charge of the methyl group in the cluster than that in the respective monomer indicates an electron-donating effect of the methyl group upon the formation of a dihydrogen bond.

When M-H (M = Be and Mg) forms a dihydrogen bond with a HCCH or HCCCH₃ molecule, charge transfers from the M-H σ bond orbital to the anti-bond orbital of CH group leads to a decrease of electron density on the M-H σ bond in the proton acceptor and increase of electron density on the H-C bond in the proton donor. Thus, it is helpful for the stabilization of dihydrogen bond if the proton acceptor has an electron-donating group and the proton donor has an electron-withdrawing group. Now, the methyl group in the

proton donor and acceptor is electron-donating. Thus, the methyl group in the proton acceptor has an enhancing effect on the strength of dihydrogen bond, whereas in the proton donor it has a weakening effect on the strength of dihydrogen bond.

In the O \cdots HO hydrogen bond between DMSO and methanol molecules, the methyl group in the proton acceptor is electron-donating, while in the proton donor it is electron-withdrawing [22]. Clearly, the methyl group in the proton acceptor plays the same role in the two types of hydrogen bonds, whereas in the proton donor it plays a different role in the two types of hydrogen bonds. In the O \cdots HO hydrogen bond, the electron-donating role of the methyl group in the proton acceptor and its electron-withdrawing role in the proton donor has a positive contribution to the formation of a hydrogen bond. In the dihydrogen bond, however, the electron-donating role of the methyl group in the proton donor is a negative contribution. Therefore, we think that the results reported here can be taken as a beneficial makeup for the role of methyl group in the formation of hydrogen bond.

CONCLUSIONS

By employing the method of quantum chemical calculations at the MP2/6-311++G(3df,2p) level, we optimized the structures of HBeH-HCCH, CH₃BeH-HCCH, FBeH-HCCH, HBeH-HCCCH₃, HBeH-HCCF, HMgH-HCCH, CH₃MgH-HCCH, FMgH-HCCH, HMgH-HCCCH₃, and HMgH-HCCF complexes. The bond lengths, infrared spectra, interaction energies, and charge changes are calculated. When

Table 4. Mulliken Charges (q/e) of the Methyl Groups and their Changes ($\Delta q/e$) in the Selected Complexes^a

	$q_m(A)$	$q_c(A)$	$\Delta q(A)$	$q_m(D)$	$q_c(D)$	$\Delta q(D)$
CH ₃ BeH-HCCH	-0.2300	-0.1746	0.0554			
HBeH-HCCCH ₃				-0.1896	-0.0011	0.1885
CH ₃ MgH-HCCH	-0.4786	-0.3092	0.1694			
HMgH-HCCCH ₃				-0.1896	-0.0044	0.1852

^aThe subscript of m and c represents monomer and complex, respectively. A and D represent the proton acceptor and donor, respectively.

the proton acceptor adjoins with a methyl group, the dihydrogen bond is enhanced. The effect of an F atom in the proton acceptor is the same as that of the methyl group. When the proton donor adjoins with a methyl group, the dihydrogen bond is weakened. The effect of an F atom in the proton donor is different from that of the methyl group. The charge analyses indicate that the methyl group in the proton acceptor and donor is electron-donating. The electron-donating role of methyl group in the proton acceptor is favorable for the formation of dihydrogen bond, whereas its role in the proton donor is unfavorable for the formation of dihydrogen bond. The former is similar to that in O \cdots HO hydrogen bond, whereas the latter is different from that in O \cdots HO hydrogen bond. The result is thus a good makeup for the role of methyl group in the formation of hydrogen bond.

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References

- [1] R. Custelcean, J.E. Jackson, *Chem. Rev.* 101 (2001) 1963.
- [2] V.I. Bakhmutov, *Dihydrogen Bond: Principles, Experiments and Applications*, Wiley Publisher, 2008, and references contained therein.
- [3] M. Solimannejad, S. Scheiner, *J. Phys. Chem. A* 109 (2005) 11933.
- [4] S.J. Grabowski, *J. Phys. Chem. A* 104 (2000) 5551.
- [5] G.N. Patwari, A. Fujii, N. Mikami, *J. Chem. Phys.* 124 (2006) 241103.
- [6] H.Y. Liao, *Chem. Phys. Lett.* 424 (2006) 28.
- [7] S. Berskia, J. Lundell, Z. Latajka, *J. Mol. Struct.* 552 (2000) 223.
- [8] J.G. Planas, C. Vinas, F. Teixidor, A. Comas-Vives, G. Ujaque, A. Lledos, M.E. Light, M.B. Hursthouse, *J. Am. Chem. Soc.* 127 (2005) 15976.
- [9] S.A.C. McDowell, T.S. Forde, *J. Chem. Phys.* 117 (2002) 6032.
- [10] I. Alkorta, J. Elguero, O. Mo, M. Yanez, J.E. Del Bene, *J. Phys. Chem. A* 106 (2002) 9325.
- [11] P. Lipkowski, S.J. Grabowski, T.L. Robinson, J. Leszczynski, *J. Phys. Chem. A* 108 (2004) 10865.
- [12] I. Alkorta, K. Zborowski, J. Elguero, M. Solimannejad, *J. Phys. Chem. A* 110 (2006) 10279.
- [13] W.T. Klooster, T.F. Koetzle, P.E.M. Siegbahn, T.B. Richardson, R.H. Crabtree, *J. Am. Chem. Soc.* 121 (1999) 6337.
- [14] R.H. Crabtree, P.E.M. Siegbahn, O. Eisenstein, A.L. Rheingold, T.F. Koetzle, *Acc. Chem. Res.* 29 (1996) 348.
- [15] N.V. Belkova, E.S. Shubina, L.M. Epstein, *Acc. Chem. Res.* 38 (2005) 624.
- [16] W.K. Fung, X. Huang, M.L. Man, S.M. Ng, M.Y. Hung, Z.Y. Lin, C.P. Lau, *J. Am. Chem. Soc.* 125 (2003) 11539.
- [17] R.M. Bullock, *Chem. Eur. J.* 10 (2004) 2366.
- [18] G.R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier Science Publishers B.V. Amsterdam, 1989.
- [19] Q. Dai, C.Y. Xu, Y. Sato, K. Yoshimoto, S. Nishizawa, N. Teramae, *Anal. Sci.* 22 (2006) 201.
- [20] K. Chenoweth, C.E. Dykstra, *Chem. Phys. Lett.* 402 (2005) 329.
- [21] K.-H. Choi, H.-J. Lee, A. Karpfen, C.-J. Yoon, J. Park, Y.-S. Choi, *Chem. Phys. Lett.* 345 (2001) 338.
- [22] Q.Z. Li, G.S. Wu, Z.W. Yu, *J. Am. Chem. Soc.* 128 (2006) 1438.
- [23] Q.Z. Li, X.L. An, F. Luan, W.Z. Li, B.A. Gong, J.B. Cheng, *J. Phys. Chem. A* 112 (2008) 3985.
- [24] Q.Z. Li, X.L. An, F. Luan, W.Z. Li, B.A. Gong, J.B. Cheng, J.Z. Sun, *Int. J. Quantum Chem.* 108 (2008) 558.
- [25] X.L. An, H.P. Liu, Q.Z. Li, B.A. Gong, J.B. Cheng, *J. Phys. Chem. A* 112 (2008) 5258.
- [26] I. Alkorta, J. Elguero, S. J. Grabowski, *J. Phys. Chem. A* 112 (2008) 2721.
- [27] S.J. Grabowski, W.A. Sokalski, J. Leszczynski, *J. Phys. Chem. A* 108 (2004) 5823.
- [28] P.C. Singh, G. Naresh Patwari, *J. Phys. Chem. A* 111 (2007) 3178.
- [29] Y. Wu, L. Feng, X.D. Zhang, *J. Mol. Struct. (THEOCHEM)* 851 (2008) 294.
- [30] S.F. Boys, F. Bernardi, *Mol. Phys.* 19 (1970) 553.

- [31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A.J. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
- [32] Q.Z. Li, X.L. An, B.A. Gong, J.B. Cheng, *Vib. Spectrosc.* 46 (2008) 28.
- [33] B.Q. Wang, Z.R. Li, D. Wu, X.Y. Hao, R.J. Li, C.C. Sun, *Chem. Phys. Lett.* 375 (2003) 91.
- [34] S. Scheiner, S.J. Grabowski, T. Kar, *J. Phys. Chem. A* 105 (2001) 10607.
- [35] Y. Feng, L. Liu, Y. Fang, Q.X. Guo, *J. Phys. Chem. A* 106 (2002) 11518.