Infrared-Optical Double-Resonance Measurements on O−H···H−Ge Dihydrogen-Bonded Phenol−Triethylgermanium Hydride Complex in the Gas Phase

Prashant Chandra Singh,[†] **Dilip K. Maity,**[‡] **and G. Naresh Patwari***[,†]

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India, and Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India

Received: February 4, 2008; Revised Manuscript Received: April 2, 2008

Spectroscopic investigation of a dihydrogen-bonded complex between phenol and triethylgermanium hydride is reported here. Laser-induced fluorescence excitation, fluorescence-detected infrared, and IR−UV hole-burning spectroscopic studies were carried out in supersonic jet to investigate the complex formation between phenol and triethylgermanium hydride. The lowering of the O−H stretching frequency of the phenol moiety in the complex with triethylgermanium hydride clearly establishes the role of phenol as hydrogen bond donor. The experimental results together with the ab-initio calculations unambiguously confirm formation of an O−H···H−Ge dihydrogen-bonded complex between phenol and triethylgermanium hydride

Introduction

Dihydrogen bonding is an interaction analogous to hydrogen bonding between two oppositely charged hydrogen atoms.[1] The formation of dihydrogen bonding is well-characterized in crystal structures,[2] in gas-phase clusters,[3] and by theoretical means.[4] The dihydrogen-bonded interaction brings two hydrogen atoms together, which under some conditions can lead to dehydrogenation. It has now been shown, both experimentally and theoretically, that dihydrogen bonding is a precursor to dehydrogenation reactions.[5,6] Thus, dihydrogen bonding can be envisaged as a medium to store molecular hydrogen. Boron and other metal/nonmetal hydrides have been viewed as efficient chemical hydrogen storage materials for their potential application in hydrogen fuel cells.[7] In this regard borane−amines in general and borane−ammonia in particular have been investigated extensively to understand their ability to release molecular hydrogen.[8] Several groups have investigated the dehydrogenation of borane−ammonia using various methodologies, such as thermal decomposition and acid-catalyzed reaction.[9,10] It was also shown, in many cases, that the dehydrogenation of borane−ammonia proceeds via a dihydrogen-bonded intermediate.[5–10] Apart from their role in hydrogen storage materials, dihydrogen bonds, similar to conventional hydrogen bonds, can be used in molecular recognition and crystal engineering. The crystal structure of cyclotrigallazane [$(GaH_2NH_2)_3$] reported by Campbell et al. clearly demonstrates the potential of dihydrogen bonding in crystal engineering.[11]

Mikami and co-workers have extensively worked on dihydrogen-bonded complexes involving borane-amines in the gas phase.[3] Dehydrogenation reaction was also reported from the dihydrogen-bonded complex between phenol with borane−trimethylamine following its photoionization.[5d] More recently, Ishikawa et al. have reported the formation of dihydrogen-bonded complex between phenol and diethylmethylsilane.[12] At this stage, a natural extension would be investigate the formation of dihydrogen-bonded complexes involving germanium hydrides. This exercise will allow us to compare the energetics of dihydrogen bond formation involving various hydrides and to evaluate their potential as hydrogen storage materials. This provides impetus to investigate dihydrogen-bonded complexes involving germanium hydrides. We report here electronic and vibrational spectroscopic evidence for the formation of O−H···H−Ge dihydrogen-bonded complex between phenol and triethylgermanium hydride in the gas phase.

Experiment

The details of the complete experimental setup can be found elsewhere.[13] Briefly, laser-induced fluorescence (LIF) excitation, fluorescence-detected infrared (FDIR), and IR−UV hole-burning spectra were recorded on a jet-cooled mixture of phenol (SRL Chemicals) and triethylgermanium hydride (Aldrich). Helium buffer gas was passed over the reagents kept separately at room temperature and expanded supersonically through a 0.5 mm diameter pulsed nozzle (Series 9, Iota One; General Valve Corp.). In our experiments the UV laser was a frequency-doubled output of a second harmonic Nd:YAG laser (Continuum, Surelite I-10) pumped dye laser (Radiant Dyes, Narrow Scan G-R) operating with rhodamine-19 dye. Total florescence was detected using a photomultiplier tube (PMT; Electron Tubes Ltd., 9780SB + 1252−5F)/filter (WG305 + BG3) combination. The tunable IR source was an idler output of a $LiNbO_3$ optical parametric oscillator (Euroscan Instruments, Custom $LiNbO_3$-OPO) pumped with an injection-seeded−single-mode Nd:YAG laser (Quantel, Brilliant B). The IR OPO was calibrated by recording the photoacoustic spectrum of ambient water vapor. The typical bandwidth of both UV and IR lasers is about 1 cm^{-1}, and the absolute frequency calibration is within ±2 cm^{-1}.

Results and Discussion

The LIF excitation spectrum of phenol is shown in Figure 1A, and the transition at 35974 cm^{-1}, marked with “p”, is its band origin.[14] Upon addition of triethylgermanium hydride (TEGH), at least five new transitions, marked “a” though “e”, appear in the LIF excitation spectrum, which is shown in Figure 1B. This spectrum is very similar to the one observed in the case of the dihydrogen-bonded complex of phenol with dieth-

---

* To whom correspondence should be addressed. E-mail: naresh@chem.iitb.ac.in.

[†] Indian Institute of Technology Bombay.

[‡] Bhabha Atomic Research Center.

10.1021/jp801035u CCC: $40.75

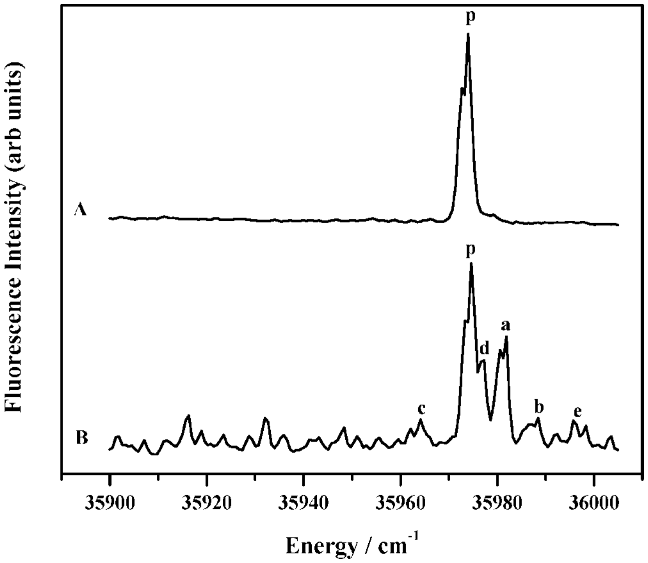

Figure 1. LIF excitation spectrum of (A) phenol and (B) phenol in the presence of TEGH. Transitions marked with the lowercase alphabet appeared in the presence of TEGH.

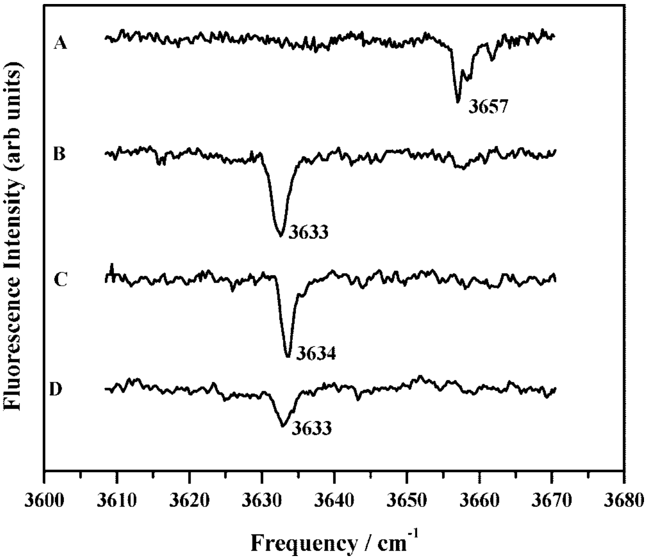

Figure 2. FDIR spectra of (A) phenol, (B) phenol−TEGH probed at “a”, (C) phenol−TEGH probed at “b”, and (D) phenol−TEGH probed at “c”.

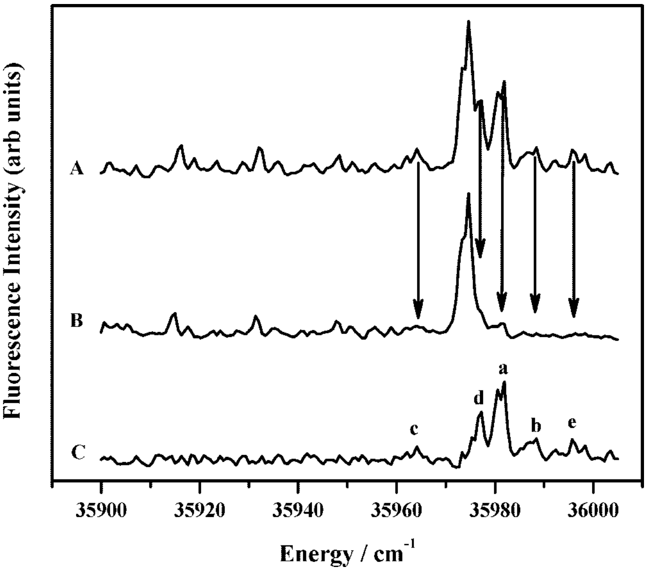

Figure 3. (A) LIF excitation spectrum with IR off and (B) LIF excitation spectrum with the IR laser frequency fixed to the O−H stretching vibration of phenol−TEGH complex (IR−UV hole-burnt spectrum). (C) The LIF excitation spectrum of phenol−TEGH complex obtained by subtracting B from A. The arrows point to the bands with reduced intensities in the hole-burnt spectrum.

ylmethylsilane.[12] The shifts in the electronic transitions were −10, +3, +8, +14, and +22 cm^{-1} relative to phenol band origin and most likely are due to conformational isomers of the complex. Though the bands b, c, and e are very low intensity and are barely above the noise level, these bands consistently appear in the presence of TEGH and stand out in the IR−UV hole-burning spectroscopy; vide infra. Though the shifts in the electronic transitions are marginal, these shifts do not necessarily indicate the strength of hydrogen/dihydrogen bonding present in the present complexes. However, in the present scenario, they provide evidence for the formation of binary clusters and also provide discrete bands to selectively record the vibrational spectra in the O−H stretching region.

Vibrational spectroscopy in the hydride (X−H, where X = O, N, C) stretching region is a convenient tool to investigate the formation of hydrogen bonding. This is due to the fact that these stretching frequencies are very sensitive to hydrogen-bonded structures, as they are directly involved in hydrogen bond formation and show a characteristic shift to a lower frequency.[15] FDIR spectra were recorded in order to understand the nature of the interaction of TEGH with phenol, which are depicted in Figure 2. Trace A shows the FDIR spectrum of bare phenol in the O−H stretching region, which shows a lone transition at 3657 cm^{-1}.[16] The observed structure in the O−H stretching vibration is due to modulation of the IR power as a result of ambient water vapor absorption. Trace B depicts the FDIR spectrum of the phenol−TEGH complex probed at the transition marked “a” in the LIF excitation spectrum (Figure 1B). A lone transition in this spectrum at 3633 cm^{-1} can be assigned to the O−H stretching frequency of the complex, which is shifted to a lower frequency by 24 cm^{-1}, relative to bare phenol. Since the O−H stretching frequency of the complex is shifted by 24 cm^{-1} to a lower frequency, this spectrum clearly indicates that the OH group of phenol is hydrogen-bonded to the TEGH moiety. This however does not indicate which part of TEGH is interacting with phenol. Traces C and D in Figure 2 were recorded by probing the transitions marked “b” and “c”, respectively, in the LIF excitation spectrum. Even these spectra show that the O−H stretching frequency is positioned around 3633 cm^{-1}. The shift in the O−H stretching frequency in the present phenol−TEGH complex is comparable to that of the dihydrogen-bonded phenol−diethylmethylsilane complex (∼25 cm^{-1})[12] but far lower than the dihydrogen-bonded phenol−borane trimethylamine complex (143 cm^{-1}).[3b] This straightforwardly indicates that the strength of dihydrogen-bonded complexes of borane−amines is far greater than those of the corresponding silanes and germanes.

As stated earlier, a large number of transitions appeared in the LIF excitation spectrum of phenol−TEGH (Figure 1B). IR−UV hole-burning spectroscopy was carried out to verify the origin and the nature of the new transitions appearing in the LIF excitation spectrum, and the results are presented in Figure 3. Trace A is an UV-only spectrum in the absence of IR laser and is almost identical to the LIF excitation spectrum shown in Figure 1B. Trace B was recorded by pumping the O−H vibrational transition of the phenol−TEGH complex at 3633 cm^{-1} with an IR laser, prior to the UV excitation, i.e. the

TABLE 1: Relative Heats of Formation and Their Population of Various Conformers of TEGH Calculated at the B3LYP/6-311++G(d,p) Level at 298 K

conformers	$\Delta H°$/(kJ mol^{-1})	population
[t-t-t]	9.0	0.00
[t-t-g_1] [g_1-t-t [t-g_1-t] [t-t-g_2] [g_2-t-t] [t-g_2-t]	3.6	0.10
[t-g_1-g_1] [g_1-t-g_1] [g_1-g_1-t] [t-g_2-g_2] [g_2-t-g_2] [g_2-g_2-t]	0.5	0.34
[t-g_1-g_2] [g_1-t-g_2] [g_1-g_2-t]	0.3	0.19
[t-g_2-g_1] [g_2-t-g_1] [g_2-g_1-t]	3.0	0.05
[g_1-g_1-g_2] [g_1-g_2-g_1] [g_2-g_1-g_1] [g_2-g_2-g_1] [g_2-g_1-g_2] [g_1-g_2-g_2]	2.1	0.18
[g_1-g_1-g_1] [g_2-g_2-g_2]	0.0	0.14

IR-UV hole-burnt spectrum. The hole-burnt spectrum reveals that all five newly appearing transitions in the vicinity of the phenol band origin have diminished intensities. Trace C is the LIF excitation spectrum of the phenol−TEGH system, which was obtained by subtracting trace B from trace A. This implies that the O−H stretching frequency of all five newly appeared transitions is at 3633 cm^{-1}. The results of IR−UV hole-burning spectroscopy can be interpreted in two ways. First, all of the transitions appearing in the LIF excitation spectrum are vibronic bands of a single isomer. Second, the transitions might originate from two different structural isomers; however, their interaction strength is almost identical such that the shift in the O−H stretching frequency of phenol moiety lies within the bandwidth of 1 cm^{-1} of the IR laser.

To supplement the experimental observation, we carried out quantum chemical calculations using the GAUSSIAN-03[17] and GAMESS[18] suit of programs. TEGH (triethylgermanium hydride), as the name suggests, has three ethyl groups bound to the germanium atom. Each ethyl group can in principle have three possible conformations, trans (t), gauche$_1$ (g_1), and gauche$_2$ (g_2). These conformations arise due to different orientations of the terminal carbon atom with respect to the hydrogen atom attached to the germanium atom. The trans configuration has the dihedral angle of 180°, while gauche$_1$ and gauche$_2$ have dihedral angles of +60 and −60°, respectively. The three ethyl groups on TEGH lead to a total of 27 possible configurations. However, for single-ethyl groups the two gauche configurations g_1 and g_2 are isoenergetic; therefore, in the case of TEGH only seven sets of independent configurations arise, which are listed in Table 1. The entries in each set are conformational enantiomers; for example, the conformers [g_1-g_1-g_1] and [g_2-g_2-g_2] are isoenergetic but are non-superimposable. Table 1 also lists their relative heats of formation calculated at the B3LYP/6-311++G(d,p) level. The all-gauche conformers [g_1-g_1-g_1] and [g_2-g_2-g_2] have the lowest heat of formation, while the all-trans conformer of [t-t-t] has the highest. Table 1 also lists the relative populations for each set of conformers (scaled with the degeneracy of the set) at 298 K. The relative populations of the [t-t-t] and [t-g_2-g_1] sets of conformers are very low, 5% or less, and can perhaps be neglected. Therefore the observed transitions in the LIF excitation spectrum of phenol−TEGH should arise out of the remaining five sets of conformations of TEGH.

To determine the intermolecular structure of phenol−TEGH complexes, the geometries of the monomers and the complexes were optimized without any constraints at the MP2/cc-PVDZ level of theory for the five most abundant TEGH isomers.[19] The nature of the stationary point obtained on the potential energy surface (PES) was confirmed by calculating the vibrational frequencies at the same level of theory. The calculated vibrational frequencies were scaled by a factor of 0.954 to correct for the basis set truncation, partial neglect of the electron correlation, and harmonic approximation and then compared with the experimentally observed values. The stabilization energies were corrected for the zero point energy (ZPE) and the basis set superposition error (BSSE) using counterpoise method. According to Kim et al., 100% of BSSE correction often underestimates the interaction energy and 50% correction is a good empirical approximation.[20] Therefore, we report the stabilization energies with 50% BSSE correction. Figure 4 shows the structures of the five phenol−TEGH complexes, and Table 2 lists the binding energies, the intermolecular H···H distance along with the O−H stretching frequencies, and the shifts in the phenol−TEGH complexes. In all cases the two oppositely changed hydrogen atoms are in the proximity with the H···H interaction distance around 2.4 Å (twice the van der Waals radius of hydrogen atom) or less, therefore qualifying as dihydrogen-bonded complexes.[1] The binding energies are in the

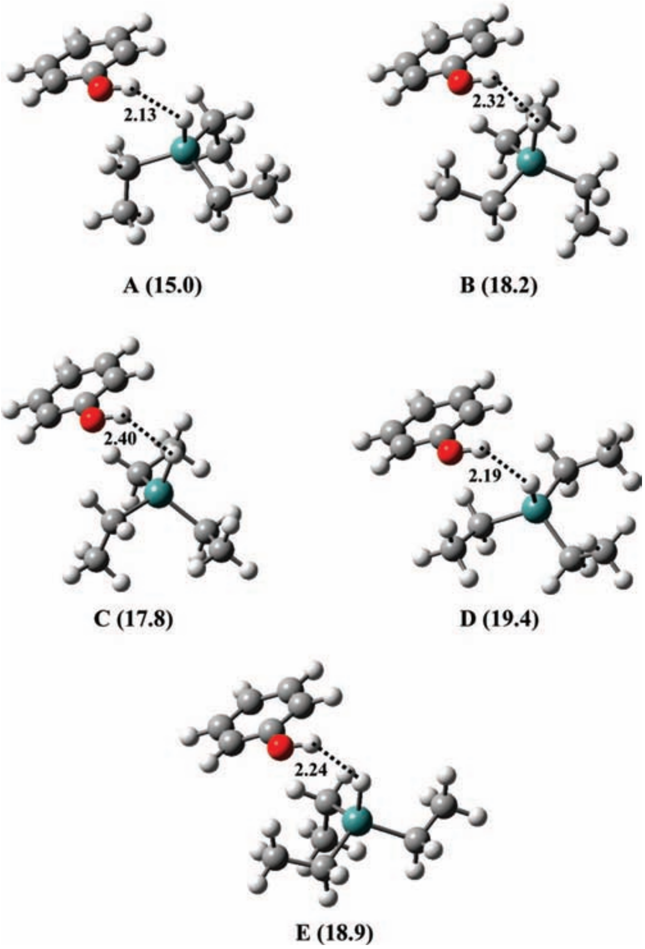

Figure 4. Calculated structures of phenol−TEGH complexes at MP2/cc-pVDZ level of theory. The distances are shown in angstroms and the binding energies (kJ mol^{-1}) are shown in parentheses.

TABLE 2: Binding Energies, H···H Distances and Scaled Vibrational Frequencies and Their Shifts for Various Isomers of Phenol−TEGH Complexes Calculated at the MP2/cc-PVDZ Level of Theory

	ΔE (kJ mol^{-1})	H···H (Å)	ν_{O-H} (cm^{-1})	$\Delta\nu_{O-H}$ (cm^{-1})
phenol			3657	
A [t-t-g_1]	15.0	2.13	3630	−27
B [t-g_1-g_1]	18.2	2.32	3628	−29
C [t-g_1-g_2]	17.8	2.40	3643	−14
D [g_1-g_1-g_2]	19.4	2.19	3634	−23
E [g_1-g_1-g_1]	18.0	2.24	3619	38

range of 15.0−19.4 kJ mol^{-1}. Apart from the H···H interaction, these complexes are characterized by the presence of dispersive interaction between the CH groups of TEGH and π electron density of the benzene ring. It is not very easy to separate out the contribution between the H···H and C−H···π interactions. However, in complex **A**, the H···H interaction distance is minimum at 2.13 Å and it appears that the C−H···π interaction in this complex is minimal due to unfavorably disposed ethyl groups of the [t-t-g_1] confomer of TEGH relative to the benzene π electron cloud. This places the upper limit for the H···H interaction around 15 kJ mol^{-1}. However in the complexes **B**−**E** the H···H interaction is sacrificed to gain C−H···π interaction. The shifts in the O−H stretching frequencies of the phenol moiety in these five complexes range from −14 to −38 cm^{-1}, and three out of the five complexes have O−H frequency shifts around the experimentally observed shift of −24 cm^{-1}. From Table 2 prima facie there appears no correlation between the binding energies, H···H distances, and the O−H frequency shifts. The most stable complex **D** with binding energy of 19.4 kJ mol^{-1} and H···H distance of 2.19 Å has an O−H frequency shift of −23 cm^{-1}, which is in excellent agreement with the experimental values.

Though one is tempted to assign the observed transitions to various phenol−TEGH conformational isomers, the theoretical analysis is not totally supportive of the experimental observations. UV−UV hole-burning spectroscopy would most certainly separate out the transitions into isomeric and vibronic bands. Furthermore, we had optimized one phenol complex for each isomer of TEGH; this exercise can be extended by considering the relative orientations of the ethyl groups with the benzene ring. The TEGH isomer [g_1-g_1-g_1] will result in only one possible orientation, while the isomer [t-g_1-g_2] will have three different orientations. This analysis will lead to formation of 10 different isomers of phenol−TEGH complexes against the five optimized in the present case. This further complicates the situation, and assigning the observed transition in the LIF excitation spectrum to the individual isomers would be an horrendous task. However, it can be noted that the specific details of the structure are probably not as important as the nature of interaction. Fortunately, the FDIR and the IR−UV hole-burnt spectra reveal that the nature of the interaction between phenol and TEGH in all five transitions is almost identical. On the basis of the above discussion, one can risk an assignment of phenol−TEGH complexes to the structure similar in nature to the one shown in Figure 4D. This assignment of course can only be tentative. However, the experimental observations along with the ab-initio calculations unambiguously support the formation of O−H···H−Ge dihydrogen bonding between phenol and TEGH.

Conclusions

The LIF excitation spectrum of phenol shows several new transitions in the presence of triethylgermanium hydride. The FDIR spectra reveal that the O−H stretching vibration of the complex is shifted to a lower frequency by 24 cm^{-1}. The IR−UV hole-burning spectroscopy reveals that all the newly appearing transitions have an identical shift of 24 cm^{-1} for the O−H stretching vibration of the phenol moiety. The analysis of the observed experimental results using ab-initio calculations clearly shows the formation of an O−H···H−Ge dihydrogen-bonded complex between phenol and triethylgermanium hydride. Finally, the ability of germanes and silanes to form dihydrogen bonds is much lower than boranes.

Acknowledgment. This material is based upon work supported by Department of Science and Technology (Grant No. SR/S1/PC-40/2003), Board of Research in Nuclear Sciences (Grant No. 2004/37/5/BRNS/398), and Council of Industrial and Scientific Research (Grant No. 01(1902)/03/EMR-II). P.C.S. thanks CSIR for the award of senior research fellowship.

References and Notes

(1) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. *Acc. Chem. Res.* **1996**, *29*, 348; and references therein.

(2) (a) Stevans, R. C.; Bau, R.; Milstein, R.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429. (b) Vander Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4381. (c) Richardson, T. B.; Gala, S. D.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875. (d) Klooster, W. T.; Koetzle, T. F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.

(3) (a) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2000**, *113*, 9885. (b) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2001**, *114*, 8877. (c) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **2002**, *116*, 6056. (d) Patwari, G. N.; Fujii, A.; Mikami, N. *J. Chem. Phys.* **2006**, *124*, 241103. (e) Patwari, G. N.; Ebata, T.; Mikami, N. *Chem. Phys.* **2002**, *283*, 193. (f) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 8642.

(4) (a) Kulkarni, S. A. *J. Phys. Chem. A* **1998**, *102*, 7704. (b) Kulkarni, S. A.; Srivastava, A. K. *J. Phys. Chem. A* **1999**, *103*, 2836. (c) Grabowski, S. J. *Chem. Phys. Lett.* **2000**, *327*, 203. (d) Popelier, P. L.; A, *J. Phys. Chem. A* **1998**, *102*, 1873. (e) Merino, G.; Bakhmutov, V. I.; Vela, A. *J. Phys. Chem. A* **2002**, *106*, 8491.

(5) (a) Atwood, J. L.; Koutsantonis, G. A.; Lee, F.; Raston, C. L. *J. Chem. Soc., Chem. Commun* **1994**, 91. (b) Gruet, K.; Clot, E.; Eisenstein, O.; Lee, D. H.; Patel, B.; Macchioni, A.; Crabtree, R. H. *New. J. Chem.* **2003**, *27*, 80. (c) Custelcean, R; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963. (d) Patwari, G. N.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2001**, *105*, 10753.

(6) (a) Kulkarni, S. A. *J. Phys. Chem. A* **1999**, *103*, 9330. (b) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108.

(7) (a) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283. (b) Vermeulen, P.; van Thiel, E. F. M. J.; Notten, P. H. L. *Chem. Eur. J.* **2007**, *13*, 9892. (c) Schueth, F.; Bogdanovic, B.; Felderhoff, M. *Chem. Commun. (Cambridge)* **2004**, 2249.

(8) (a) Marder, T. B. *Angew. Chem., Int. Ed.* **2007**, *46*, 8116. (b) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, *25*, 2613. (c) Zhang, X. B.; Han, S.; Yan, J. M.; Chandra, M.; Shioyama, H.; Yasuda, K.; Kuriyama, N.; Kobayashi, T.; Xu, Q. *J. Power Sources* **2007**, *168*, 167. (d) Mohajeri, N.; T-Raissi, A.; Adebiyi, O. *J. Power Sources* **2007**, *167*, 482. (e) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T *J. Am. Chem. Soc.* **2007**, *129*, 1844.

(9) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19. (b) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Rossbler, K.; Leitner, G. *Thermochim. Acta* **2003**, *391*, 159.

(10) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746. (b) Nguyen, M. T.; Nguyen, V. S.; Matus, M. H.; Gopakumar, G.; Dixon, D. A. *J. Phys. Chem. A* **2007**, *111*, 679. (c) Patwari, G. N. *J. Phys. Chem. A* **2005**, *109*, 2035.

(11) Campbell, J. P.; Hwang, J. W.; Young, V. G., Jr.; Von Dreele, R. B.; Cramer, C. J.; Gladfelter, W. L *J. Am. Chem. Soc.* **1998**, *120*, 521.

(12) Ishikawa, H.; Saito, A.; Sugiyama, M.; Mikami, N. *J. Chem. Phys.* **2005**, *123*, 224309.

(13) Singh, P. C.; Patwari, G. N. *Curr. Sci.*, submitted for publication.

(14) Abe, H.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1982**, *86*, 1768.

(15) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960.

(16) Tanabe, S.; Ebata, T.; Fujii, M.; Mikami, N. *Chem. Phys. Lett.* **1993**, *215*, 347.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, 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 03*, Revision A.1;Gaussian: Wallingford, CT, 2003.

(18) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A *J. Comput. Chem.* **1993**, *14*, 1347 (GAMESS Version-7).

(19) The phenol−TEGH complexes were also optimizd at the B3LYP/6-311++G(d,p) level of theory. At this level we found formation of dihydrogen-bonded complexes. However, the dispersion ineraction between the ethyl groups and the benzene ring were totally absent. Similar observations were made for the phenol−dimethylmethylsilane complex.[12]

(20) Kim, S. K.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.

JP801035U