Estimation of Intramolecular Hydrogen Bond Energy via Molecular Tailoring Approach

Milind M. Deshmukh,[†] Shridhar R. Gadre,[*,†] and Libero J. Bartolotti[‡]

Department of Chemistry, University of Pune, Pune 411 007, India, and Department of Chemistry, East Carolina University, Science and Technology Building, Suite 300, Greenville, North Carolina 27858-4353

Received: September 7, 2006

A novel method, based on the molecular tailoring approach for estimating intramolecular hydrogen bond energies, is proposed. Here, as a case study, the O−H···O bond energy is directly estimated by addition/subtraction of the single point individual fragment energies. This method is tested on polyhydroxy molecules at MP2 and B3LYP levels of theory. It is seen to be able to distinguish between weak (∼1 kcal mol^{-1}) and moderately strong (∼5 kcal mol^{-1}) hydrogen bonds in polyhydroxy molecules.

1. Introduction

Hydrogen bonding is an important weak interaction encountered in gas, liquid, as well as solid phases. The hydrogen bond plays a very vital role in many life processes and is one of the most frequently used terms in chemistry and biology.[1] The concept of the hydrogen bond was first highlighted by Pauling in his famous paper on the nature of the chemical bond.[2] In general, a hydrogen bond may be denoted by X−H···Y, where X−H is a proton donor and Y is a proton acceptor. Classically hydrogen bonded neutral molecular systems[1a] involve interactions such as O−H···O, N−H···O, N−H···N, S−H···O, etc. ranging from ∼1−4 kcal mol^{-1} for weak, 4−15 kcal mol^{-1} for moderate, and 15−40 kcal mol^{-1} for a very strong hydrogen bond. Typical H···Y distances for such strong, moderate, and weak hydrogen bonds are ∼1.2−3.0 Å and X−H···Y angles lie in the range 100−180° for such X−H···Y interactions.[1] The estimation of intermolecular hydrogen bond strength is much less intricate as compared to the intramolecular one. A large number of experimental as well as theoretical methods are reported in the literature aiming at quantification of the intermolecular interaction energies.[3] A direct estimation of intramolecular hydrogen bond energy is, however, rendered difficult because of the variation in the definition of such a bond,[4] and hence indirect methods have to be employed. Spectroscopic[5] and electron density topographical approaches[6] have also been applied for gauging the strength of the intramolecular hydrogen bonds. However, in general, very few direct attempts have reported for approximate theoretical estimation[7−12] of intramolecular hydrogen bond energy, wherein the energies of different conformers of the molecule are added/subtracted together. Some of these methods are briefly discussed below.

Conformational Analysis. In this method, the energy of a hydrogen bond is calculated by comparing the energy of two different conformers. Generally, these conformers are chosen such that the hydrogen bond is retained in one conformer and broken in another. The energy difference between the two conformers is then taken as the measure of intramolecular hydrogen bond. This method is generally called as cis−trans method since the hydrogen bond energy is the energy difference between the cis and trans conformers.

Ortho−Para Approach. As the name suggests, the hydrogen bond energy of the X−H···Y bond formed by two ortho substituents is extracted by taking the energy difference between the ortho and para forms of the molecule under consideration. The use of this method is found to be quite convincing.[13] However, the method is applicable only to aromatic systems in which a hydrogen bond is present in two ortho substituents.

Isodesmic/Homodesmic Reactions. In this method, the intramolecular hydrogen bond making/breaking reaction is written in such a way that the numbers and types of bonds on either side of the reactions are equal.[9] Recently this method has been applied to a number of different substituents at the aromatic subtrates.[14]

The reliability of the above methods is a subject of debate. It has been shown that the cis−trans method provides reasonably accurate hydrogen bond energies.[11a] However, the recent studies reported in the literature show that the cis−trans method for catechol overestimates the hydrogen bond enthalpy[8−10] due to the repulsive interaction between the oxygen atoms in trans conformer. The enthalpy of a hydrogen bond estimated using the isodesmic reactions is in general found to be underestimated.[13] Rozas et al.[9] have remarked that the cis−trans method gives an idea about which rotamer is stable but cannot be used to estimate the hydrogen bond energy. It is shown by them that the use of isodesmic reaction provides reasonable results. However, the detailed comparison of these three methods due to Estacio et al.[13] suggests that the ortho−para method is most reliable. There are few variants of the above methods for the intramolecular hydrogen bond energy estimation.[10]

In another recent and qualitatively different method,[15] a fragment molecular orbital Hamiltonian algorithm has been applied to oligopeptides, $(Gly)_n$. An individual residue is considered as a single fragment and the interresidue interaction energy is estimated from the single point energy of the pair of fragments. This interaction energy may be approximately taken as the O···H−N intramolecular hydrogen bond energy although some other weak interactions may also be involved in this estimation.

An examination of the above-mentioned literature leads us to a query: Is a direct estimation, albeit somewhat approximate, of hydrogen bond energy theoretically possible? A method for

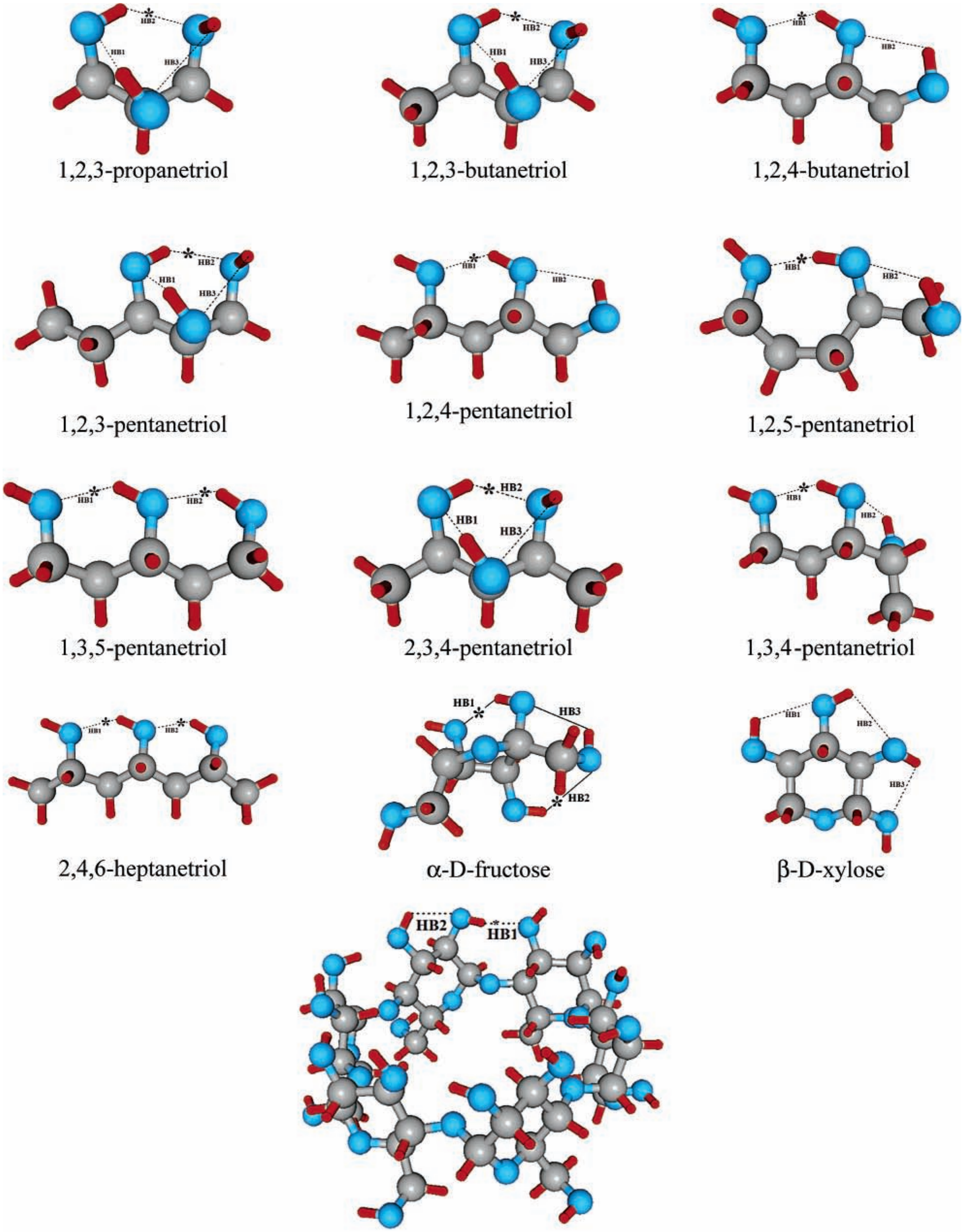
---

[*] To whom correspondence should be addressed. Email: gadre@chem.unipune.ernet.in.

[†] University of Pune.

[‡] East Carolina University.

10.1021/jp065836o CCC: $33.50



1,2,3-propanetriol
1,2,3-butanetriol
1,2,4-butanetriol
1,2,3-pentanetriol
1,2,4-pentanetriol
1,2,5-pentanetriol
1,3,5-pentanetriol
2,3,4-pentanetriol
1,3,4-pentanetriol
2,4,6-heptanetriol
α-D-fructose
β-D-xylose
α-cyclodextrin

Figure 1. Optimized geometries of some polyhydroxy compounds at MP2 (frozen core)/6-311++G(2d,2p) level, except α-cyclodextrin, which is optimized at the B3LYP/6-311++G(d,p) level. An asterisk denotes a (3,−1) density BCP. See Table 1 for energies and text for details.

this purpose, based on molecular tailoring approach (MTA),[16] recently developed in our laboratory, is proposed in the present work and applied to the intramolecular hydrogen bond energy estimation for some polyhydroxy compounds.

2. Methodology

Several polyhydroxy compounds (see Figure 1) are optimized at the MP2/6-311++G(2d,2p) (frozen core) level of theory using

TABLE 1: Hydrogen Bond Energies along with Various Properties Calculated at MP2(full)/6-311++G(2d,2p) Level of Theory[a]

molecules	O−H···O distances (Å)	E(HB) (kcal mol^{-1})	ρ at (3, -1) BCP (au)	frequency (cm^{-1})	$\Delta E^a = \lvert E_{\mathrm{M}} - E_{\mathrm{e}} \rvert$ (kcal mol^{-1})
1,2,3-propanetriol	2.16(HB1)	1.90 (2.00)[b]		3784	
E_{M}: -344.21170	2.08(HB2)	2.47 (2.56)[b]	0.02008	3765	0.50
E_{e}: -344.21091	2.58(HB3)	1.63 (1.66)[b]		3845	
1,2,3-butanetriol	2.13(HB1)	2.13		3768	
E_{M}: -383.44517	2.05(HB2)	2.72	0.02108	3745	0.50
E_{e}: -383.44437	2.58(HB3)	1.60		3844	
1,2,4-butanetriol	1.98(HB1)	2.90	0.02189	3789	
E_{M}: -383.43912	2.22(HB2)	1.75		3828	0.40
E_{e}: -383.43849				3875	
1,2,3-pentanetriol	2.13(HB1)	2.11		3769	
E_{M}: -422.67178	2.05(HB2)	2.77	0.02117	3743	0.51
E_{e}: -422.67097	2.57(HB3)	1.61		3844	
1,2,4-pentanetriol	1.97(HB1)	3.04	0.02268	3785	
E_{M}: -422.67251	2.22(HB2)	1.77		3827	0.42
E_{e}: -422.67184				3858	
1,2,5-pentanetriol	1.80(HB1)	4.97	0.03338	3669	
E_{M}: -422.66590	2.25(HB2)	1.78		3825	0.55
E_{e}: -422.66502				3865	
1,3,5-pentanetriol	1.94(HB1)	2.91	0.02251	3763	
E_{M}: -422.66727	1.96(HB2)	2.90	0.02393	3792	0.58
E_{e}: -422.66635				3875	
2,3,4-pentanetriol	2.12(HB1)	2.18		3759	
E_{M}: -422.67861	2.02(HB2)	2.94	0.02231	3731	0.52
E_{e}: -422.67778	2.56(HB3)	1.50		3820	
1,3,4-pentanetriol	1.91(HB1)	2.86	0.02527	3756	
E_{M}: -422.67242	2.23(HB2)	2.58		3805	0.50
E_{e}: -422.67163				3874	
2,4,6-heptanetriol	1.92(HB1)	3.02	0.02495	3753	
E_{M}: -501.13408	1.93(HB2)	2.94	0.02420	3773	0.65
E_{e}: -501.13304				3857	
α-D-fructose	2.08(HB1)	3.08	0.01855	3755	
E_{M}: -686.05951	2.44(HB2)	2.85	0.00988	3816	0.14
E_{e}: -686.05929	2.48(HB3)	2.83		3839	
β-D-xylose	2.41(HB1)	1.81		3834	
E_{M}: -571.71462	2.45(HB2)	1.75	-	3837	0.01
E_{e}: -571.71463	2.48(HB3)	2.12		3842	
α-cyclodextrin[c]	1.94(HB1)	4.58	0.02426	3605	0.28
E_{M}: -3665.68068	2.38(HB2)	2.40		3780	
E_{e}: -3665.68024					

[a] The average error $\lvert E_{\mathrm{M}} - \mathrm{Ee} \rvert$ of all the 12 cases (excluding Cyclodextrin) turns out to be 0.44 kcal mol^{-1}. [b] The respective hydrogen bond energy calculated at MP2(full)/ AUG-cc-pVTZ level. [c] Optimized geometry at B3LYP/6-311++G(d,p) level is used. [d] The energies in au of the original molecules (E_{M}) and those calculated by fragmentation (E_{e}) are also shown in the first column. See text for details.

the Gaussian package.[17] This list of molecules includes 10 triols (propanetriol to heptanetriol), two sugar molecules, and α-cyclodextrin (which is optimized at the B3LYP/6-311++G(d,p) level). For the case of triols and sugars, at least 15 different conformers of each were employed as starting geometries. The lowest-energy conformers were verified to be local minima on the potential energy surface by carrying out frequency calculations. The corresponding O−H stretching frequencies are also evaluated from these calculations (see Table 1). Further, the topography of the molecular electron density, $\rho(\mathbf{r})$, is mapped[18] for these molecules. The intramolecular hydrogen bond energy is calculated for these molecules using the fragmentation approach.[16] The present fragmentation procedure is illustrated for 1,2,4-pentanetriol in Figure 2. Here, the original molecule (M) is cut into three overlapping fragments F1, F2, and F3 that are obtained by replacing a −OH group with a hydrogen atom. These cut regions are shown by dotted circles on the original molecule. Fragments F4, F5, and F6 are obtained by taking the intersection of these basic fragments, i.e., (F1∩F2), (F1∩F3), and (F2∩F3), respectively. The fragment F7 is the common intersection of three fragments F1, F2, and F3, i.e., (F1∩F2∩F3). A single point energy evaluation has been carried out on all seven fragments obtained by above fragmentation procedure at the MP2(full)/6-311++G(2d, 2p) level of theory. The fragments are *not optimized* so that conformational changes in them are avoided. An approximate estimation of energy of medium-sized molecules has been proposed by Collins and co-workers[19] using the divide-and-conquer approach. Such an energy estimation has also recently been independently proposed and tested for a set of overlapping fragments in our laboratory.[16c] The results of the intramolecular hydrogen bond energies of the chosen set of molecules along with the benchmark estimation of the respective molecular energies are presented in the following section.

3. Results and Discussion

We first present the results of the MTA approach for the case of the 1,2,4-pentanetriol molecule discussed above. The approximate estimated energy (E_{e}) for this molecule, employing the fragmentation scheme in Figure 2, is given as: $E_{\mathrm{e}} = E_{\mathrm{F1}} + E_{\mathrm{F2}} + E_{\mathrm{F3}} - E_{\mathrm{F4}} - E_{\mathrm{F5}} - E_{\mathrm{F6}} + E_{\mathrm{F7}} = -422.67184$ au. The actual energy of the original molecule (M) is $E_{\mathrm{M}} = -422.67251$ au, confirming that the error in the MTA-based energy calculation is indeed rather small, viz. $\sim$0.42 kcal mol^{-1}. Thus the present approach is capable of providing a good estimate of molecular energy by using the fragments of the molecule. The hydrogen bond energy E_{HB1} for 1,2,4-pentanetriol is calculated as $(E_{\mathrm{F1}} + E_{\mathrm{F2}} - E_{\mathrm{F4}}) - E_{\mathrm{e}} = -422.66700 - (-422.67184) = 0.00485$ au $= 3.04$ kcal mol^{-1}. Similarly, E_{HB2} evaluated from F2, F3, and F6 turns out to be 1.77 kcal mol^{-1}.

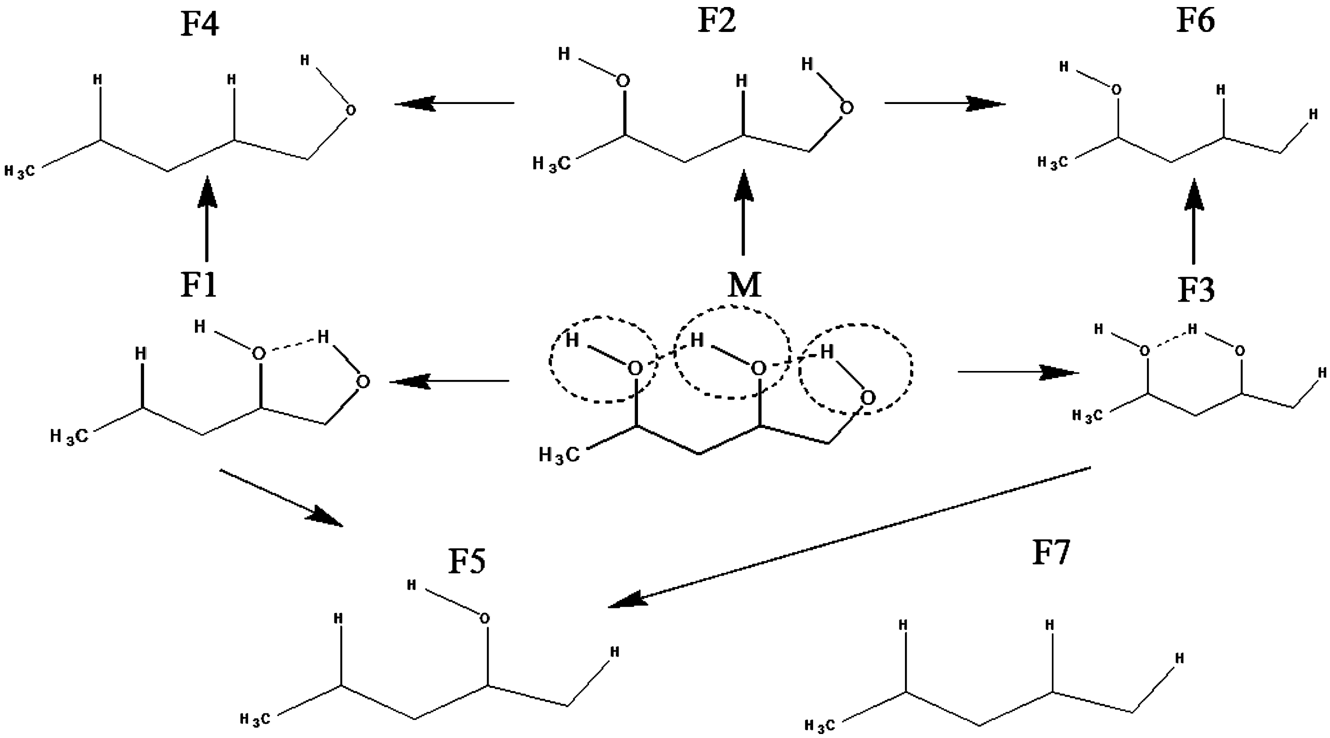


Figure 2. Fragmentation scheme for 1,2,4-pentanetriol (shown as M) at MP2(full)/6-311++G(2d,2p) level. See text for details of fragmentation. The energies of fragments F1−F7 and M are: −347.54088, −347.53867, −347.55112, −272.41256, −272.42050, −272.42077, −197.29500, and −422.67251 au, respectively.

In a similar fashion, the hydrogen bond energies are estimated for all the other molecules. Table 1 displays the calculated hydrogen bond energies of the polyhydroxy molecules ranging from 1,2,3-propanetriol to α-cyclodextrin molecule. The estimated hydrogen bond energies (E_{HB1}, E_{HB2}, and E_{HB3}) for 1,2,3-propanetriol at two different levels of theory, viz. MP2(full)/6-311++G(2d,2p) and MP2(full)/AUG-cc-pVTZ are (1.90, 2.47, and 1.63 kcal mol^{-1}) and (2.00, 2.56, and 1.66 kcal mol^{-1}), respectively (see Table 1 for details). This suggests that, for good-quality basis sets, the relative magnitudes of the hydrogen bond energies are *only marginally* dependent on the basis set employed. It is difficult to estimate the basis set superposition error (BSSE) for these molecules due to the methodology involved. However, the use of triple-ζ quality basis set such as 6-311++G(2d,2p) is expected to reduce significantly the BSSE correction.[20] By consideration of this accuracy, we estimate the error associated with our calculated hydrogen bond energies to be in the range of ±0.5 kcal mol^{-1}. This is based on the average error in calculating E_e for 12 molecules using MTA approach. It is clear from Table 1 that the estimated hydrogen bond energies fall in a range expected from chemical intuition and are able to distinguish the strong and weak hydrogen bonds. The hydrogen bond energies vary between 1.50 and 4.97 kcal mol^{-1}. Particularly noteworthy is the strongest hydrogen bond (4.97 kcal mol^{-1}) among the alkanetriols, viz. that for 1,2,5-pentanetriol.

The distinction between the two types of hydrogen bonds in α-cyclodextrin is also quite prominent. The corresponding hydrogen bond energies in this case turn out to be 2.40 and 4.58 kcal mol^{-1} at the B3LYP/6-311++G(d,p) level. The O−H stretching frequencies for the case of α-cyclodextrin molecule are also in line with the estimated hydrogen bond energies. It may be noted that these calculations are at B3LYP/6-311++G(d,p) level of theory and hence the frequency values are not quantitatively comparable to those for the other cases.

An empirical equation suggested by Espinosa et al.[21] gives the hydrogen bond energy to be half of the potential energy density at (3,−1) $\rho(\mathbf{r})$ bond critical point (BCP) at the H−O···H bond. The works due to Espinosa et al.[6b] and Klein[6c,6d] have employed this relation for the estimation of hydrogen bond energies. On the other hand, our method offers a direct energy based approach toward such estimation. We present below a very brief discussion on connection with the electron density topography and vibrational O−H stretching frequencies (cf. Table 1).

The presence of (3,−1) $\rho(\mathbf{r})$ BCP at O−H···O bond is generally considered as the manifestation of hydrogen bond.[6] However, such a (3,−1) BCP at O−H···O bond is seen to be conspicuous by its absence in all the polyols having an O−H···O interactions between vicinal −OH groups.[6c−e,9] From Table 1, it is seen that the $\rho(\mathbf{r})$ value corresponding to the strongest hydrogen bond ($E_{\mathrm{HB}} = 4.97$ kcal mol^{-1}), at (3,−1) BCP is the highest (0.03338 au). In case of weakest hydrogen bond ($E_{\mathrm{HB1}} = 1.50$ kcal mol^{-1}), (3,−1) BCP at O−H···O bond is absent. To the best of the authors' knowledge, the absence of (3,−1) BCP for the O−H···O bond formed between vicinal −OH groups was first noticed by Klein.[6c,6d] However, the existence of the intramolecular hydrogen bond between the vicinal −OH group in 2,3-butanediol is suggested in the literature[22] with the corresponding enthalpy of such a H-bond being estimated between 1.3 and 1.9 kcal mol^{-1} even though there is no (3,−1) $\rho(\mathbf{r})$ BCP found in this case. This is in agreement with our energies for hydrogen bond formed between vicinal −OH groups. Also the absence of (3,−1) BCP is reported in the literature[9] when there is a formation of a five-membered ring and BCP is found only for the case of a six- or higher-membered ring.[9] The strongest hydrogen bond ($E_{\mathrm{HB1}} = 4.97$ kcal mol^{-1}) is noticed for 1,2,5-pentanetriol, involving the formation of a seven-membered ring. The $\rho(\mathbf{r})$ value at the (3,−1) O−H···O

BCP lies typically between 0.009 and 0.033 au for all the relevant cases.

Similarly, a reasonable qualitative agreement between the estimated hydrogen bond energies and the respective unscaled O−H bond stretching frequencies is seen for all the cases. Here the strongest hydrogen bond is found in 1,2,5-pentanetriol ($E_{\mathrm{HB1}} = 4.97$ kcal mol^{-1}) with the corresponding O−H bond stretching frequency of value 3669 cm^{-1} (see Table 1) and the weakest bond ($E_{\mathrm{HB}} = 1.50$ kcal mol^{-1}) is noticed in 2,3,4-pentanetriol with the corresponding O−H bond stretching frequency of value 3820 cm^{-1}. The calculated hydrogen bond energies show a good qualitative rank-order relationship with the corresponding calculated O−H bond stretching frequencies. It is seen from Table 1 that the signature of an −OH group getting involved in hydrogen bonding is reflected in corresponding O−H stretching frequency being less than 3845 cm^{-1}. The hydrogen bond energy is generally found to lie between 1.5 and 5 kcal mol^{-1} with the corresponding O−H stretching frequency ranging between 3845 and 3669 cm^{-1}. In summary, the estimated H-bond energies show a good qualitative rank-ordering with O−H stretching frequencies as well as $\rho(\mathbf{r})$ at (3,−1) BCP.

4. Concluding Remarks

In conclusion, a novel method for the estimation of intramolecular hydrogen bond energy based on the MTA has been proposed in this article. The present approach is tested out on some polyhydroxy compounds wherein only the single point energies of fragments are used for the estimation of intramolecular hydrogen bond energy. The average error in the estimation of total energy of molecules is less than 0.5 kcal mol^{-1}. The estimated intramolecular hydrogen bond energies range from ∼1 to 5 kcal mol^{-1}. The estimated hydrogen bond energies show a qualitative rank ordering with the corresponding −OH stretching frequencies and $\rho(\mathbf{r})$ value at (3,−1) BCP. It is hoped that the method proposed in this article, being quite general, finds wide applications to interesting diverse chemical and biological systems.

Acknowledgment. Authors are thankful to Mr. V. Ganesh, P. Balanarayan, and Dr. S. P. Gejji for the useful discussions. We are also grateful to the Centre for Developing Advanced Computing, Pune, as well as the University Grants Commission (UGC), New Delhi, for support under CAS (Pune University), and UPE program of the University of Hyderabad for the Computer time. M.M.D. is thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, for the award of a Fellowship.

Supporting Information Available: Table showing the optimized geometries of various polyhydroxy compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Jeffery, G. A. *An Introduction to Hydrogen bonding*; Oxford University Press: New York 1997. (b) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: Oxford, 1999.

(2) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 167.

(3) (a) Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533. (b) Sánchez-García, E.; George, L.; Montero, L. A.; Sander, W. *J. Phys. Chem. A* **2004**, *108*, 11846. (c) Munshi, P.; Row: T. N. G. *J. Phys. Chem. A* **2005**, *109*, 659. (d) Cockroft, S. L.; Hunter, C. A.; Lawso, K. R.; Perkins, J.; Urch, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 8594.

(4) (a) Kollman, P. A.; Leland, C. A. *Chem. Rev.* **2001**, *101*, 1385. (b) Grabowski, S. J. *J. Phys. Org. Chem.* **2004**, *17*, 18.

(5) (a) Bellamy. *Advances in Infrared Group Frequencies*; Methuen: London, 1968; p 241. (b) Glasel, J. A. In *Water: A Comprehensive Treatise*; Frank, F., Ed.; Plenum Press: New York & London, 1982; Vol. 1, Chapter 6, p 223. (c) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(6) (a) Fuster, F.; Silvi, B. *Theor. Chem. Acc.* **2000**, *104*, 13 and references therein. (b) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. *J. Chem. Phys.* **2002**, *117*, 5529 and references therein. (c) Klein, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 13931. (d) Klein, R. A. *J. Comput. Chem.* **2003**, *24*, 1120 and references therein. (e) Deshmukh, M. M.; Sastry, N. V.; Gadre, S. R. *J. Chem. Phys.* **2004**, *121*, 12402. (f) Grabowski, S. J.; Sokalski, W. A.; Leszczyñski, J. *J. Phys. Chem. B* **2006**, *110*, 6444.

(7) Kovács, A.; Szabó, A.; Hargittai, I. *Acc. Chem. Res.* **2002**, *35*, 887.

(8) Chung, G.; Kwon, O.; Kwon, Y. *J. Phys. Chem. A* 1**997**, *101*, 9415.

(9) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2001**, *105*, 10462 and references therein.

(10) Lipkowski, P.; Koll, A.; Karpfen, A.; Wolschann, P. *Chem. Phys. Lett.* **2002**, *360*, 256.

(11) (a) Buemi, G.; Zuccarello, F. *J. Mol. Struct. THEOCHEM* **2002**, *581*, 71. (b) Korth, H.-G.; de Heer, M. I.; Mulder, P. *J. Phys. Chem. A* **2002**, *106*, 8779. (c) Kjaergaard, H. G.; Howard, D. L.; Schofield, D. P.; Robinson, T. W.; Ishiuchi S.; Fujii, M. *J. Phys. Chem. A* **2002**, *106*, 258. (d) Foti, M. C.; Johnson, E. R.; Vinqvist, M. R.; Wright, J. S.; Barclay, L. R. C.; Ingold, K. U. *J. Org. Chem.* **2002**, *67*, 5190.

(12) (a) Zhang, H.-Y.; Sun, Y.-M.; Wang, X.-L. *Chem.*−*Eur. J.* **2003**, *9*, 502. (b) Bakalbassis, E. G.; Lithoxoidou, A. T.; Vafiadis, A. P. *J. Phys. Chem. A* **2003**, *107*, 8594.

(13) Estacio, S. G.; Cabral do Counta, P.; Costa Cabral, B. J.; Minas Da Piedade, M. E.; Martinho Simoes, J. A. *J. Phys. Chem. A* **2004**, *108*, 10834 and references therein.

(14) Roy, D.; Sunoj, R. B. *J. Phys. Chem. A* **2006**, *110*, 5942.

(15) Ishimoto, T.; Tokiwa, H.; Teramae, H.; Nagashima, U. *J. Chem. Phys.* **2005**, *122*, 094905.

(16) (a) Babu, K.; Ganesh, V.; Gadre, S. R.; Ghermani, N. E. *Theor. Chem. Acc.* **2004**, *111*, 255. (b) Gadre, S. R.; Babu, K.; Ganesh, V. In *Proceedings of NRB Seminar*; Maheshwari, S. N., Ed.; Viva Books: New Delhi, 2005, p 86. (c) Ganesh, V.; Dongare, R. K.; Balanarayan, P.; Gadre, S. R. *J. Chem. Phys.* **2006**, *125*, 104109.

(17) Frisch, M. J., Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; 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.; Petresson, P. G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; 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 C.02, Gaussian, Inc.; Wallingford, CT, 2004.

(18) Program UNIPROP, the molecular property calculation package, developed by Theoretical Chemistry Group, Department of Chemistry, University of Pune, Pune, India. See: (a) Bapat, S. V.; Shirsat, R. N.; Gadre, S. R. *Chem. Phys. Lett.* **1992**, *200*, 373. (b) Balanarayan, P.; Gadre, S. R *J. Chem. Phys.* **2003**, *119*, 5037.

(19) Deev, V.; Collins, M. A. *J. Chem. Phys.* **2005**, *122*, 154102.

(20) Scheiner, S. *Hydrogen bond*; Oxford, New York, 1997.

(21) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170.

(22) Jesus, A. J. L.; Rosado, M. T. S.; Reva, I.; Fausto, R.; Eusebio, M. E.; Redinha, J. S. *J. Phys. Chem. A* **2006**, *110*, 4169.