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Ab initio studies of methanol, methanethiol and methylamine dimer

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Received 27 April 2002; accepted 26 June 2002

Abstract

Quantum chemical calculations are used to provide structural, vibrational and energetical information on the dimers of the methanol, methylamine and methanethiol systems. These systems were studied employing the DFT(B3LYP) and MP2 methods together with the 6-31 + G** and 6-311 + G** basis sets. We found two distinct potential minima for methylamine (one of them is a transition structure) and methanethiol, and one for the methanol dimer. The properties of these dimers are compared with those of the dimers (H₂O)₂, (NH₃)₂ and (CH₃SH)₂. The interactions in these dimers were analyzed using electron density properties at the bond critical point. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bonds; Methanethiol; Methylamine dimer

1. Introduction

Understanding the properties of solutions from the peculiarities of their components is of key importance in chemistry. Molecules in clusters or solutions are usually bound to each other via weak van der Waals or stronger hydrogen-bonded interactions. The role of hydrogen bonds (HB) in the structure and stability of molecular complexes in solution remains an area of active research [1,2]. This type of interaction causes a red shift in the frequencies of vibrational modes specifically involved in the interaction.

There are a large number of original and review articles covering the properties of hydrogen-bonded dimers [1–7]. The application of ab initio methods to this type of problems has already indicated that the Hartree Fock (HF) method inaccurately predicts

geometries and interaction energies of hydrogen-bonded system. On the other hand, it has been shown that the hybrid type density functional theory (B3LYP) predicts hydrogen bonding geometries and energies that are in good agreement with MP2 results [4].

In the present article we report a study of the methanol (CH₃OH), methylamine (CH₃NH₂) and methanethiol (CH₃SH) dimers using B3LYP density functional theory and MP2 ab initio methods with various basis sets. The hydrogen bond between methanol molecules has already been the subject of an extensive research [8–12]. Previous studies mainly examined the structure and binding energies of this dimer, and rarely the vibrational frequencies, which are frequently used to characterize the hydrogen bond. We found only one ab initio calculation in the literature for the methylamine clusters consisting of up to four molecules. Cabalaeiro-Lago et al., studied these clusters by using HF, DFT/B3LYP and MP2

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ab initio methods using the 6-31 + G* basis set [13–15]. According to their results, the minimum energy on the potential surface of methylamine dimer is about -13 kJ/mol. The structural and energetic properties of the methanethiol dimer were studied only at the HF level [16].

The H₂O, NH₃ and H₂S dimers, which are the simple analogs of the methanol, methylamine and methanethiol molecules, respectively, have already been studied [3,17–19]. The dimer properties of these hydrogenated complexes were compared with our results. The main goal of the present work was to characterize the strength of the HB in these dimers.

1.1. Computational methods

All calculations were performed using the GAUSSIAN98 program system [20]. The structures of dimers were fully optimized with B3LYP/6-31 + G**, B3LYP/6-311 + G**, MP2/6-31 + G** and MP2/6-311 + G** levels of theory. It has already been shown in several examples that a proper description of hydrogen-bonded clusters requires the use of a flexible basis set, which should include diffuse components [8,21]. The nature of the calculated stationary point was always characterized by their harmonic vibrational frequencies. The interaction energies for each minimum were corrected for basis set superposition error (BSSE) with the full counterpoise (CP) procedure resulting in a more reliable estimate of the interaction energy [22]. Harmonic frequencies were used without any scaling factor to evaluate the zero-point energy (ZPE) correction.

2. Results

2.1. Methanol

The key features of the hydrogen bond in methanol dimers are the typically short O...O distance and the near linearity of the OH...O arrangement. The structural data and the interaction energies corresponding the global energy minimum configuration (Fig. 1) are shown in Table 1. These results indicate that the HB lengths are quite similar using the two methods. Our data are in good agreement with earlier results [8–12]. It can be seen in Table 1 that the OH

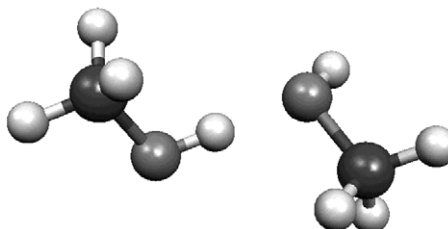


Fig. 1. The optimized structure of the methanol dimer (M1).

stretching frequency of the dimer undergoes red shift by about $130\text{--}177\text{ cm}^{-1}$ using either the B3LYP or MP2 method. The observed experimental red shift of the OH frequency is about $130\text{--}160\text{ cm}^{-1}$ [12]. Fig. 1 illustrates the energy minimum configuration of methanol dimers. The total interaction energy is about $14.6\text{--}15.0$ kJ/mol.

2.2. Methanethiol

During the optimization of methanethiol dimers two energy minimum configurations were obtained by both the B3LYP and MP2 methods. Fig. 2 shows the structures of both dimer configurations; Table 2 lists the intra and intermolecular distances and the intermolecular energy of the methanethiol dimers (T1, T2).

The T2 dimer corresponds to an open hydrogen bond like structure in agreement with the previous calculation [16]. The intermolecular SS distances are about 10% shorter than those obtained by the HF method [16]. The total binding energy is smaller by about $1.0\text{--}1.3$ kcal/mol using the present B3LYP density functional theory. The frequency red shift for this dimer to about $50\text{--}30\text{ cm}^{-1}$ for the B3LYP or

Table 1
Calculated properties for methanol dimer

	B3lyp/b	B3lyp/c	Mp2/b	Mp2/c
Dipole(mo)	1.90	1.89	2.07	2.02
Dipole(di)	2.99	3.15	3.10	3.29
O–O	2.86	2.87	2.85	2.84
O–H	1.89	1.90	1.891	1.88
F(O–H1)	3841(3842)	3844(3845)	3890(3899)	3905(3913)
F(O–H2)	3680	3691	3722	3782
$\Delta E1$	4.15	3.35	3.46	3.50

Distances are given in Å, and dipole moment in Debye and energetic properties in kcal/mol (monomer data are in parentheses).

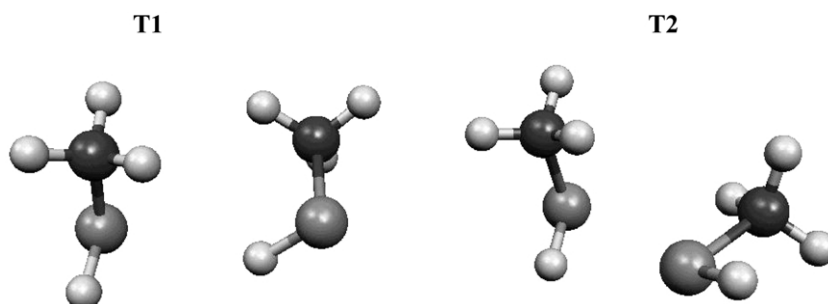


Fig. 2. The optimized structures of methanethiol dimers (T1,T2).

MP2 method, respectively. This is the global minimum on the interaction energy surface if we apply the B3LYP method.

The COH planes of the molecules in the T1 dimer are almost perpendicular to each other. Here the S–S distance is shorter by about 0.1–0.3 Å and the S–H distance is longer by about 0.5–0.3 Å than in the T2 dimer. The corresponding frequency shift with respect to the methanethiol monomer is 1–4 cm^{−1}. This shift is significantly smaller than the same value in the T2 dimer. The total dipole moment in this dimer is higher than in the T1 dimer.

Novoa and Sosa [3] have already shown that density functional theory is not an appropriate model for study of the energetics of weakly hydrogen-bonded complexes. We believe that the MP2 results give a proper description for this type of dimers.

2.3. Methylamine monomer and dimer

The results for the methylamine monomer obtained with the different basis sets and computational methods are found in Table 3. These results are very similar to those obtained at the MP2/6-311 + G(3df,2p) level in a previous study of methylamine monomer [13,15]. The experimental dipole moment of methylamine molecule is about 1.31 Debye [13]. It can be seen in Table 3 that the monomer dipole moment is about 10–15% higher than the experimental value. The discrepancy is likely due to the limitation of the basis sets used in our calculations.

We found two different dimer configurations for methylamine (A1,A2). These dimers are shown in Fig. 3 and the most important structural and energetic data for the dimers are found in Table 3.

One of them (A2) is an open type hydrogen-bonded structure. A similar dimer configuration was found in the earlier work using a different basis set [13]. The main differences between the results provided by the two different methods used here were in the hydrogen-bonded distance and the interaction energy. The hydrogen-bonded distance is about 0.06–0.08 Å shorter if we apply the DFT/B3LYP method. The interaction energy provided by the DFT/B3LYP method is about 20–30% smaller than the value, which is obtained using the MP2 method. This type of deficiency of DFT/B3LYP method has already been pointed out by Novoa and Sosa [3].

Table 2
Calculated properties for methanethiol (T1,T2) dimers

	B3lyp/b	B3lyp/c	Mp2/b	Mp2/c
<i>T1 structure</i>				
S–S	4.10	4.13	4.07	4.08
S–H	2.82	2.80	2.82	2.82
Dipole(mo)	1.76	1.703	1.81	1.77
Dipole(di)	1.40	1.61	1.59	1.05
<i>F</i> (S–H1)	2679(2684)	2669(2668)	2824(2829)	2806(2807)
<i>F</i> (S–H2)	2633	2617	2799	2783
Δ <i>E</i> 1	0.7	0.47	0.52	0.56
<i>T2 structure</i>				
S–S	3.99	4.05	3.79	3.78
S–H	3.48	3.47	3.16	3.19
Dipole(mo)	1.76	1.70	1.81	1.77
Dipole(di)	1.72	1.70	2.25	2.21
<i>F</i> (S–H1)	2687(2684)	2667(2668)	2826(2829)	2803(2807)
<i>F</i> (S–H2)	2683	2671	2829	2806
Δ <i>E</i> 1	0.49	0.34	0.87	1.04

Distances are given in Å, and dipole moment in Debye and energetic properties in kcal/mol (monomer data are in parentheses).

Table 3

Calculated properties for methylamine (A1(transition structure), A2) dimers

	B3lyp/b	B3lyp/c	Mp2/b	Mp2/c
<i>A1 structure</i>				
N···N	3.23	3.24	3.16	3.16
N···H	2.22	2.24	2.21	2.21
Dipole(mo)	1.47	1.41	1.55	1.52
Dipole(di)	2.49	2.43	2.09	2.046
<i>F</i> (N–H1)	3590, 3505 3567, 3437 (3599, 3511)	3573,3499 3567, 3434 (3582, 3505)	3681, 3533 3663, 3577 (3697, 3590)	3637,3619 3544, 3498 (3651, 3555)
$\Delta E1$	1.95	1.64	2.79	2.91
<i>A2 structure</i>				
N···N	3.19	3.20	3.10	3.13
N···H	2.54	2.546	2.44	2.48
Dipole(mo)	1.47	1.41	1.55	1.52
Dipole(di)	0.293	0.272	0.072	0.15
<i>F</i> (N–H1)	3587(3599)	3571(3582)	3679,3667	3635,3623
<i>F</i> (N–H2)	3493(3511)	3489(3505)	3575,3552	3542,3508
$\Delta E1$	1.6	1.32	1.87	2.45

Distances are given in Å, and dipole moment in Debye and energetic properties in kcal/mol (monomer data are in parentheses).

The other dimer (A1) is a typical example of the two molecules arranged with an anti parallel dipole orientation. This conclusion is drawn from the total dipole moment of this dimer, which is close to zero. The interaction energy of this dimer is about 10–20% smaller than that of the other dimer, but it is quite high. This dimer exhibits a single imaginary frequency range from 36 cm^{-1} with DFT to 16 cm^{-1} with MP2. This means that this is a transition structure. This observation corresponds to the results of Cabalaeiro-Lago et al. [23].

The methylamine presents two N–H stretching modes. The calculated frequencies for the monomer and dimer are shown in Table 3. It can be seen that the A2 dimer shows a large red shift of $30\text{--}70\text{ cm}^{-1}$ and the A1 dimer's red shift is only $10\text{--}20\text{ cm}^{-1}$. In

both cases the N–H symmetric vibration has a higher red shift. The BSSE and ZPE corrections of the interaction energies have been estimated for all the optimized complexes. It can be seen that the BSSE at MP2 level is much higher in the A1 dimer, but in the A2 dimer the two methods give mainly the same BSSE. The ZPE corrections without any scaling factor are larger at the MP2 level by about 30–50%.

In addition to this it is also important to note that the basis set effects is small on the geometries of the dimers. The intermolecular distances in the two dimer configuration do not change by more than 1–2% if we apply the more flexible 6-311 + G** basis set. This effect can mainly be seen in the change of the interaction energy.

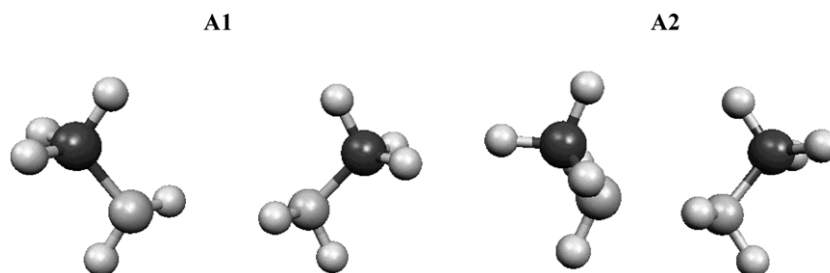


Fig. 3. The optimized structures of methylamine dimers (A1,A2).

Table 4

The selected topological properties of electron density at bcps from MP2/6-311 + G** calculations

Methanol	$\Delta\rho(\text{O}-\text{H}_\text{o})$ 0.10	ρ 0.0275	ϵ 0.053	$\alpha(\text{bcpOH}_\text{o})$ 5.36
Methanethiol T1	$\Delta\rho(\text{S}-\text{H}_\text{s})$ 0.0224	ρ 0.00899	ϵ 0.0346	$\alpha(\text{bSH}_\text{s})$ 10.98
	$\Delta\rho(\text{S}-\text{H}_\text{c})$ 0.0177	ρ 0.0049	ϵ 3.26	$\alpha(\text{bH}_\text{c}\text{S})$ 54.36
Methanethiol T2	$\Delta\rho(\text{S}-\text{H}_\text{c})$ 0.021	ρ 0.0079	ϵ 0.10	$\alpha(\text{bSH}_\text{c})$ 24.9
	$\Delta\rho(\text{S}-\text{H}_\text{s})$ 0.018	ρ 0.0049	ϵ 1.39	$\alpha(\text{bSH}_\text{s})$ 71.39
Methylamine A1	$\Delta\rho(\text{S}_\text{c}-\text{H}_\text{c})$ 0.0074	ρ 0.0021	ϵ 0.0071	$\alpha(\text{bH}_\text{c}\text{H}_\text{c})$ 21.5
	$\Delta\rho(\text{H}_\text{n}-\text{H}_\text{n})$ 0.0504	ρ 0.0116	ϵ 11.29	$\alpha(\text{bH}_\text{n}\text{H}_\text{n})$ 78.9
Methylamine A2	$\Delta\rho(\text{N}-\text{H}_\text{n})$ 0.055	ρ 0.0179	ϵ 0.0105	$\alpha(\text{bNH}_\text{n})$ 5.47
	$\Delta\rho(\text{H}_\text{c}-\text{H}_\text{c})$ 0.0105	ρ 0.0274	ϵ 1.74	$\alpha(\text{bH}_\text{c}\text{H}_\text{c})$ 38.5

3. Topological analysis

The theory of atoms in molecules (AIM) [24] has been widely applied to many chemical problems including the description of hydrogen-bonded systems [25–30]. Topological properties of the conventional $\text{O}-\text{H}\cdots\text{O}$ or $\text{N}-\text{H}\cdots\text{N}$ HB [25,26] and unconventional [26–30] $\text{C}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\pi$ and antihydrogen and dihydrogen bonds were also investigated with this method. The intermolecular bond properties were characterized in terms of the properties of bond critical point ($\nabla_{\rho_\text{c}} = 0$, bcp) like charge density, bond ellipticity (defined as $\epsilon = \lambda_1/\lambda_2 - 1$ where λ_1 and λ_2 are the two negative eigenvalues of the Hessian matrix, and the Laplacian of the charge density. It has already been shown that a correlation exists between the electron density at the bond critical point and

the hydrogen bond energy especially in a system with strong conventional and unconventional HB.

Table 4 reports the computed local topological properties of the electron density of the investigated dimers. Comparing all data for the $\text{N}-\text{H}\cdots\text{N}$, $\text{S}-\text{H}\cdots\text{S}$ and $\text{O}-\text{H}\cdots\text{O}$ bonds it is clear that the methanol dimer, the methylamine dimer A2, and methanethiol dimer T1 are very similar in terms of the topological properties at the bcp. All three have a relatively large electron density at the bcp and the ellipticities of the bcps are also small; this provides a measure for its structural stability. The strongest HB interaction exists between the two-methanol molecules, which correlates well with the corresponding electron density at bcp. In the methylamine dimer A1 a dihydrogen bonded [29] interaction exists between the two molecules. The charge density and the Laplacian of the charge density of this bcp is similar to that found in conventional $\text{N}-\text{H}\cdots\text{N}$ HB like bonds in methylamine dimer A1. In this case the ellipticity of this bonds is extremely high. In the methanethiol dimer T2 two different types of bcp were found. One of them describes an unconventional $\text{C}-\text{H}\cdots\text{S}$ like bonds and the other one a $\text{S}-\text{H}\cdots\text{S}$ like bonds. The charge densities at these bcp are small.

4. Conclusion

The H_2O dimer is a typical example of a moderately strong hydrogen bond. In the NH_3 and H_2S dimers the hydrogen bond is relatively weak. The CH_3 substituted analogs of these dimers were investigated in this paper. The calculated interaction energy with together the corresponding hydrogen bond distances (OO, NN, SS), respectively, are shown in Table 5. For methanol and methylamine the H-bond is stronger than for H_2O and NH_3 . On the other hand in the H_2S dimer the hydrogen bond is stronger than in the methanethiol dimer.

Table 5

The selected properties of methanol, water, H_2S , CH_3SH , NH_3 and methylamine dimers

	MeOH	H ₂ O [3]		MeSH	H ₂ S [17]		MeNH ₂	NH ₃ [3]
OO	2.87	2.90	SS	4.1	4.13	NN	3.24	3.29
−ΔE	4.73	4.48	−ΔE	1.1	0.75	−ΔE	2.71	2.36

We found only one energy minimum in the dimer configuration for methanol and two for CH_3SH and CH_3NH_2 . This methanol dimer configuration is a typical H-bonded complex. One of the minima of the potential energy surface of the methylamine dimer is a hydrogen-bonded like arrangement, but the other transition structure on this surface corresponds to an anti dipole configuration. The $(\text{CH}_3\text{SH})_2$ dimer global minimum has a quadruple like L shape arrangement. The local minimum is the hydrogen-bonded complex. The hydrogen bond strength decrease in the order from $\text{CH}_3\text{OH} > \text{CH}_3\text{NH}_2 > \text{CH}_3\text{SH}$.

Acknowledgments

This work was supported by the Hungarian National Science Foundation OTKA(Grant No: F029738).

References

- [1] G. Jeffrey, G.A. Sanger, Hydrogen Bonding in Biological Structures, Springer, Berlin, 1991.
- [2] A.J. Stone, The Theory of Intermolecular Forces, Clarendon Press, Oxford, 1996.
- [3] J.J. Novoa, C. Sosa, J. Phys. Chem. 99 (1995) 15837.
- [4] M. Lozynski, D. Rusinka-Roszak, H. Mack, J. Phys. Chem. 102 (1998) 2899.
- [5] S. Arulmozhuraja, P. Kolandaivel, J. Mol. Struct. 366 (1996) 123.
- [6] L. Turi, J. Phys. Chem. 100 (1996) 11285.
- [7] A.D. Buckingham, P.W. Fowler, J.M. Hudsud, Chem. Rev. 88 (1988) 963.
- [8] O. Mo, M. Yanez, J. Elguero, J. Chem. Phys. 107 (1997) 3592.
- [9] R.D. Parra, X.C. Zeng, J. Chem. Phys. 110 (1999) 6329.
- [10] I.A. Topol, S.K. Burt, A.A. Rushin, Chem. Phys. Lett. 247 (1995) 112.
- [11] A. Bleiber, J. Sauer, Chem. Phys. Lett. 238 (1995) 243.
- [12] A. Schriver, A. Burneau, J.P. Perchard, J. Chem. Phys. 77 (1982) 4926.
- [13] E.M. Cabaleiro-Lago, M.A. Rios, J. Chem. Phys. 112 (2000) 2155.
- [14] E.M. Cabaleiro-Lago, M.A. Rios, J. Chem. Phys. 113 (2000) 9523.
- [15] G.I. Csonka, L. Sztraka, J. Mol. Struct. 410–411 (1997) 387.
- [16] A.K. Sum, S. Sandler, J. Phys. Chem. A 104 (2000) 1121.
- [17] G. de Oliveira, C.D. Dykstra, Chem. Phys. Lett. 243 (1995) 358.
- [18] A. Bleiber, J. Sauer, Chem. Phys. 238 (1995) 243.
- [19] T.H. Tang, S.J. Knak Jensen, I.G. Csizmadia, J. Mol. Struct. (Theochem) 487 (1999) 275.
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN98 (Revision A. 7), Gaussian Inc., Pittsburgh, PA, 1998.
- [21] G. Alagona, C. Ghio, J. Comput. Chem. 11 (1990) 930.
- [22] S. Boys, F. Bernandi, Mol. Phys. 19 (1970) 553.
- [23] E.M. Cabaleiro-Lago, J. Rodriguez-Otero, J. Mol. Struct. (Theochem) 586 (2002) 225.
- [24] R.F.W. Bader, Atoms in Molecules, Clarendon Press, Oxford, 1990.
- [25] O. Galvez, P.C. Gomez, L.F. Pacios, J. Chem. Phys. 115 (2001) 11166.
- [26] A. Vila, R.A. Mosquera, J.M. Hermida-Ramon, J. Mol. Struct. (Theochem) 541 (2001) 149.
- [27] S. Wojtulewski, S. Grabowski, J. Mol. Struct. (Theochem) 605 (2001) 235.
- [28] S. Grabowski, Chem. Phys. Lett. 338 (2001) 361.
- [29] N.G. Fidanza, F.D. Suvire, G.L. Sosa, R.M. Lobayan, R.D. Enriz, N.M. Perucha, J. Mol. Struct. (Theochem) 543 (2001) 185.
- [30] M.J. Calhorda, P.M. Lopes, J. Organometall. Chem. 609 (2000) 53.