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Computational Methods for Study of Hydrogen Bonding Between Phenol Derivatives with Ethanol

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It is common practice in computational chemistry to model the behaviour of bulky compounds from simplified structures. This procedure enables the use of higher computational levels, with generally improved results. The most crucial problem in this methodology is choosing how simple the structures in question should be. In fact, oversimplification in this context can lead to a highly different behavior relative to starting one. In order to check how valid this approach is, in this work the author modelled intermolecular hydrogen bonding between phenol derivatives with ethanol. The calculations were carried out with the Gaussian 98 suite of programs. The geometry of all structures involved in gas phase is fully optimized at HF at the 6-31G** level. The result shows that strength of hydrogen bonding and the dipole moment in *meta* position is larger than other positions in all system.

Key Words: Hydrogen bonding, *ab initio*, Optimization, Phenol derivatives, Ethanol.

INTRODUCTION

Among all non-covalent interactions, the hydrogen bonding types are particularly significant. Although the term 'hydrogen bond' is widely used, it seems that a precise definition of this phenomenon (accounting for all of its relevant aspects) has not yet been fully agreed upon. Recently a large number of studies devoted to the hydrogen bonding phenomenon have been published (from both experimental and theoretical view points[1,2]), between closed-shell systems[3] or open-shell systems[4] as well as cooperative effect in hydrogen bonded clusters[5-7].

Hydrogen bonding plays one of the most important roles in an arrangement of molecules in crystals[8,9]. A large number of papers appeared dealing with the Lewis acidity and basicity of functional groups involved in H-bonds as for example:nitro[10], formyl[11], carboxylic[12], carbonyl[13,14], hydroxyl[15], *etc.*

Interactions between the hydrogen atom of the phenol group and the solvent reduce the amount of free phenol and the apparent rate constant for hydrogen atom abstraction (PhOH + RO → PhO + ROH) is lower in HB accepting solvents. It is common practice in computational chemistry to model the behavior of bulky compounds from simplified structures. This procedure enables the use of higher computational levels, with generally improved results. The most crucial problem in this methodology is choosing how simple the structures in question should be. In fact, over simplification in this context can lead to a highly different behavior relative to starting one. In order to check how valid this approach is, in this work the author modelled intermolecular hydrogen bonding between {phenol + phenol (A-A), ethanol + ethanol (B-B), phenol + ethanol (A-B), *ortho* methyl phenol + ethanol (C1-B), *meta* methyl phenol + ethanol (C2-B), *para* methyl phenol + ethanol (C3-B), *ortho* chloro phenol + ethanol (D1-B), *meta* chloro phenol + ethanol (D2-B), *para* chloro phenol + ethanol (D3-B), *ortho* flouro phenol + ethanol (E1-B), *meta* flouro phenol + ethanol (E2-B), *para* flouro phenol + ethanol (E3-B), *ortho* nitro phenol + ethanol (F1-B), *meta* nitro phenol + ethanol (F2-B), *para* nitro phenol + ethanol (F3-B)}. The calculations were carried out with the Gaussian 98 suite of programs. Thermo chemical properties have been calculated and analyzed after vibration analysis carried out at the same level of theory with the same basis set. The analysis of the electrical properties was based on atomic electric charges and electric dipole moments and polarizability tensor elements. The aim of the present study is to introduce a new measure to estimate the H-bond strength for heterogeneous systems. This measure is to be useful for typical intermolecular H-bonds and in such cases where the direct estimation of H-bond energy is not possible.

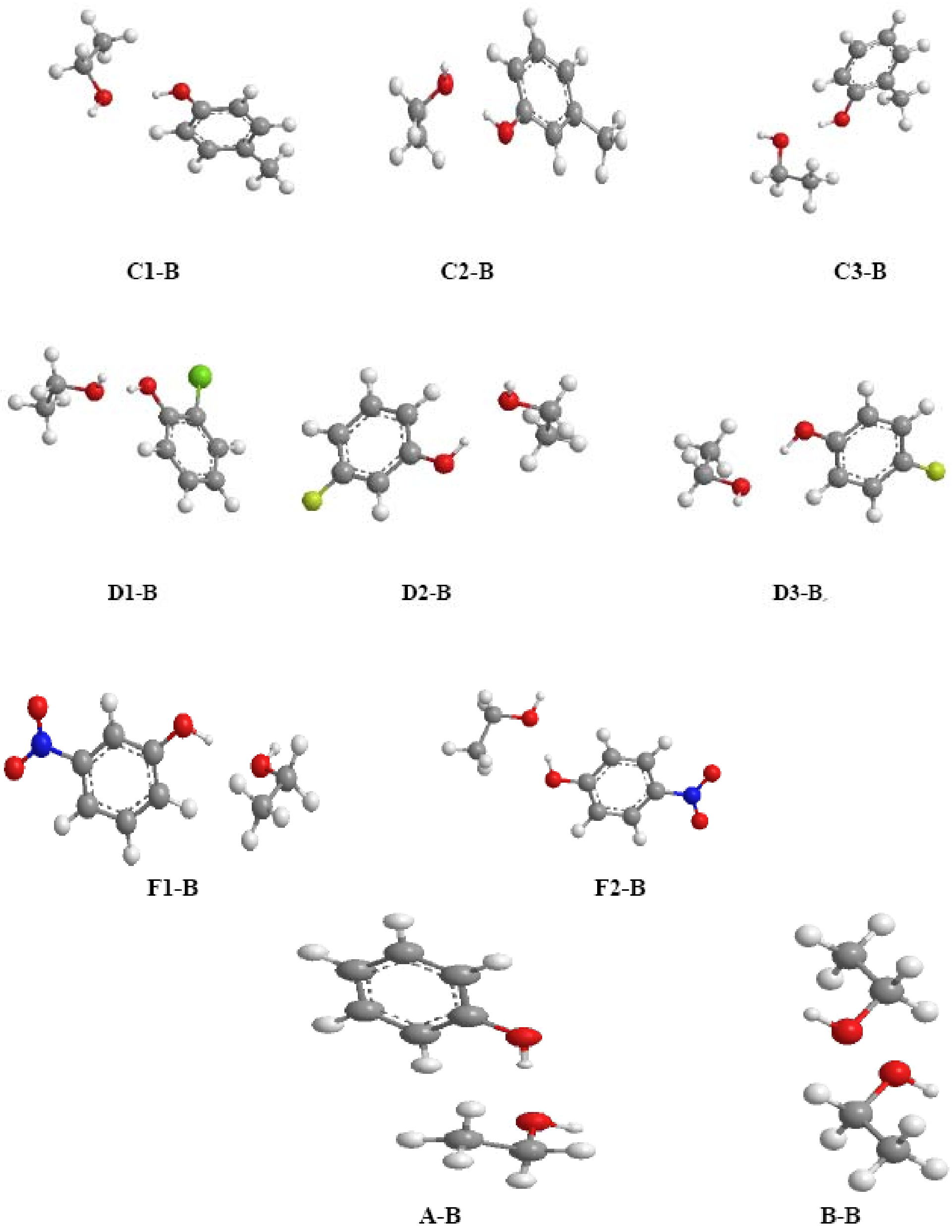
COMPUTATION DETAILS

Calculations were performed using the Gaussian 98 system of codes[16]. The geometries of all components were fully optimized at Hartree Fock computational levels using the basis sets 6-31G**. Calculations were performed on a Pentium-PC computer with a 3000 MHz processor. A starting molecular-mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program[17].

RESULTS AND DISCUSSION

Since intermolecular forces are much weaker than intramolecular ones, standard computational methods of electronic structure theory are not very well suited for applications to intermolecular interactions. In the present study, the geometry optimizations and frequency calculations were performed at the HF level using basis sets 6-31G**. In the Fig. 1 shows the optimized geometrical structures as well as the Wiberg bond orders and the atom-atom overlap–weighted NAO (natural atomic orbital) bond orders. These bond orders are two distinct forms of doing the population analysis as is described elsewhere[18]. Association of one molecule of phenol derivatives with one molecule of ethanol leads to formation of two 1:1 complexes that denotes (C-B[CH_3-phenol + ethanol], {D-B[X-phenol + ethanol] X=F, Cl, Br}, F-B [NO_2-phenol + ethanol].

Tables 1and 2 present geometrical and energetic of the pure compound in the gas phase. The results show that total atomic charge on the oxygen and hydrogen and dipole moment of phenol derivatives depended on position of (X).



C1-B C2-B C3-B

D1-B D2-B D3-B

F1-B F2-B

A-B B-B

Fig. 1. Schematic representation of H-bond clusters between phenol derivatives and Ethanol optimized at HF/6-31G(d,p)

In the *ortho* position the dipole moment is large and the total atomic charge on (O) and (H) depends on induction effect substitution. The angle of (< O–H) in the *para*-position for all derivatives is large.

TABLE-1
CALCULATED TOTAL ENERGY (SUM OF ELECTRONIC AND ZERO-POINT ENERGIES), DIPOLE MOMENT, TOTAL ATOMIC CHARGES (O) AND TOTAL ATOMIC CHARGES (H) FOR SOLVENT

Compound		ZPE + Ele (hartree)	Dipole moment (debye)	Total atomic charges (O)	Total atomic charges (H)
Phenol	(A)	-305.4457	1.4513	-0.7568	0.4564
Ethanol	(B)	-153.9895	1.8220	-0.7338	0.1698
o-Methyl phenol	(C1)	-344.4535	1.2209	-0.7607	0.4570
m-Methyl phenol	(C2)	-344.4540	1.2245	-0.7576	0.4561
p-Methyl phenol	(C3)	-344.4528	1.4566	-0.7595	0.4554
o-Chloro phenol	(D1)	-764.3517	3.4109	-0.7366	0.4627
m-Chloro phenol	(D2)	-764.3556	3.3748	-0.7506	0.4605
p-Chloro phenol	(D3)	-764.3551	2.4700	-0.7527	0.4597
o-Fluoro phenol	(E1)	-404.2992	3.0137	-0.7403	0.4600
m-Fluoro phenol	(E2)	-404.3064	2.9716	-0.7510	0.4604
p-Fluoro phenol	(E3)	-404.3034	2.0336	-0.7580	0.4574
o-Nitro phenol	(F1)	-508.9021	6.5467	-0.7046	0.4678
m-Nitro phenol	(F2)	-508.9117	6.2206	-0.7482	0.4629
p-Nitro phenol	(F3)	-508.9160	5.4359	-0.7405	0.4666

TABLE-2
CALCULATED LENGTHS OF BINDING OF (C-O) AND (O-H) AND ANGLE OF (O-H) FOR PURE SOLVENT

Compound		D(C-O)	D(O-H)	< (O-H)
Phenol	(A)	1.3527	0.9469	110.6600
Ethanol	(B)	1.4036	1.0821	105.7754
o-Methyl phenol	(C1)	1.3560	0.9467	110.5523
m-Methyl phenol	(C2)	1.3528	0.9468	110.5652
p-Methyl phenol	(C3)	1.3542	0.9468	110.5485
o-Chloro phenol	(D1)	1.3445	0.9470	110.5923
m-Chloro phenol	(D2)	1.3489	0.9471	110.8666
p-Chloro phenol	(D3)	1.3501	0.9470	110.9210
o-Fluoro phenol	(E1)	1.3486	0.9469	110.4501
m-Fluoro phenol	(E2)	1.3479	0.9471	110.7726
p-Fluoro phenol	(E3)	1.3543	0.9468	110.7842
o-Nitro phenol	(F1)	1.3330	0.9478	110.1357
m-Nitro phenol	(F2)	1.3480	0.9471	111.2048
p-Nitro phenol	(F3)	1.3406	0.9476	111.3770

The sum of electronic and zero-point energies (ZPE+Ele), different energy between binary system and pure compound, {ΔE = (ZPE(bin) – [ZPE(i)+ZPE(j)]}, dipole moment and different dipole moment between binary system and pure compound, [Δ(dipole)] and total atomic charge of O_1 are listed in Table-3 and calculated lengths of binding of (C–O) and (O–H) and angle of (O–H) for binary system listed in Table-4. The results show that the calculated energies of interactions are within the range 5-8 kcal/mol and they are typical for hydrogen bond energies of middle strength. It should be noted that theory indicates that strongly hydrogen bonding in all derivatives is formed in *meta* position. The order of hydrogen bond strength in all system is:

TABLE-3
CALCULATED TOTAL ENERGY (SUM OF ELECTRONIC AND ZERO-POINT ENERGIES), ΔE, DIPOLE MOMENT, Δ(DIPOLE),TOTAL ATOMIC CHARGES (O) AND TOTAL ATOMIC CHARGES (H) FOR BINARY MIXTURES

Compd.	ZPE + Ele (hartree)	ΔE (kcal mol^{-1})	Dipole moment	Δ(dipole)	Total atomic charges (O1)
A-A	-344.3247	0	1.8511	0	-0.3806
B-B	-307.9811	0	2.3456	0	-0.7422
A-B	-459.4454	-6.84	3.7058	0.4325	-0.2920
C1-B	-498.4531	-6.99	3.7486	0.1057	-0.8131
C2-B	-498.4536	-7.09	3.4647	0.4182	-0.8137
C3-B	-498.4523	-6.29	3.5191	0.2405	-0.8146
D1-B	-918.3529	-7.13	4.9891	-0.2430	-0.7926
D2-B	-918.3565	-7.15	6.0351	0.8383	-0.8065
D3-B	-918.3560	-7.12	5.6303	1.3383	-0.8082
E1-B	-558.2999	-7.02	4.5868	-0.2490	-0.7967
E2-B	-558.3070	-7.03	5.5223	0.7287	-0.8069
E3-B	-558.3037	-6.78	5.0362	1.1806	-0.8138
F1-B	-662.9321	-7.51	7.0895	-1.2790	-0.8111
F2-B	-662.9139	-7.91	9.0340	0.9914	-0.8048
F3-B	-662.9172	-7.29	8.3662	1.1083	-0.8179

TABLE-4
CALCULATED LENGTHS OF BINDING OF (C–O) AND (O–H) AND ANGLE OF (O–H) FOR BINARY SYSTEM

Compd.	D(C1-O1)	D(C2-O2)	(O1-H)	(O2-H)	< (O1-H)	< (O2-H)
A-A	1.3676	1.3893	0.9579	0.94977	111.2383	110.7138
B-B	1.4079	1.4079	0.9471	0.94719	109.2925	109.2943
A-B	1.3463	1.4149	0.9537	0.94755	111.3777	110.1127
C1-B	1.3493	1.4148	0.9537	1.08629	111.3390	110.1167
C2-B	1.3463	1.4147	0.9536	0.94753	111.3327	110.1233
C2-B	1.3478	1.4147	0.9535	0.94752	111.2592	110.1106
D1-B	1.3373	1.4164	0.9549	0.94774	111.3918	110.0518
D2-B	1.3419	1.4159	0.9546	0.94767	111.5727	110.0985
D3-B	1.3432	1.4158	0.9544	0.94764	111.5718	110.1165
E1-B	1.3420	1.4159	0.9543	0.94768	111.0876	110.0663
E2-B	1.3409	1.4156	0.9545	0.94762	111.5396	110.1220
E3-B	1.3479	1.4155	0.9537	0.94761	111.3796	110.0969
F1-B	1.3371	1.4189	0.9570	0.94710	111.8373	110.0810
F2-B	1.3408	1.4171	0.9552	0.94783	111.7764	110.0359
F3-B	1.3418	1.4170	0.9551	0.94753	111.7064	110.0759

meta > *ortho*> *para*

The calculated results show that the order of dipole moment is:

meta > *para* > *ortho*

The total atomic charge on the oxygen of phenol derivatives depends on the position of subistituent and the order of atomic charge is decrease:

para > *meta* > *ortho*

It is also intriguing to compare the dihedral OH out-of-the aromatic plane angles in the hydrogen-bonded complexes. The O-H group lies in the plane of the aromatic ring for phenol and its *o*-methyl derivatives. Such planar structures have energy minima for $\hat{E}$ close to 0° with rotation barriers of about 3.5 kcal /mol.

The results show that the hydrogen bonding energy and dipole moment in *meta*-nitro phenol with ethanol is larger than other component and the energy between binary system and pure compound in this position is -7.91 kcal/mol and the dipole moment is 9.034.

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