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## Computational Study of Hydrogen Bonding in Substituted Phenol-Acetonitrile-Water Clusters

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The calculations for a water-acetonitrile-substituted phenols system and the comparison with the experimental parameters will be given. Here we study change in the nature of the interactions into the system with donor and acceptor electron substituents on the phenolic ring, the structures, relative energies and harmonic frequencies. The conformers showed a significant difference in the OH and CN band shift depending on the type of the hydrogen bond formed and the position of the substituent on the phenolic ring. The cyclical hydrogen bonds between water-acetonitrile and substituted phenol OH are important evidence of the relative stability in the system under study.

**Keywords:** Phenol-Acetonitrile-Water cluster; Hydrogen bonding; Quantum chemical computations.

### INTRODUCTION

The object of studying cluster systems is to demonstrate the effects of the solute-solvent interaction on the different chemical, physical and/or physicochemical properties of the solute. In addition, our purpose is to demonstrate the noticeable influence of some substituent groups on the type of formed clusters. The existing bibliographical information has mainly been focused in pure clusters that consist of identical molecules<sup>1-3</sup> as in the case of water, methanol, ammonia, etc. Nevertheless, the cluster systems that consist of a solute that interacts with diverse molecules of solvent display more interesting and complex properties.<sup>4-10</sup> In these systems, the different types of functional groups can interact to generate a series of conformers with interesting thermodynamic properties.

In our work we studied cluster systems of the substituted phenol-acetonitrile-water type as a comparison to the non-substituted phenol cluster<sup>4</sup> to examine the nature of the interactions between the solute and the different types of solvent. We mainly focused on the substituent effects of the nitro, methoxy, chlorine and amino group as donating/attracting electrons on the type of formed cluster.<sup>11-15</sup> The properties of the stable conformers with different types of hydrogen bonds, such as harmonic frequencies, heat of for-

mation, bond distances, electrostatic potential, among others, were calculated and compared with the non-substituted phenol cluster.

### CALCULATION METHODS

The calculations were performed with the PC SPARTAN PRO program. The semi-empirical methods used were AM1 and PM3. The data collected with the AM1 method displayed a great deviation with respect to the non-substituted phenol-acetonitrile-water cluster,<sup>4</sup> so the calculated PM3 properties were exclusively taken into account.

### RESULTS AND DISCUSSION

The spectroscopic properties of phenol in the substituted phenol-acetonitrile-water clusters depend significantly on the disposition of the solvent molecules and on the position of the substituent in the phenolic ring. This effect is markedly seen on the IR band of the OH.

The two types of clusters studied are represented in Fig. 1.

In cluster type 1, the OH group of phenol acts as a proton-donating group while forming a hydrogen bond with the water molecule; in cluster type 2 this group also

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acts like a proton donor when connecting with the nitrogen of acetonitrile.

These two structures have an energy difference of 1.17 Kcal/mol; therefore, cluster type 1 shows a greater stability. This can be attributed to water being a better proton acceptor than acetonitrile, and it may form a stronger bond with phenolic OH. At the spectroscopic level it is possible to mention a difference as to the IR signal bands of OH and CN. Comparing the frequencies ( $\text{OH} = 3888.88 \text{ cm}^{-1}$  and  $\text{CN} = 2461.82 \text{ cm}^{-1}$ ) of free phenol and acetonitrile molecules with the frequencies presented in cluster type 1, a difference of  $155.31 \text{ cm}^{-1}$  for the OH and  $13.14 \text{ cm}^{-1}$  for the CN can be seen. In cluster 2 the difference is 245.89 and  $15.86 \text{ cm}^{-1}$ , respectively. These band displacements towards greater wavelengths characterize the formed cluster.

More interesting characteristics are shown with the presence of a substituent in the phenolic ring. Initially we substituted the phenolic ring with the nitro group, which is a powerful electron attractor, analyzing the influence of this on the cluster system. We observed that the incidence of the nitro group on the system varies with the position of this in the phenolic ring (*orto*, *meta* and *para*).

In Fig. 2 the structures of a type of cluster system of substituted phenol in their different positions (*orto*, *para* and *meta*) with acetonitrile and water are shown. Based on the system energy of different clusters of substituted phenol, we can infer that the presence of the nitro group increases the stability of the system, having lower relative energies than the system of non-substituted phenol; in addition it generates variations in the IR bands of the phenolic OH and CN groups.

In the cluster formed by *o*-nitrophenol, the presence of the nitro group causes a lowering in the harmonic frequencies of the phenolic OH of  $243.34 \text{ cm}^{-1}$ , generating a displacement of the band towards greater wavelengths with

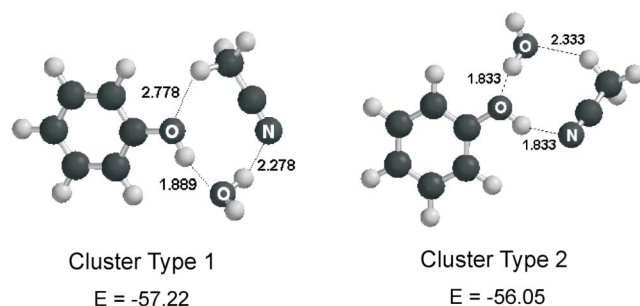


Fig. 1. Structures, relative energies in Kcal/mol and bond distances in Å of phenol-acetonitrile-water clusters.

respect to the cluster system phenol-acetonitrile-water type 1, whereas in group CN the displacement of the band is towards smaller wavelengths, due to an increase of the harmonic frequencies of  $9.25 \text{ cm}^{-1}$ .

In the system conformed by *m*-nitrophenol a lowering of the harmonic frequencies for the phenolic OH as for the CN group of the order of 18.27 and  $7.92 \text{ cm}^{-1}$  is observed respectively; both tend to move towards greater wavelengths, unlike the system conformed by *o*-nitrophenol. The cluster system conformed by *p*-nitrophenol shows that the tendency of the harmonic frequencies of the phenolic OH and CN group is towards greater values of the order of 52.27 and  $2.13 \text{ cm}^{-1}$  respectively, causing a displacement of the bands towards smaller wavelengths.

The type 2 cluster systems formed by *orto*, *meta* and *para* nitrophenol are represented in Fig. 3. In these systems it can be seen that the presence of the nitro group diminishes the harmonic frequencies of the phenolic OH and CN group in comparison with the non-substituted cluster type 2, generating a displacement of the IR bands towards greater wavelengths. The variations are displayed in Table 1.

In the study of the nitrosubstituted systems the length of the hydrogen bonds does not vary significantly in comparison with the non-substituted cluster system, and its strength is affected by the position of the nitro group in the phenolic ring. This can be due to the availability of the hydrogen of the phenolic OH depending on the position in

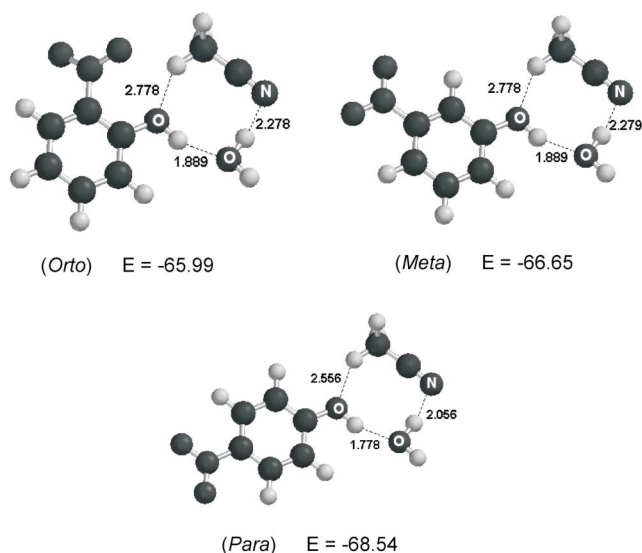


Fig. 2. Structures, relative energies in Kcal/mol and bond distances in Å for *orto*, *meta* and *para* nitrophenol-acetonitrile-water type 1 clusters.

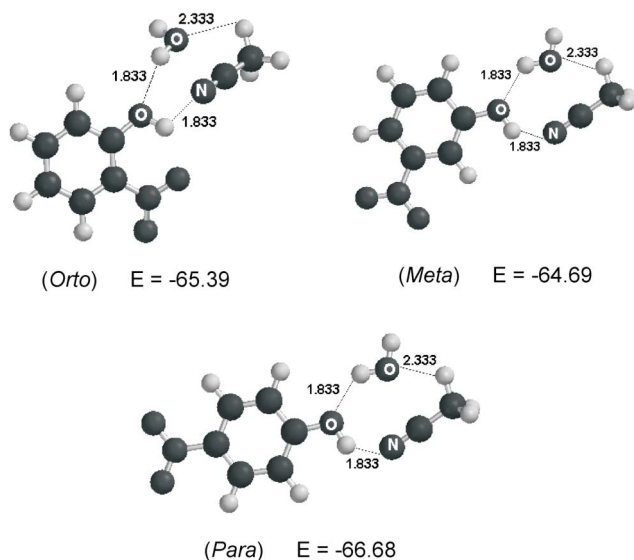
Table 1. Displacement of the bands for the cluster systems of substituted phenol type 2

Cluster type 2		Harmonic frequencies $\text{cm}^{-1}$	
		Calculated	Variation
<i>o</i> -nitrophenol	O-H	3602.21	40.78
	C≡N	2442.81	3.15
<i>m</i> -nitrophenol	O-H	3629.96	13.03
	C≡N	2441.45	4.51
<i>p</i> -nitrophenol	O-H	3610.56	32.43
	C≡N	2444.14	1.82

which the group nitro is. This substituent has an intensity of considerable positive charge on nitrogen, attracting the delocalized  $\pi$  electrons in the ring, forming a double bond with the adjacent carbon, which generates an increase in the electrostatic potential of the ring forcing the lone pair of electrons of the OH to migrate towards the ring.

The *ortho* and *para* positions favor the migration of the nitrogen positive charge towards the adjacent carbon to the OH group, which stimulates the oxygen lone pair electrons to migrate with greater intensity towards this carbon atom, so the hydrogen is more acidic. This effect is reflected in the hydrogen electrostatic potential of 65.79 and 72.47 eV for the *ortho* and *para* positions, respectively, being more available to form stronger hydrogen bonds (see Fig. 4).

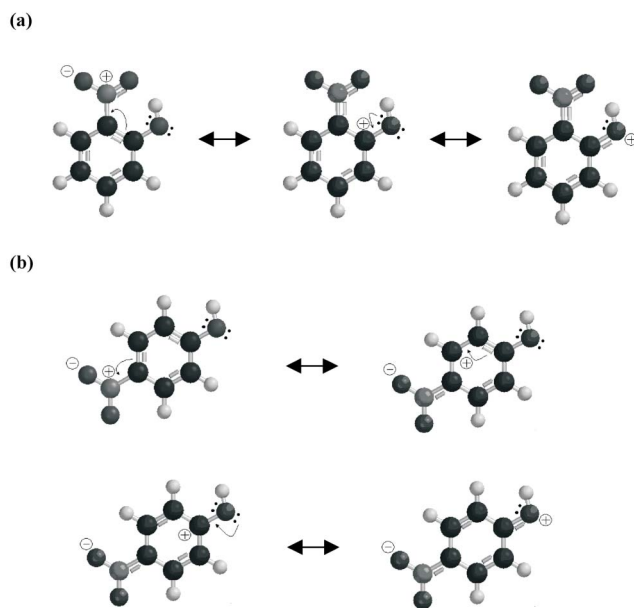
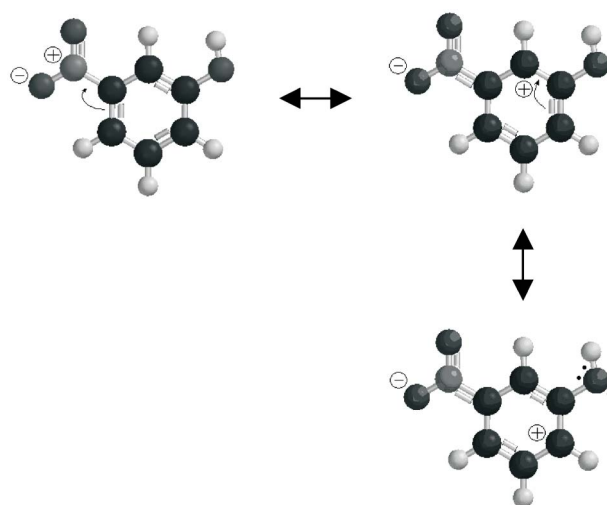
The displacement of the positive charge to the OH adjacent carbon is not favored in the *meta* position; therefore,

Fig. 3. Structures, relative energies in Kcal/mol and bond distances in Å for clusters of *ortho*, *meta* and *para* nitrophenol-acetonitrile-water type 2.

the tendency of the oxygen non-bonding electrons to migrate towards the ring will be smaller, and the hydrogen bonds formed will be weaker (Fig. 5).

It is possible to indicate that the presence of the nitro group in any one of the possible positions favors the stability of the hydrogen bond if it is compared with the non-substituted cluster.

Water, having a more electronegative atom than the nitrogen of acetonitrile has greater capacity to accept the

Fig. 4. Structures of resonance and mechanisms of electron migration for *o*-nitrophenol (a) and *p*-nitrophenol (b).Fig. 5. Structures of resonance and mechanisms of electron migration for *m*-nitrophenol.

proton of the phenolic OH; therefore, the nitrosubstituted type 1 clusters have greater stability than the type 2 cluster systems presented in their structure with this type of bonding. This is reflected in the energy values of the different systems.

In the *orto* position of type 1 a phenomenon is observed that does not appear in the other positions, which is the disturbance produced to the OH owing to the nitro group oxygens generating a diminution in the harmonic frequency of the OH, that is to say, a displacement of the band  $243.34\text{ cm}^{-1}$  towards longer wavelengths. Whereas in the system conformed by the type 2 *o*-nitrophenol, an electrostatic attraction exists between the water hydrogens, which have a partial positive and the nitro group oxygens, which have a high electron density. This causes the required energy to excite the molecule to the vibrational tension state to be greater, since it would be the summation of the necessary energy to overcome the electrostatic attraction and the magnitude of the difference in the vibrational states.

In the substitution with the methoxy group, which is donating electrons, the relative energies of the system display variations of up to 38.7 Kcal/mol compared with the non-substituted cluster system.

The most stable position of the substituent with respect to the ring for type 1 and 2 clusters is our goal, showing relative energies of -95.94 Kcal/mol in the type 1 cluster and -94.26 Kcal/mol in the type 2 cluster. When comparing the relative energies an energy difference of 1.68 Kcal/mol is evident, being more stable than the type 1 cluster system.

Based on the energies shown in Fig. 6 it could be said that the cluster systems to which the methoxy group was inserted are those that have a greater stability as far as the energy of all the system is concerned (Summation of all the energies of the cluster).

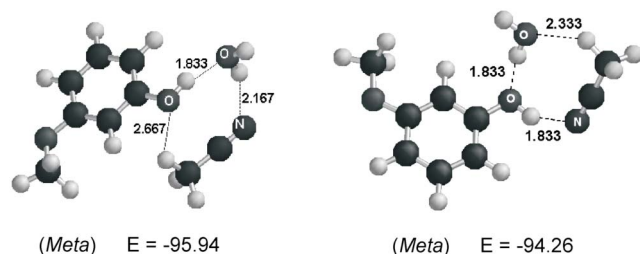


Fig. 6. Structures, relative energies in Kcal/mol and bond distances in Å for *meta* methoxysubstituted type 1 and 2 clusters.

Table 2. Displacements of the  $\Delta\nu$  bands in  $\text{cm}^{-1}$  and energy variations  $\Delta E$  of clusters type 1 and 2-methoxysubstituted

	type 1 Cluster			type 2 Cluster		
	<i>orto</i>	<i>meta</i>	<i>para</i>	<i>orto</i>	<i>meta</i>	<i>para</i>
$\Delta\nu_{\text{CN}}$	3.68	3.65	3.38	1.70	0.26	0.37
$\Delta\nu_{\text{OH}}$	6.37	45.35	44.88	1.32	4.48	4.28
$\Delta E$	35.55	38.72	37.62	35.60	38.21	37.24

This effect causes some significant displacements in the bands of the IR spectra of OH and CN groups, with some differences between cluster type 1 and type 2 (see Table 2). In the *orto* position of the type 1 cluster, there was a displacement towards long wavelengths compared with the non-substituted cluster, whereas in the *meta* and *para* positions the displacement was in the opposite direction, indicating that more energy is needed to excite these systems to the vibrational state and that they have a greater stability as far as the hydrogen bonds are concerned (between the methoxy substituted systems type 1).

When the substitution is accomplished with the chlorine atom (attractor of electrons) the stability of the system was favored with a diminution of its relative energies as much as in the type 1 cluster as in the type 2 cluster. This diminution is marked in the *para* substitution of both clusters, which indicates that these structures are most stable (Fig. 7).

As far as the displacements of the IR bands of groups OH and CN, it was observed that for the type 2 cluster the tendency was towards longer wavelengths in the different positions (diminution of the frequencies).

For the type 1 cluster, the OH frequency presented in the *orto* position shows a decrease and an increase for

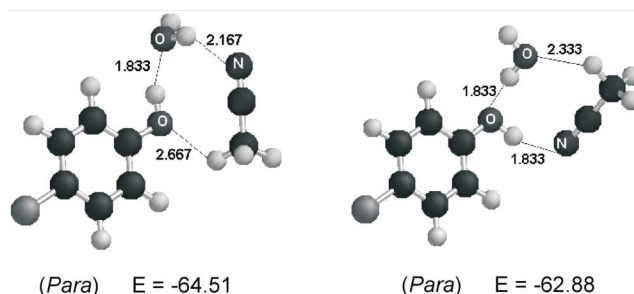


Fig. 7. Structures, harmonic frequencies (CN and OH) in  $\text{cm}^{-1}$ , relative energies in Kcal/mol and bond distances in Å for chlorosubstituted type 1 and 2 clusters.



Table 3. Displacements of the  $\Delta\nu$  bands in  $\text{cm}^{-1}$  and energy variations  $\Delta E$  of chlorosubstituted type 1 and 2 clusters

	type 1 Cluster			type 2 Cluster		
	<i>orto</i>	<i>meta</i>	<i>para</i>	<i>orto</i>	<i>meta</i>	<i>para</i>
$\Delta\nu_{\text{CN}}$	4.17	3.19	3.29	0.95	0.67	0.44
$\Delta\nu_{\text{OH}}$	6.41	41.89	42.03	52.94	6.90	4.92
$\Delta E$	6.54	7.25	7.39	5.46	6.82	6.83

group CN, whereas the observed ones in the *meta* and *para* positions show an increase for both groups. The values of these displacements are shown in Table 3.

In general terms, in the substitution with the amino group, the stability of the system is favored with a diminution in its relative energies of about 2.55 Kcal/mol. The *meta* position was the most stable in both clusters.

As far as the displacements in the IR band are concerned, in the type 1 cluster in the *meta* position, the tendency is towards shorter wavelengths as much as for the OH as for the CN, with variations of 39.38 and 3.83  $\text{cm}^{-1}$ , respectively.

For the type 2 cluster in the *orto* and *meta* positions the displacements are towards longer wavelengths, whereas in the *para* position, the tendency is towards shorter wavelengths (see Table 4).

## CONCLUSION

In general type 1 clusters displayed a greater stability, without concerning the substituent group, shown in the given energy values, when comparing them with the non-substituted cluster systems. This can be due, as was already mentioned previously, to the spatial orientation of the molecules that form this cluster, the phenolic hydroxile being a donor of protons when forming a hydrogen bond with the water oxygen, whereas in the type 2 cluster it is connected

Table 4. Displacements of the  $\Delta\nu$  bands in  $\text{cm}^{-1}$  and energy variations  $\Delta E$  of type 1 and 2 aminosubstituted clusters

	type 1 Cluster			type 2 Cluster		
	<i>orto</i>	<i>meta</i>	<i>para</i>	<i>orto</i>	<i>meta</i>	<i>para</i>
$\Delta\nu_{\text{CN}}$	3.79	3.83	3.46	0.52	0.67	0.09
$\Delta\nu_{\text{OH}}$	24.48	39.38	46.98	3.39	1.01	7.53
$\Delta E$	1.20	2.56	1.79	0.65	2.47	1.52

with the acetonitrile nitrogen; this is the fundamental difference between these two structures (type 1 and 2 clusters). For the substituted systems with electron attractor groups, such as chloro and nitro groups, within the three possible sites of substitution in the ring, *orto*, *meta* and *para*, the systems that displayed a greater stability according to their relative energies were the substituted ones on the *para* position, since it is in this position where a more favored tendency of the oxygen lone pair electrons to migrate towards the ring is seen, providing a more acidic character to phenolic hydroxide hydrogen, whereas for the substituted systems with donating electron groups like the methoxy and amino groups the position of substitution with a greater stability was *meta*. The displacements of the IR bands of the substituted systems with donating electron groups showed the following tendencies cluster 1 increased the frequencies for group CN in the three positions and for the OH group increased in the *meta* and *para* positions; type 2 cluster frequencies diminished as much as for group OH as for the CN in the three positions. For the substitution with the electron attractor groups the tendency was the following one: in cluster 1 the frequency of the OH group diminished and the CN increased for the *orto* position, whereas in the *para* position both frequencies increased; in cluster 2 the tendency was a diminution of the frequencies for both groups in the three different positions. These displacements of the bands implied directly in the formation of hydrogen bonds (OH and CN) can be very useful at the time of determining experimentally the cluster type formed in a sample with different conformers.

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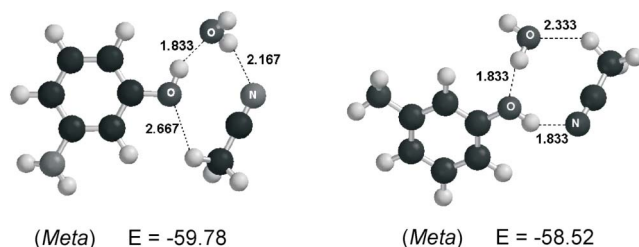


Fig. 8. Structures, harmonic frequencies (CN and OH) in  $\text{cm}^{-1}$ , relative energies in Kcal/mol and bond distances in Å for *meta* aminosubstituted type 1 and 2 clusters.

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