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Density Functional Theory Calculations on Hydrogen-Bonded Tropolone−$(H_2O)_2$ Clusters

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The geometries, harmonic vibrational frequencies, and binding energies of tropolone−H_2O and tropolone−$(H_2O)_2$ complexes have been investigated through the use of the B3LYP density functional approach. The geometries of the different complexes were optimized using 6-31G(d) and 6-31+G(d) basis sets. The harmonic frequencies were evaluated using the latter basis. The binding energies for the most stable clusters were calculated at the B3LYP/6-311+G(3df,2p) level. We have located nine different local minima which meet the general criteria posed by the experimental infrared spectra of possessing at least one free OH oscillator and only two hydrogen-bonded oscillators, which act as proton donors. However, only the two most stable complexes present frequency gaps between the free OH and the hydrogen-bonded OH stretching modes in agreement with the experimental values. These two species, **Tw2ring** and **Tw2ext**, are very near in energy to one another, although they present very different bonding characteristics since in the former the intramolecular hydrogen bond of the tropolone moiety is broken, while this is not the case for the latter. The binding energies of both complexes (10.0 and 9.9 kcal/mol, respectively) are sizably larger than those predicted for tropolone−H_2O complexes. This indicates that significant cooperative effects appear when a second water molecule is added to the system. These cooperative effects are reflected in the strengths of the intra- and intermolecular hydrogen bonds and in the shiftings of the vibrational modes affected by the hydrogen bonding. Although using the available experimental information, one cannot favor one isomer over the other, according to our results they could be discriminated in terms of the shifting of the O−H stretching and bending modes of the tropolone moiety. For **Tw2ext** the stretching mode should appear slightly blue-shifted, while for **Tw2ring** it should appear red-shifted. Similar differences in the out-of-plane bending mode should also be observed. Both complexes have also quite different rotational constants, so nonnegligible dissimilarities should be observed in their microwave spectra.

Introduction

Tropolone is a non-benzenoid seven-membered ring which has been extensively studied, both from the experimental and the theoretical viewpoints,[1−24] notably because it presents an intramolecular hydrogen bond (IHB) with a symmetric double-minimum potential energy function and constitutes a typical example of multidimensional tunneling.[22] There exists experimental evidence showing that at least three fundamental vibrations present large tunneling splittings.[14]

Experimental studies based on the fluorescence excitation spectra of tropolone−water clusters revealed[8] that this symmetric double-minimum potential is destroyed by the formation of intermolecular hydrogen bonds between tropolone and water. Actually the cluster bands show no doublet structure, which indicates that H-atom tunneling in tropolone is effectively quenched by a water molecule. These findings stimulated interest in tropolone−water clusters, and recently, Sekiya et al.,[25] Frost et al.,[26] and Mitsuzuka et al.[27] reported infrared spectroscopy studies on these complexes. The work of Frost et al.[26] was limited to the tropolone−H_2O clusters, while Mitsuzuka et al.[27] explored the tropolone−$(H_2O)_n$ ($n = 1−3$) and tropolone−$(CH_3OH)_n$ ($n = 1, 2$) complexes. Although in the work of Frost et al.[26] a complete characterization of the possible structures of tropolone−H_2O complexes was given by means of ab initio and density functional theory (DFT) techniques, in the work of Mitsuzuka et al.[27] only some possible structures for tropolone−$(H_2O)_2$ were suggested on the basis of the characteristics of the infrared spectra of these species as compared with the spectra of tropolone−$(CH_3OH)_2$ complexes. The aim of this paper is to investigate, through the use of DFT approaches, the structure, relative stability, and vibrational frequencies of tropolone−$(H_2O)_2$ clusters. A second goal of our study will be the analysis of some possible cooperative effects in these clusters, which juxtapose the properties of the tropolone IHB and several intermolecular hydrogen bonds (HBs), in an effort to investigate under which circumstances the different HBs of the complex perturb each other.

Computational Details. The geometries of the different systems investigated were initially optimized using a B3LYP density functional approach together with a 6-31G(d) basis set expansion. The B3LYP method is a hybrid density functional theory approach which combines Becke's three-parameter nonlocal exchange potential[28] with the nonlocal correlation functional of Lee, Yang, and Parr.[29] It is generally accepted that a proper description of hydrogen-bonded complexes requires the inclusion of diffuse components in the basis set. Therefore, the geometries of the six most stable tropolone−$(H_2O)_2$ clusters were refined using a 6-31+G(d) basis set expansion. The harmonic vibrational frequencies were obtained at the same level of theory used in the geometry optimizations. This allowed us to classify the stationary points found as local minima or transition states and to estimate the corresponding zero point energies (ZPE), which were scaled by the empirical factor 0.98 proposed by Bauschlicher.[30]

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TABLE 1: Total Energies (*E*, in hartrees), Zero Point Energies (ZPE, in hartrees), Rotational Constants (*A*, *B*, *C*, in kilohertz), and Binding Energies (BE, in kilocalories per mole) for Tropolone−$(H_2O)_2$ and Tropolone−H_2O Complexes, with Relative Energies (Δ*E*, in kilocalories per mole) Given within Parentheses[a]

	B3LYP/6-31G(d)		B3LYP/6-31+G(d)					B3LYP/6-311+G(3df,2p)	
system	*E* (Δ*E*)	ZPE	*E* (Δ*E*)	ZPE	*A*	*B*	*C*	*E* (Δ*E*)	BE
Tw2ab(ud)	−573.61919 (6.0)	0.16451	−573.660 67 (4.8)	0.163 45	1250.5	643.1	424.7	−573.872 36 (3.8)	6.2
Tw2ab(uu)	−573.61910 (6.1)	0.16450							
Tw2ac(ud)	−573.62443 (3.0)	0.16489	−573.664 04 (3.0)	0.163 99	1201.0	744.6	460.8	−573.875 46 (2.2)	7.8
Tw2ac(uu)	−573.62404 (3.2)	0.16483							
Tw2bc(ud)	−573.62140 (4.6)	0.16448	−573.661 36 (4.4)	0.163 53	1146.7	756.7	456.7	−573.872 60 (3.7)	6.3
Tw2bc(uu)	−573.62101 (4.8)	0.16443							
Tw2cage	−573.62596 (2.4)	0.16551	−573.663 18 (3.8)	0.164 43	1787.6	585.3	476.4	−573.873 20 (3.9)	6.2
Tw2ext	−573.62211 (4.3)	0.16465	−573.669 21 (0.4)	0.165 00	1388.7	633.7	436.2	−573.879 73 (0.1)	9.9
Tw2ring	−573.62985 (0.0)	0.16555	−573.669 26 (0.0)	0.164 46	1918.1	563.7	436.7	−573.879 39 (0.0)	10.0
Tw2abTS1[b]	−573.61747	0.16377							
Tw2abTS2	−573.61752	0.16377							
Tw2acTS1	−573.62001	0.16359							
Tw2acTS2	−573.62211	0.16407							
Tw2bcTS1	−573.61674	0.16313							
Tw2bcTS2	−573.61958	0.16374							
Tw1a	−497.19949 (0.0)	0.14043	−497.230 13 (0.0)					−497.403 36 (0.0)	3.8
Tw1b	−497.20075 (−0.9)	0.14021	−497.230 07 (0.1)					−497.402 87 (0.2)	3.6
Tw1c	−497.19536 (2.2)	0.13979	−497.226 08 (2.1)					−497.399 39 (2.1)	1.7
tropolone	−420.77548	0.11568	−420.795 41	0.115 34				−420.930 22	
water	−76.40895	0.02115	−76.422 57	0.021 08				−76.463 19	

[a] Both Δ*E* and BE include the corresponding scaled ZPE corrections. [b] For each type of tropolone−$(H_2O)_2$ clusters the TS1 refers always to the transition state associated with the OH flipping of the water molecule which solvates the carbonyl group, while TS2 refers to the OH flipping of the other water molecule.

To get reliable binding energies, the final energies of the monomers, and those of the most stable tropolone−H_2O and tropolone−$(H_2O)_2$ clusters, were calculated in B3LYP/6-311+G(3df,2p) single point calculations carried out on the aforementioned B3LYP optimized geometries. We have shown previously[31−34] that this level of theory provides energetics for hydrogen-bonded clusters in good agreement with high-level ab initio G2-type[35] calculations, which for systems of this size are computationally unaffordable.

To investigate the bonding features of the most stable clusters, and in particular to characterize the different hydrogen bonds formed in each cluster, we used the atoms in molecules (AIM) theory of Bader.[36] Using this formalism, we have located the bond critical points (i.e. points where the electron density function, $\rho(\mathbf{r})$, is a minimum along the bond path and a maximum in the other two directions) because the values of the charge density and its Laplacian at these critical points give useful information regarding the strength of the linkages. Actually, it has been reported previously in the literature[37,38] that there exists a good linear correlation between the charge density at the hydrogen bond critical point (bcp) and the strength of the linkage. This relationship is particularly useful when describing cooperative effects,[31,37,38] i.e., the reinforcement of a given hydrogen bond due to the presence of other hydrogen bond(s) in the complex. As we shall show later, the complexes between tropolone and water offer good examples for illustrating this phenomenon. The Laplacian of the density, $\nabla^2\rho(\mathbf{r})$, identifies regions of the space wherein the electronic charge is locally depleted ($\nabla^2\rho > 0$), as in hydrogen bonds or ionic bonds, or built up ($\nabla^2 \rho < 0$), as in covalent linkages. There are however significant exceptions, mainly when the atoms involved in the bond are very electronegative. These exceptions do not appear when the energy density, $H(\mathbf{r})$, is used.[39] Negative values of $H(\mathbf{r})$ indicate that a stabilizing charge concentration takes place in the bonding region; hence, changes in the value of $H(\mathbf{r})$ are associated with changes in the strength of the bond.

All calculations have been carried out using the GAUSSIAN-94 series of programs.[40] The AIM analysis was performed using the AIMPAC series of programs.[41]

Results and Discussion

We have located nine different local minima for the tropolone−$(H_2O)_2$ clusters. Their total energies and the unscaled zero point energy corrections have been summarized in Table 1. The optimized geometries of the six more stable complexes are given in Figure 1. Although the structures and energetics of the tropolone−H_2O complexes have been described already in the literature[26] at similar levels of theory, they have been included also in Figure 1 and in Table 1 for the sake of comparison.

Three of the tropolone−$(H_2O)_2$ minima, namely, **Tw2ac**, **Tw2ext**, and **Tw2ring**, were proposed by Mitsuzuka et al.[27] as suitable structures of tropolone−$(H_2O)_2$ clusters. In ref 27 a fourth structure, called "top" (see Chart 1) was also envisioned. However, all attempts to locate a stationary point with this structure failed, since all arrangements in which the second water molecule interacts as a HB acceptor of the first one collapsed either to the **Tw2ring** or to the **Tw2cage** local minima.

The different minima can be classified in two groups. The first group contains those complexes, namely, **Tw2ac**, **Tw2bc**, **Tw2ring**, and **Tw2cage**, in which at least one water molecule acts as a proton acceptor of the hydroxyl group of tropolone. In fact, with only the exception of **Tw2ring**, in these clusters a water molecule is hydrogen bonded to both active sites of the tropolone moiety simultaneously, behaving as a HB donor with respect to the carbonyl group and as a HB acceptor with respect to its hydroxyl group. The second set includes clusters **Tw2ab** and **Tw2ext**, where the intramolecular HB of tropolone is not directly perturbed, in the sense that the OH group of tropolone still acts as a proton donor to the carbonyl group. In **Tw2ab** both water molecules behave as HB donors with respect to the carbonyl and the hydroxyl groups of tropolone, while in **Tw2ext** the first molecule acts as a HB donor to the carbonyl group and the second water molecule solvates the first one.

As we shall see in forthcoming sections, the first set includes complexes where the IHB disappears, while the complexes included in the second set retain some degree of its intramolecular hydrogen bonding. The nomenclature adopted for complexes **Tw2ab**, **Tw2ac**, and **Tw2bc** is consistent with the

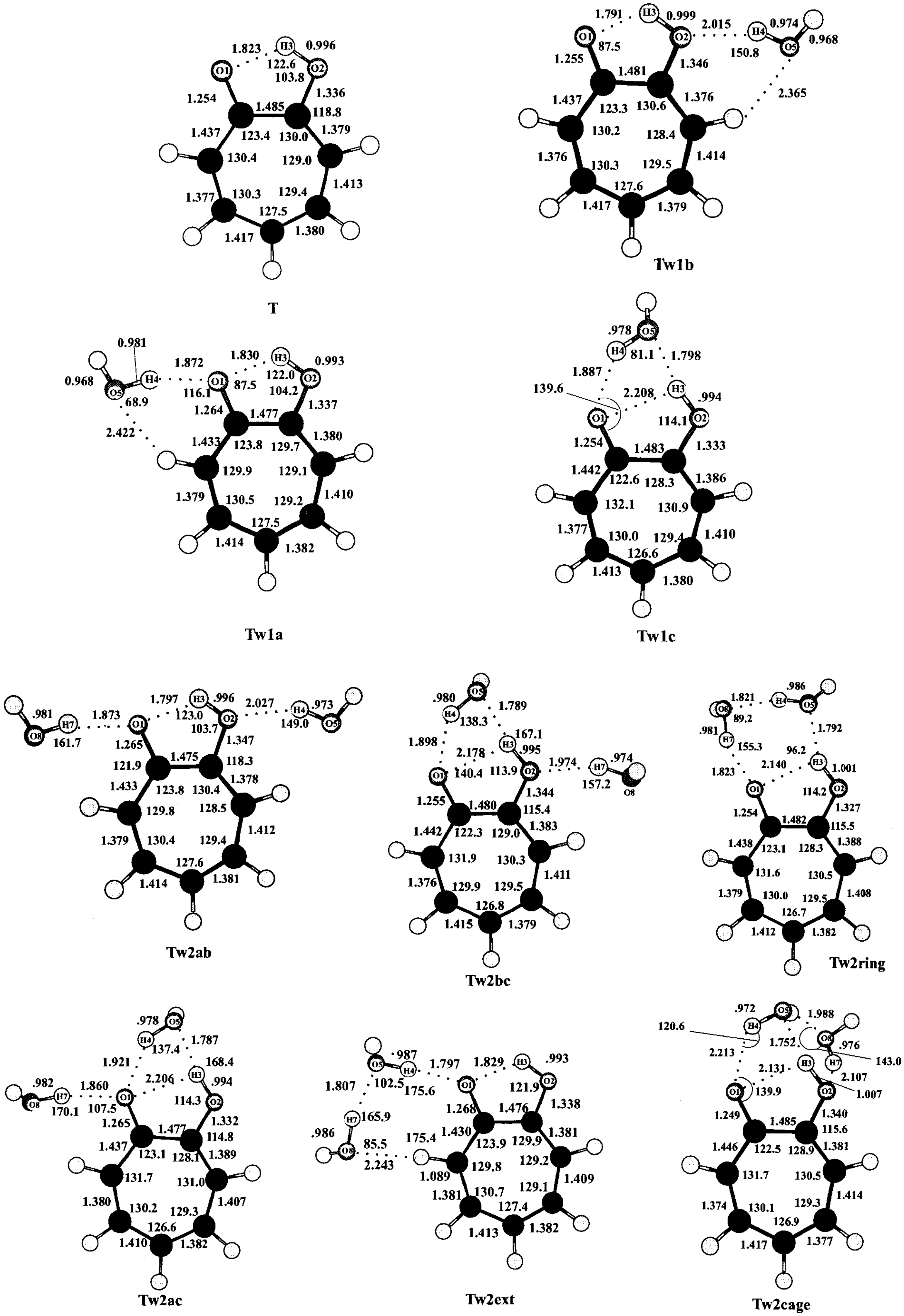
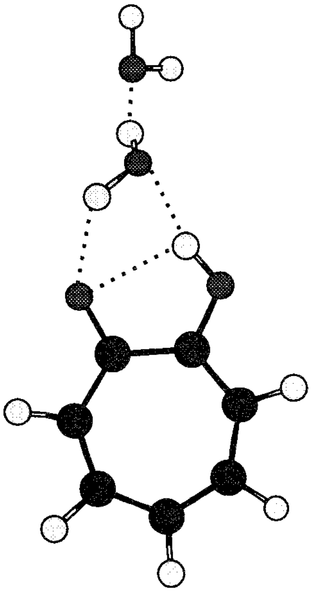


Figure 1. B3LYP/6-31+G(d) optimized geometries of tropolone, tropolone$-H_2O$, and tropolone$-(H_2O)_2$ complexes. Bond legths are in angstroms and bond angles in degrees. The O$-$H$\cdots$O distance in the water dimer at the same level of theory is 1.906 Å.

fact that they can be viewed as the result of juxtaposing the appropriate tropolone$-H_2O$ complexes, **Tw1a**, **Tw1b**, and **Tw1c**. Structure **Tw2ext** can also be considered as the result of solvating complex **Tw1a** by a second water molecule, while

CHART 1



top

Tw2ring and **Tw2cage** could be envisioned as the result of solvating the ring complex **Tw1c** by a second water molecule.

Within the subset formed by **Tw2ab**, **Tw2ac**, and **Tw2bc** complexes there are two conformers which differ in the relative positions of the free OH groups of the water molecules. If they are at opposite sites of the tropolone plane, i.e., one above and the other one below that plane will be designated as **ud** and, if both are at the same side of the molecular plane, will be named as **uu**, following the nomenclature first used by Schütz et al. for water clusters.[42] According to our results (see Table 1), within each set the **ud** conformer is always the most stable, so for the sake of simplicity we have included in Figure 1 exclusively the optimized geometries of the **ud** conformers.

We have also located the transition states which connect the **uu** and the **ud** conformers, which correspond to the flipping of the free OH group of one of the water molecules. The optimized geometries of these transition states will not be discussed here for the sake of conciseness, buy they are available from the authors upon request. It is worth mentioning, however, that the flipping of the water hydrogens implies very low energy barriers, so likely tunneling effects must be important. It is worth mentioning that these barriers are very similar to those reported by Schütz et al. for the flipping of the free OH groups in the water trimer.[42]

Relative Stabilities and Binding Energies. The first conspicuous feature of Table 1 is that the relative stability of the different complexes is rather sensitive to the flexibility of the basis set expansion used in our DFT calculations. Importantly, the effect of diffuse components in the basis set is particularly large. This is something well-established in the ab initio treatment of hydrogen-bonded clusters;[43] however, since the basis set requirements of density functional methods are not necessarily the same as those of ab initio calculations, we also thought it of interest to verify that when DFT techniques are used, this requirement still holds. In this respect it must be also mentioned that the effect of the diffuse basis functions is apparent not only in the relative stability of the hydrogen-bonded complexes but also in their optimized structures. The most significant changes affect the HB lengths and, in some specific cases, the relative orientation of the water molecules with respect to the tropolone moiety. These differences are reflected in changes in the calculated rotational constants, which for the most stable complexes, **Tw2ring** and **Tw2ext**, differ as much as 9% and 32%, respectively.

Tw2ring is predicted to be the global minimum at all levels of theory considered; however, when a G2-type 6-311+G(3df,2p) basis set is used, the energy gap with respect to **Tw2ext** local minimum becomes very small (0.1 kcal/mol). The estimated entropies for both clusters are almost equal, so both complexes are also very near to one another in terms of free energies. The other local minima lie at least 2.0 kcal/mol higher in energy. It must be taken into account, however, that in complexes **Tw2ring** and **Tw2ext** the two water molecules close a six-membered and an eight-membered ring, respectively, so both complexes have lower entropies than other local minima of the potential energy surface (PES). This implies that the gaps between free energies are not necessarily equal to those between energies. Actually, the energy gap between these two clusters and **Tw2ac** is about 0.8 kcal/mol greater than the gap between the corresponding free energies, due to the aforementioned entropic effect. Nevertheless, since the energy differences between **Tw2ring** and **Tw2ext** and the remaining local minima of the PES are large, while the differences between their estimated entropies are small, one should expect these two complexes to be also the global minima of the free energy surface.

It is important also to note that the binding energies of these two species are almost three times greater than those estimated for the two most stable tropolone−H_2O complexes (see Table 1). This is a first indication, as we shall discuss later, of the existence of sizably large cooperative effects in tropolone−$(H_2O)_2$ clusters.

Bonding Characteristics and Cooperative Effects. As we have mentioned in the Introduction, one important goal of our study is to know how the water molecules affect the intramolecular hydrogen bond of tropolone. In principle the IHB can be broken because the hydroxyl group prefers to act as a proton donor to water, and it is important to know if this interaction is favored when the size of the cluster increases. A second point of interest is to understand how the intermolecular HBs of tropolone−H_2O complexes are affected when a second water molecule is added to the system, i.e., whether cooperative effects are important in complexes containing two water molecules. In general, these cooperative effects are reflected in significant frequency shifts of the vibrational modes affected by the hydrogen bonding.[31,37,44]

The bonding characteristics of the tropolone−H_2O complexes show that the IHB of tropolone is perturbed in different ways depending on the basic center which is solvated. The interaction of the water molecule with the carbonyl group (**Tw1a**) leads to a weakening of the IHB, while it becomes reinforced when the interaction involves the hydroxyl group (**Tw1b**). These changes can be easily rationalized in terms of acid−base criteria.[37] In the **Tw1b** complex the acidic character of the hydroxyl group, which behaves as a HB acceptor with respect to the water molecule, is enhanced, and this leads to a reinforcement of the IHB. Accordingly, the charge density at the corresponding bond critical point increases (see Table 2), the O···H distance shortens, and the donor O−H bond lengthens. In **Tw1a** the basicity of the carbonyl group, which behaves also as a HB acceptor with respect to the water molecule, decreases and the IHB weakens. Consistently, the charge density at the bcp decreases (see Table 2), the O···H distance increases, and the donor O−H bond shortens. In complex **Tw1c** no bond critical

TABLE 2: Bonding Characteristics of Tropolone and the Stable Tropolone−H_2O and Tropolone−$(H_2O)_2$ Clusters, with Charge Densities (ρ) and Energy Densities ($H(\mathbf{r})$) in au, Obtained at the B3LYP/6-31+G(d) Level

	tropolone		Tw1a		Tw1b		Tw1c		Tw2ab		Tw2ac		Tw2bc		Tw2ring		Tw2ext		Tw2cage	
	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$
hydrogen bonds[a]																				
O1···H3	0.039	−0.001	0.038	−0.001	0.042	−0.001			0.041	−0.001							0.038	−0.001		
O1···H4			0.031	−0.001			0.029	0.000			0.027	0.000	0.028	0.000			0.035	−0.001	0.016	0.001
O1···H7									0.031	−0.001	0.032	−0.001			0.034	−0.001				
O2···H4					0.021	0.000			0.021	0.000										
O2···H7													0.024	0.000			0.036[b]	−0.001[b]	0.018	0.000
O5···H3							0.036	−0.001			0.037	−0.001	0.037	−0.001	0.048	−0.004			0.042	−0.002
O8···H4															0.034	−0.001			0.024[c]	−0.001[c]
CH···O8(5)			0.009	0.001	0.010	0.001			0.010	0.001	0.008	0.001	0.009	0.001			0.015	0.000		
									0.009	0.001										
covalent bonds																				
C−O1	0.378	−0.641	0.369	−0.619	0.377	−0.638	0.375	−0.632	0.367	−0.618	0.366	−0.612	0.375	−0.632	0.372	−0.624	0.365	−0.612	0.381	−0.645
C−O2	0.309	−0.490	0.309	−0.489	0.301	−0.470	0.310	−0.490	0.300	−0.470	0.310	−0.491	0.301	−0.470	0.318	−0.508	0.308	−0.488	0.304	−0.478
O2−H3	0.316	−0.466	0.318	−0.472	0.312	−0.458	0.311	−0.466	0.314	−0.465	0.311	−0.466	0.309	−0.463	0.293	−0.425	0.319	−0.473	0.298	−0.436
O5−H4			0.329	−0.494	0.338	−0.509	0.329	−0.500	0.338	−0.510	0.332	−0.505	0.329	−0.501	0.319	−0.476	0.321	−0.484	0.339	−0.512
O5−H6			0.347	−0.514	0.346	−0.514	0.344	−0.513	0.346	−0.515	0.344	−0.513	0.344	−0.513	0.344	−0.511	0.345	−0.513	0.332	−0.500
O8−H7									0.329	−0.495	0.329	−0.494	0.337	−0.508	0.326	−0.492	0.323	−0.484	0.336	−0.505
O8−H9									0.346	−0.514	0.346	−0.513	0.346	−0.514	0.345	−0.510	0.346	−0.513	0.344	−0.514

[a] The charge density at the HB in water dimer, at the same level of theory, is 0.028 au. [b] O5···H7 bond. [c] O8···H6 bond.

point is found between the hydroxyl and the carbonyl groups of tropolone, indicating that a single water molecule perturbs dramatically the IHB. The topology of the charge density (see Table 2) clearly shows that in this complex the hydroxyl group is really acting as a proton donor to the water molecule. This is consistent with the large increase in the COH bond angle, described by Frost et al.,[26] when this complex is formed. This situation will be found again in several tropolone−$(H_2O)_2$ complexes.

In the three tropolone−H_2O complexes the water molecule behaves as a proton donor−acceptor. This is obvious in complex **Tw1c**, where the water molecule behaves as a proton acceptor of the hydroxyl group and as a proton donor to the carbonyl group. In complexes **Tw1a** and **Tw1b** water behaves as a proton donor to the carbonyl and the hydroxyl groups, respectively, but also as a proton acceptor of a CH group of tropolone. As expected, due to the small polarity of the C−H linkages, these C−H····O HBs are much weaker than the O−H····O ones. Accordingly they exhibit a much smaller charge density at the corresponding bcp (see Table 2), as well as much longer bond distances and, as we shall show later, smaller stretching frequencies.

The effect of the second water molecule on the strength of the different HBs is not negligible in any case. As shown in Table 2 the IHB in complex **Tw2ab** is stronger than in **Tw1a** and weaker than in **Tw1b**. Solvation of **Tw1a** by a second water molecule to yield **Tw2ab** enhances the donor capacity of the hydroxyl group and therefore reinforces the IHB. On the contrary, solvation of **Tw1b** by a second water molecule to yield **Tw2ab** decreases the acceptor capacity of the carbonyl group and therefore the IHB weakens. The same kind of interactions explain why the O1···H4 linkage in complex **Tw1c** is stronger than in species **Tw2ac**, while its O5···H3 hydrogen bond is weaker than in cluster **Tw2bc**. For similar reasons the O1···H4 linkage in **Tw2ext** and the O5···H3 hydrogen bond in **Tw2ring** are stronger than the corresponding ones in **Tw1a** and **Tw1c**, respectively. The strongest HB is found between O5 and H3 in complex **Tw2cage**. This simply reflects the high acceptor capacity of the water molecule, which behaves simultaneously as a double proton donor (see Figure 1) and the enhanced donor ability of the O−H group of tropolone, which behaves simultaneously as proton acceptor. As we shall discuss in forthcoming sections this will be reflected in dramatic shifts of the vibrational modes associated with the hydroxyl group of tropolone. Hence, from the bonding analysis discussed above we may conclude that **Tw2ab** and **Tw2ext** are the only tropolone−$(H_2O)_2$ complexes which retain almost intact its intramolecular hydrogen bond.

It can be also useful to notice that the most stable complexes, namely, **Tw2ring** and **Tw2ext**, can be alternatively considered as the association of a water dimer to tropolone. In both cases the intermolecular HB of the $(H_2O)_2$ moiety is sizably stronger than in the isolated water dimer (see Table 2 and Figure 1), as should be expected in light of the acid−base arguments employed in our previous discussion. Also importantly, all the intermolecular hydrogen bonds between the water molecules and tropolone in these two tropolone−$(H_2O)_2$ complexes are stronger than those found in the tropolone−H_2O analogues, **Tw1a** and **Tw1c**. This indicates that for the most stable tropolone−$(H_2O)_2$ clusters cooperative effects are important. To quantify these effects from the energetic point of view, we have considered it of interest to evaluate the so-called additive interaction energy, (ΔE_{add}, defined as:

$$\Delta E_{\mathrm{add}} = \Delta E_{\mathrm{ABC}} - \Delta E_{\mathrm{AB}} - \Delta E_{\mathrm{AC}} - \Delta E_{\mathrm{BC}}$$

where ΔE_{ABC} is the binding energy of the tropolone−$(H_2O)_2$ complex and the remaining terms in the right-hand side of the equation represent the association energies of the different dimers which can be defined within the trimer. In our notation A corresponds always to the molecule of tropolone.

At the highest level of theory used in this work the values of ΔE_{add} for the two most stable clusters, **Tw2ext** and **Tw2ring**, are 3.7 and 7.0 kcal/mol, respectively. The first value is rather close to that estimated, at the same level of theory, for other similar hydrogen-bonded such clusters as water[37] and methanol[31] trimers. The value of ΔE_{add} obtained for the global minimum is quite high due mainly to two factors. On one hand the water molecules must reorient to favor the formation of the cyclic hydrogen-bonded structure, and, as a consequence, the HBs with the hydroxyl and the carbonyl groups are weaker than expected. On the other hand, and more importantly, the IHB is practically broken and this decreases significantly the stability of the dimers AB and AC. This loss in stability is compensated for, however, by the formation of a third HB between both water molecules (dimer BC).

Vibrational Frequencies. When dealing with hydrogen-bonded clusters, a primary point of comparison with experiment is via the frequency shifts undergone by the intramolecular vibrations of the different subunits forming the cluster. Also of relevance can be the intermolecular vibrations since they provide some clue to the relative strengths of the corresponding hydrogen bonds. Hence, in what follows we shall concentrate our attention on the O−H stretching frequencies of both water molecules ($\nu_1-\nu_4$), the OH stretching mode of tropolone (ν_5), the bending motions of both water molecules (ν_6, ν_7), the C═O (ν_8), and the C−OH (ν_9) stretching modes, the two O−H (in-plane (ν_{10}) and out-of-plane (ν_{11})) bending motions of tropolone, the in-plane O−O wagging of tropolone (ν_{12}), and the intermolecular stretching vibrations associated with each HB ($\nu_{13}-\nu_{15}$).

Since the harmonic vibrational frequencies of tropolone−H_2O complexes were discussed in detail by Frost et al.,[26] we shall limit our analysis to the tropolone−$(H_2O)_2$ complexes. In clusters **Tw2ab**, **Tw2bc**, **Tw2ac**, and **Tw2cage** the two highest vibrational frequencies (ν_1, ν_2) correspond to the asymmetric stretching modes of both water molecules, while the next two (ν_3, ν_4) are associated with the corresponding symmetric modes. Consistently with the fact mentioned above, that the two most stable complexes, **Tw2ring** and **Tw2ext**, can be viewed as clusters between a water dimer and tropolone, in both clusters the two highest vibrational frequencies (ν_1, ν_2) correspond to the in-phase and the out-of-phase combinations of the stretching modes of the two free OH groups. The next two (ν_3, ν_4) are the analogous combinations of the OH stretching modes of the two hydrogen-bonded OH groups. In all cases the predicted frequency values are sizably lower than those estimated for the isolated water molecule. Also, for all the complexes studied, the two absorptions associated with the corresponding water bending modes (ν_6, ν_7) have higher frequencies than in the water monomer. It can be also observed that these shiftings are particularly large for the two most stable complexes, **Tw2ext** and **Tw2ring**.

There are significant differences between the different tropolone−$(H_2O)_2$ complexes as far as the OH stretch of the tropolone moiety (ν_5) is concerned. For **Tw2ext** this vibrational mode appears blue-shifted with respect to isolated tropolone, while in the remaining cases it undergoes a red-shifting. This frequency change is particularly large for **Tw2cage**, in agreement with our previous discussion. As a consequence, in this complex the OH stretching band of tropolone appears at lower frequencies than the corresponding C−H stretching modes (see Table 3). As expected, the sign of the shifting of the out-of-plane OH bending (ν_{11}) is the opposite. For **TW2ext** it appears red-shifted by 18 cm^{-1}, while for the remaining complexes it appears blue-shifted. Again this shifting is particularly large for the **Tw2cage** cluster.

For this latter complex the C═O stretching vibrational mode (ν_8) appears slightly blue-shifted, while for the remaining complexes is always slightly shifted to lower frequency values. It must be emphasized that this behavior is in agreement with the topology of the corresponding charge distributions, which shows that only for **Tw2cage**, the C═O linkage is reinforced with respect to the tropolone monomer (see Table 2). The C−OH stretching mode (ν_9) appears blue-shifted for clusters **Tw2ac** and **Tw2ring**, again consistently with the values of the charge densities at the corresponding bcps. The estimated blue-shifting in both cases (+14 and +20 cm^{-1}) is similar to the experimental value (+14 cm^{-1}) reported for this shifting in tropolone−H_2O complexes.[26]

The in-plane OH bending of tropolone (ν_{10}) is blue-shifted only in complex **Tw2ab** which presents an IHB stronger than that of tropolone (see Table 2). Complex **Tw2ext** retains also the IHB, but it is weaker than that of tropolone (see Table 2), and accordingly the in-plane OH bending is slightly shifted to lower frequencies. In all the remaining complexes, where the IHB is practically broken, this vibrational mode undergoes a significant red-shifting. This seems to be consistent with the fact that the in-plane O−O wagging motion appears at higher frequencies in clusters **Tw2ab** and **Tw2ext** which preserve the IHB, while it is red-shifted in all the other complexes. The predicted blue-shiftings (29 and 24 cm^{-1}) for the aforementioned clusters are higher than the experimental value (+11 cm^{-1}) reported for tropolone−H_2O complexes,[26] likely reflecting the influence of the second water molecule on the IHB.

The intermolecular stretching frequencies are found typically in the 300−400 cm^{-1} region, although the stretching frequencies of the CH···O hydrogen bonds appear at lower frequency values (95−170 cm^{-1}).

From hole-burning and infrared spectroscopic analysis of tropolone−$(H_2O)_2$ and tropolone−$(CH_3OH)_2$ clusters, Mitsuzuka et al.[27] concluded that: (i) the water site has at least one free OH oscillator, (ii) the other two OH oscillators are acting as proton donors, and (iii) only two hydrogen-bonded OH oscillators are observed. On these grounds it is difficult to discriminate among the different local minima we have located in the potential energy surface, since all of them seem to fulfill these requirements. On the other hand the information on the vibrational frequencies of tropolone−$(H_2O)_2$ complexes is restricted[27] to the stretching modes of the free and the hydrogen-bonded OH groups of the water molecules. Nevertheless, this information can be enough to discard the less stable complexes in terms of the frequency gaps between the free OH and the hydrogen-bonded OH stretching modes. Actually, the experimental gaps[27] (228 and 307 cm^{-1}) are significantly higher than those estimated for all the complexes with the only exception of **Tw2ring** and **Tw2ext** (see Table 3). On the other hand, the agreement between experimental and calculated values (227 and 345 cm^{-1}) is remarkably good for the former. For the latter the accord is poorer, although similarly large (311 and 317 cm^{-1}) gaps are predicted.

TABLE 3: Harmonic Vibrational Frequencies (cm^{-1}) of Tropolone, Water, and Tropolone−$(H_2O)_2$ Complexes, with Values Obtained at the 6-31+G(d) Level

Tw2ab	Tw2bc	Tw2ac	Tw2cage	Tw2ext	Tw2ring	tropolone
27	29	33	34	32	24	115
44	48	49	43	42	42	185
62	51	51	85	57	79	364 (ν_{12})
68	85	88	105	95 (ν_{15})	99	375
75	95	129	132	124	163	376
80	125	140	163 (ν_{15})	173	164 (ν_{15})	402
120	145 (ν_{15})	162	191	175	184	449
124 (ν_{15})	182	181 (ν_{14})	200 (ν_{13})	190	201	546
175	185	183	201	241	249	597
191	298	277	287 (ν_{14})	259 (ν_{13})	261 (ν_{13})	694
345 (ν_{13})	330 (ν_{14})	335	343 (ν_{12})	371 (ν_{14})	331	723
378	338	366 (ν_{12})	368	381	352 (ν_{12})	752
387	365 (ν_{12})	375	377	387 (ν_{12})	375	772
393 (ν_{12})	375	380 (ν_{13})	405	403	391 (ν_{14})	815 (ν_{11})
408	385 (ν_{13})	396	416	425	403	877
437 (ν_{14})	404	409	445	436	453	888
454	459	458	509	458	518	946
467	526	540	523	556	555	977
561	543	599	576	601	604	1013
611	604	626	601	700	605	1030
644	642	687	691	737	698	1081
702	697	718	718	746	730	1245
733	721	732	725	756	756	1249
752	751	752	752	774	772	1295
781	776	771	775	797 (ν_{11})	839	1327 (ν_{10})
811 (ν_{11})	868 (ν_{11})	869 (ν_{11})	875	887	870	1349 (ν_9)
894	892	894	889	891	891	1454
900	905 (ν_{11})	915 (ν_{11})	945	899	935 (ν_{11})	1480
976	967	960	985	965	954 (ν_{11})	1523
985	991	997	1012	985	989	1540
1031	1025	1017	1030	1019	1015	1618 (ν_8)
1044	1031	1041	1055 (ν_{11})	1061	1027	1664
1088	1078	1081	1085	1087	1075	1675
1242 (ν_9)	1240 (ν_{10})	1241 (ν_{10})	1238	1249	1219 (ν_{10})	3161
1259	1243	1251	1252	1257	1248	3170
1316	1291 (ν_{10})	1277	1286	1301 (ν_{10})	1275	3185
1335 (ν_{10})	1309	1330	1313 (ν_{10})	1336 (ν_9)	1307	3191
1351	1344 (ν_9)	1363 (ν_9)	1346 (ν_9)	1357	1369 (ν_9)	3196
1457	1454	1458	1450	1458	1451	3327 (ν_5)
1497	1466	1460	1455	1487	1456	
1515	1525	1518	1525	1510	1524	water
1541	1538	1535	1538	1538	1532	1663
1602 (ν_8)	1605 (ν_8)	1583 (ν_8)	1621 (ν_8)	1600 (ν_8)	1610 (ν_8)	3734
1661	1652	1650	1655	1660	1650	3858
1665	1667	1662	1672	1667	1666	
1682 (ν_7)	1685 (ν_7)	1676 (ν_7)	1680 (ν_7)	1707 (ν_7)	1690 (ν_7)	
1703 (ν_6)	1688 (ν_6)	1698 (ν_6)	1697 (ν_6)	1729 (ν_6)	1730 (ν_6)	
3167	3162	3164	3111 (ν_5)	3166	3160	
3176	3172	3171	3160	3172	3168	
3190	3185	3186	3167	3178	3184	
3195	3190	3188	3181	3187	3187	
3199	3197	3197	3189	3196	3195	
3317 (ν_5)	3310 (ν_5)	3326 (ν_5)	3195	3374 (ν_5)	3237 (ν_5)	
3562 (ν_4)	3614 (ν_4)	3547 (ν_4)	3620 (ν_4)	3446 (ν_4)	3479 (ν_4)	
3694 (ν_3)	3672 (ν_3)	3645 (ν_3)	3669 (ν_3)	3506 (ν_3)	3597 (ν_3)	
3828 (ν_2)	3819 (ν_2)	3815 (ν_2)	3779 (ν_2)	3816 (ν_2)	3823 (ν_2)	
3843 (ν_1)	3831 (ν_1)	3824 (ν_1)	3831 (ν_1)	3817 (ν_1)	3824 (ν_1)	

Hence on these bases alone a clear preference for one of the two forms cannot be established. There are however some important structural differences between both complexes which should be reflected in their infrared spectra. The most important one is that while **Tw2ext** still has an IHB in **Tw2ring**, the IHB was replaced by an intermolecular HB in which the hydroxyl group acts as a proton donor to water. Since, as discussed above, the formation of **Tw2ext** implies a weakening of the IHB of tropolone, it is not surprising to find that the OH stretch of the tropolone moiety (ν_5) appears slightly shifted (47 cm^{-1}) to the blue, while in the **Tw2ring** species the same band should appear red-shifted by almost 100 cm^{-1}. Hence, the detection of this band in the infrared spectrum would allow one to clearly discriminate between both forms. Particularly sensitive to the characteristics of the IHB is the out-of-plane OH bending. As mentioned above in the **Tw2ext** complex, where the IHB is weaker than in isolated tropolone, this bending mode is red-shifted by 18 cm^{-1} (see Table 3). In contrast, in the **Tw2ring** structure, where the IHB has been replaced by a stronger intermolecular HB between the hydroxyl group and one water molecule, this vibrational mode is blue-shifted by more than 120 cm^{-1}.

The quite different arrangements of the monomers within both complexes is also reflected in sizable differences between their rotational constants (see Table 1). Hence significant differences should be also observed in their microwave spectra. It is also quite possible that other spectroscopic techniques such as rotational coherence or high-resolution electronic spectroscopy could be used for this purpose.

Conclusions

In our survey of the tropolone−$(H_2O)_2$ potential energy surface through the use of B3LYP calculations we have located nine different local minima which meet the general criteria posed by the experimental infrared spectra of possessing at least one free OH oscillator and only two hydrogen-bonded oscillators, which act as proton donors. However, only the two most stable complexes present frequency gaps between the free OH and the hydrogen-bonded OH stretching modes in agreement with the experimental values. These two species, **Tw2ring** and **Tw2ext**, are very near in energy to one another, although they present very different bonding characteristics since in the former the intramolecular hydrogen bond of the tropolone moiety is broken, while this is not the case for the latter. Both isomers had been proposed by Mitsuzuka et al.[27] as the most probable structures of tropolone−$(H_2O)_2$ complexes. Our results confirm these predictions, but since, as mentioned above, both forms are almost degenerate, one cannot on this basis alone favor one isomer over the other. Due to the similarity between the estimated entropies for both complexes, one should not expect a higher gap between their free energies either. Unfortunately the discrimination between both isomers is also not possible using the available experimental information. Nevertheless in the light of our calculations we can conclude that both species could be distinguished in terms of the shifting of the O−H stretching and bending modes of the tropolone moiety. For **Tw2ext** the stretching mode should appear slightly blue-shifted, while for **Tw2ring** it should appear red-shifted. Similar differences in the out-of-plane bending mode should also be observed. Nonnegligible dissimilarities in their microwave spectra should also be expected in light of the significant differences between their rotational constants.

The binding energies of both complexes (10.0 and 9.9 kcal/mol, respectively) are sizably larger than those predicted for tropolone−H_2O complexes. This indicates that significant cooperative effects appear when a second water molecule is added to the system. These cooperative effects are reflected in the strength of the intra- and intermolecular hydrogen bonds and in the shiftings of the vibrational modes affected by them.

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