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Bonding in Tropolone, 2-Aminotropone, and Aminotroponimine: No Evidence of Resonance-Assisted Hydrogen-Bond Effects

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Abstract: The properties of the intramolecular hydrogen bond (IMHB) in tropolone, aminotropone, and aminotroponimine have been compared with those in the corresponding saturated analogues at the B3LYP/6-311+G(3df,2p)//B3LYP/6-311+G(d,p) level of theory. In general, all those compounds in which the seven-membered ring is unsaturated exhibit a stronger IMHB than their saturated counterparts. Nevertheless, this enhanced strength is not primarily due to resonance-assisted hydrogen-bond effects, but to the much higher intrinsic basicity and acidity of the hydrogen-bond acceptor and donor groups, respectively, in the unsaturated compounds. These acidity and basicity enhancements have a double origin: 1) the unsaturated nature of the moiety to which the hydrogen-bond donor and acceptor are attached and 2) the cyclic nature of the compounds under scrutiny. As has been found for hydroxymethylene and aminomethylene cyclobutanones, and cyclobutenones and their nitrogen-containing analogues, the IMHB strength follows the [donor, acceptor] trend: [OH, C=NH] > [OH, C=O] > [NH_2, C=NH] > [NH_2, C=O] and fulfills a Steiner–Limbach correlation similar to that followed by intermolecular hydrogen bonds.

Keywords: density functional calculations · hydrogen bonds · resonance · tropolone

Introduction

We have devoted four papers to discussing the concept of resonance-assisted hydrogen bonds (RAHBs), first defined by Gilli et al.,[1] by using as a model the enol forms of β-diketones and the compounds resulting from replacing one or both O atoms by NH atoms.[2–5] Although there is no clear-cut definition of RAHBs, it was firstly introduced as "the interplay between hydrogen bond and heterodienes (or more generally heteroconjugated systems) leading to a strengthening of the hydrogen bond itself".[1] In general, it is viewed as an increase in the donor and acceptor strengths through a charge flow in suitable polarizable π-bond systems,[6,7] which is reflected in the very short donor–acceptor distances. However, the evidence that intramolecular hydrogen bonds (IMHBs) are stronger in unsaturated compounds than in their saturated analogues does not necessarily imply the existence of an RAHB phenomenon, but simply characteristics of the σ-skeleton framework that in the unsaturated compounds force the donor and acceptor to be in closer proximity than in the saturated compound. The crucial role of the σ-skeleton framework was clearly illustrated for a series of hydroxymethylene and aminomethylene cyclobutanones and cyclobutenones, in which some saturated derivatives exhibited stronger IMHBs than their unsaturated counterparts due to the geometric constraints imposed by the σ-skeleton framework.[5]

Our strategy in the analysis of the existence of the RAHB phenomenon has been to attach differently sized rings (four to six carbon atoms) (**I**) and introduce different degrees of saturation (**II**) at two adjacent positions on the enol form of β-diketone (Scheme 1).

Another possibility is to link together the terminal positions of **I** to get **III**, a compound never isolated in any of its tautomeric forms although **IIIa** has been observed in planetary atmospheres and interstellar clouds.[8,9] It is also possible to imagine vinylogues of **I**, for example, **IV** (mono) and **VI** (bis), but the flexibility of the long chains could prevent the existence of an IMHB. By combining both strategies one gets compounds **V** and **1**. Tautomer **Va** has never been isolated because **Vb** (a well-known flavor) is much more

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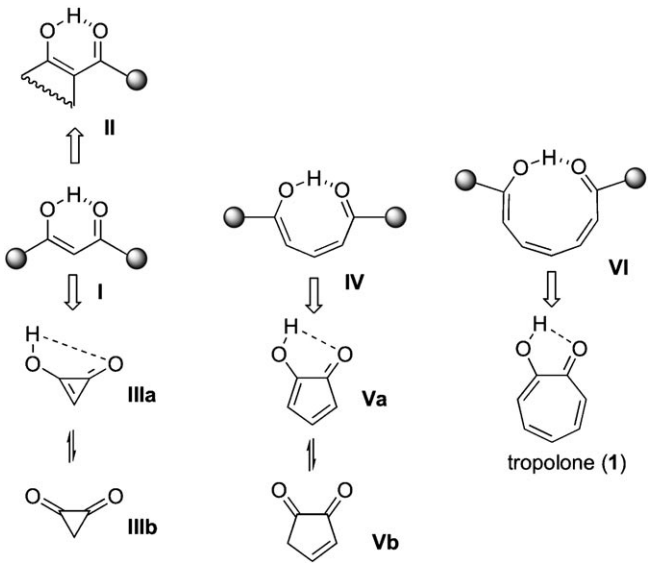


Scheme 1. The strategy used to establish compounds for the analysis of the existence of the RAHB effect. The gray spheres represent rings containing four to six carbon atoms.

stable.[10–12] Fortunately, tropolone (**1**) is a stable compound that has been much studied, including theoretical research carried out by some of us.[13,14] The bibliography on tropolone is very large and will not be reported here unless it is relevant to do so. However, it is worth mentioning that in a recent study, 5-azatropolone and its protonated form were predicted to exhibit intramolecular dynamical properties parallel to those observed for tropolone.[15] NMR coupling constants across the hydrogen bonds of aminotroponimine (both O atoms of tropolone replaced by N atoms) have been experimentally studied by some of us.[16] 2-Aminotropone (only one O atom of tropolone replaced by N) is an intermediate case in which the heteroatoms involved in the IMHB are different.

The aforementioned analyses have shown that the strength of the IMHB in compounds of type **I** and **II**, which have been traditionally considered as paradigmatic examples of systems in which the IMHB is stabilized through RAHB effects, is primarily due to the constraints intrinsically imposed by the σ-skeleton framework on the disposition and proximity of the hydrogen-bond donor and acceptor groups and not to RAHB effects.[2–5]

The study of the IMHB in compounds such as tropolone, 2-aminotropone, and aminotroponimine permits one to go a step further in this analysis because in all these compounds the single bond that links both functional groups (the hydroxyl and the carbonyl in tropolone, the amino and the carbonyl in 2-aminotropone, or the amino and the imino in aminotroponimine) does not play any role in the conjugation, limited as it is to bringing the functional groups together. This should not be confused with the resonance stabilization of tropolone, which exclusively affects the seven-membered ring but not the molecular fragment involved in the IMHB.[17] Therefore, the main question we look to answer is whether the strength of the IMHBs in the aforementioned compounds differ significantly from those exhibited by their saturated analogues and whether or not the origin of the differences found between them can be associated with RAHB effects.

Computational Details

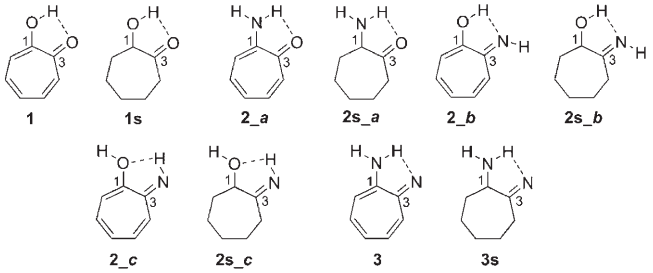
Standard B3LYP density functional theory (DFT) calculations have been performed as implemented in the Gaussian 03 suite of programs.[18] The B3LYP approach includes the Becke three-parameter nonlocal hybrid exchange potential[19] and the nonlocal correlation functional of Lee, Yang, and Parr.[20] Geometries were optimized by using a 6-311+G(d,p) basis set expansion. Very recently, an assessment of this method for the treatment of similar IMHBs has been reported.[5] In this assessment it was shown, for a large set of hydroxymethylene and aminomethylene cyclobutanones and cyclobutenones and their nitrogen-containing analogues, that although the MP2/6-311+G(d,p)-optimized values for the hydrogen-bond length and for the distance between the heteroatoms involved in the IMHB are slightly shorter than those obtained at the B3LYP level, the correlation between both sets of values is excellent.

For all the compounds under investigation we have also obtained the geometries of the transition states associated with the proton transfer between the hydrogen-bond donor and acceptor. The stationary points found were characterized as local minima or transition states by evaluating the corresponding harmonic vibrational frequencies at the same level of theory used for the geometry optimization. These frequencies were also used to estimate the corresponding zero-point energies (ZPEs), which were scaled by the empirical factor 0.9806.[21] Final energies were obtained through single-point calculations, carried out at the B3LYP/6-311+G(3df,2p) level of theory, to ensure the reliability of the calculated relative stabilities.

The characteristics of the IMHBs were analyzed in terms of the distance between the two heteroatoms involved, the length of the hydrogen bond, the redshift of the stretching frequency of the hydrogen-bond donor group (YH), and the electron population by means of the natural bond orbital (NBO) method[22] and the atoms-in-molecules (AIM) theory.[23] A hydrogen bond can be characterized by the interaction energy between the lone pair of the hydrogen-bond acceptor (X) and the σ^*_{YH} antibonding orbital of the hydrogen-bond donor (YH), obtained through the use of second-order NBO analyses.[22] This interaction leads to a charge transfer from the lone pair of the hydrogen-bond acceptor (X) into the σ^*_{YH} antibonding orbital of the hydrogen-bond donor (Y), so that the electron population of this antibonding orbital constitutes a reliable index with which to measure the relative strength of the hydrogen bond. The strength of a hydrogen bond can also be quantified by looking at the electron density at the corresponding bond critical point (bcp), and this density has been successfully used not only to characterize inter- and intramolecular hydrogen bonds[24–29] but also to design new partition schemes as useful tools to investigate the nature of these kinds of weak interactions. Furthermore, a good correlation between the strength of the interaction and the electron density at the corresponding hydrogen-bond critical point generally exists.[24,26,30–34] It has been recently found that such correlations occurred independently of the strength of the interaction and therefore are fulfilled not only by strong, but also by moderate and weak hydrogen bonds.[35] Both the NBO and AIM analyses were carried out by using a 6-311+G(d,p) basis set expansion. We assume that the conclusions obtained would not change if the basis set were enlarged. It has been shown that the values obtained with quite different basis sets, namely, 6-311+G(d,p), 6-311+G(3df,2p), aug-cc-pvDZ, and aug-cc-pVTZ, for a large set of compounds exhibiting similar IMHBs as those considered in this work, are strongly correlated[5] and therefore the trends observed in these values do not depend on the extension of the basis set used to obtain the electron density.

Results and Discussion

In what follows, and for the sake of simplicity, we will designate the heteroatom of the hydrogen-bond acceptor group as X and that of the donor group as Y, in which the X/Y atoms are O/O, O/N, N/O, and N/N (see Scheme 2).



Scheme 2. The schematic structures and the naming system of the compounds studied: **s**: saturated compound; ***a***, ***b***, ***c***: isomers of compound **2**.

The most relevant structural parameters associated with the IMHB of the species under study, namely, the heteroatomic internuclear distance (X···Y), the IMHB length (Y−H···X), the electron density at the IMHB bond critical point (ρ_{bcp}) and at the ring critical point (ρ_{rcp}), the bond length of the hydrogen-bond donor group (Y−H), and the lengths of the C^3=X and C^1−Y bonds are summarized in Table 1. The optimized geometries, the B3LYP/6-311+G(3df,2p) total energies, and the B3LYP/6-311+G(d,p) zero-point vibrational energies of the compounds investigated are summarized in Tables S1 and S2 of the Supporting Information.

Although for tropolone (**1**) and aminotroponimine (**3**) and their saturated counterparts (**1s** and **3s**, respectively) only one isomer is stable, for aminotropone (**2**) and its saturated counterpart (**2s**) there are three different isomers (named ***a***, ***b***, and ***c***) depending on the nature and disposition of the hydrogen-bond acceptor and donor groups. In isomer ***a***, the hydrogen-bond donor is an amino group and the acceptor is a carbonyl group. In isomer ***b***, the hydrogen-bond donor is a hydroxyl group and the acceptor an imino group, whereas in isomer ***c*** these roles are interchanged. At the B3LYP/6-311+G(3df,2p) level of theory isomer **2_*a*** is predicted to be 44 and 86 kJ mol^{-1} more stable than isomers **2_*b*** and **2_*c***, respectively. For their saturated counterparts these energy gaps become 21 and 38 kJ mol^{-1}, respectively.

The higher stability of the type-***a*** isomers can be understood if one takes into account that the energetic change on going from the type-***a*** to type-***b*** (or -***c***) isomers essentially measures the energy cost of changing a C=O double bond into a C−O single bond, the energy gained in changing a C−N single bond into a C=N double bond, and the energy difference between NH and OH bonds. The enthalpy associated with these changes can be adequately measured by using isodesmic reaction (1):

$$H_2CO + CH_3NH_2 \rightarrow H_2CNH + CH_3OH \qquad (1)$$

which is predicted to be endothermic by 21 kJ mol^{-1} at the B3LYP/6-311+G(3df,2p) level of theory. This confirms that the main energetic factor in favor of type-***a*** isomers is related to the presence in the system of carbonyl and NH_2 groups, with respect to the other two isomers in which these groups have been replaced by hydroxyl and imino groups, respectively.

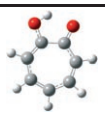
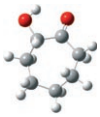
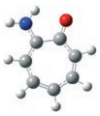
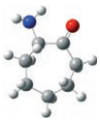
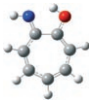
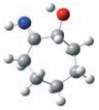
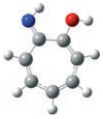
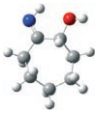
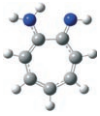
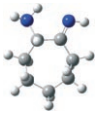
The values in Table 1 also give a clue about the origin of the enhanced stability of type-***b*** isomers relative to type-***c*** isomers, as the former have a much stronger IMHB. We will come back to this point later.

Similar to what was found for other IMHBs, those investigated here also fulfilled the Limbach–Steiner correlation, as well as the logarithmic dependence of the length on the electron density at the bcp (see the Supporting Information).

Analysis of the strength of the IMHBs: From values in Table 1, it can be seen that the strength of the IMHB involving OH and NH_2 as hydrogen-bond donors and C=O and C=NH groups as hydrogen-bond acceptors follow systematically the following [donor, acceptor] trend: [OH, C=NH] > [OH, C=O] > [NH_2, C=NH] > [NH_2, C=O]. Accordingly, the strongest IMHB is observed for the ***b***-type isomer of aminotropone. This isomer is also the one that exhibits the strongest IMHB among the corresponding saturated counterparts. The origin of this trend has been explained for a series of enols of β-diketones, generated by fusing the malonaldehyde moiety with unsaturated or saturated six-membered rings,[4] and with four-membered rings[5] and will not be repeated here. However, a cursory examination of the indexes reported in Table 1 shows that the IMHB is always stronger in the unsaturated derivatives, with the only exception being the couple **2_*c*** and **2s_*c***, in which the IMHB is stronger in the latter.

The situation discussed here is completely different from that found for the enols of β-diketones (compounds **I** and **II** in Scheme 1) in which the hydrogen-bond donor and acceptor are strictly coplanar in the unsaturated compounds but not in the saturated derivatives. Therefore, the primary reason behind the strength of the IMHBs of compounds **I** and **II** is simply the structure of the σ-skeleton framework of the system that keeps the hydrogen-bond donor and acceptor coplanar and closer to each other, rather than an RAHB effect. Similar arguments cannot be used for the compounds studied in this paper, which have the hydrogen-bond donor and acceptor coplanar in both the saturated and unsaturated compounds. Does the stronger IMHB of unsaturated compounds reflect an RAHB effect? This seems not to be the case because, as mentioned above, the single bond that links the hydrogen-bond donor and acceptor does not play any role in the conjugation. Therefore, the differences in the strength of the IHMB must be due to the effect of the ring (saturated or unsaturated) on the intrinsic basicity of the hydrogen-bond acceptor and on the intrinsic acidity of the hydrogen-bond donor.

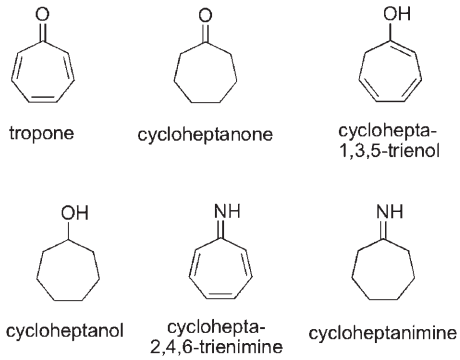
Table 1. Characteristics of the IMHB of the systems investigated: interatomic distances (X···Y, X···H, Y−H, C^3=X, C^1−Y) are in Å; ρ_{bcp} and ρ_{rcp} are the electron densities [e au^{-3}] at the IMHB bond critical point and at the ring critical point, respectively; DE [kJ mol^{-1}] is the interaction energy between the lone pair of the hydrogen-bond acceptor and the σ^*_{YH} antibonding orbital of the hydrogen-bond donor; $Pop_{\sigma^*_{YH}}$ signifies the electron population [a.u.] of the σ^*_{YH} antibonding orbital of the hydrogen-bond donor.

Compound		ρ_{bcp}	ρ_{rcp}[a]	X···Y	YH···X	Y−H	C^3=X	C^1−Y	DE	$Pop_{\sigma^*_{YH}}$
1		0.0405	0.0334	2.496	1.816	0.989	1.246	1.332	43.9	0.0468
1s		0.0282	0.0262	2.596	1.977	0.971	1.216	1.410	17.3	0.0250
2_*a*		0.0259	0.0247	2.539	2.048	1.013	1.242	1.349	13.3	0.0212
2s_*a*		0.0208	0.0206	2.647	2.152	1.015	1.214	1.458	5.4	0.0136
2_*b*		0.0463	0.0335	2.474	1.776	0.995	1.301	1.332	67.5	0.0569
2s_*b*		0.0319	0.0269	2.576	1.936	0.974	1.273	1.411	27.0	0.0289
2_*c*		0.0203	0.0201	2.654	2.129	1.019	1.291	1.363	3.5	0.0107
2s_*c*		0.0216	0.0207	2.653	2.089	1.022	1.270	1.428	5.0	0.0152
3		0.0279	0.0246	2.531	2.024	1.014	1.301	1.350	19.0	0.0235
3s		0.0213	0.0203	2.661	2.148	1.016	1.274	1.462	8.0	0.0141
2-hydroxy acryl aldehyde		–[b]	–	2.685	2.126	0.972	1.215	1.350	9.6	0.0197
2-hydroxy propanal		0.0217	0.0217	2.683	2.107	0.969	1.208	1.408	9.6	0.0183
dimer **1**		0.048	–	2.733	1.765	0.982	1.244	1.352	61.5	0.0490
dimer **2**		0.025	–	2.892	1.934	0.972	1.220	1.432	26.6	0.0265
dimer **3**		0.025	–	2.875	1.951	0.970	1.217	1.426	24.8	0.0239
dimer **4**		0.024	–	2.899	1.960	0.969	1.211	1.424	23.0	0.0226

[a] The rcp is that associated with the ring formed by the IMHB between the donor and the acceptor. [b] No hydrogen-bond bcp was found.

Let us take tropolone (**1**) and its saturated counterpart (**1s**) as suitable model compounds to investigate this question further. Taking into account that in these two compounds both the hydrogen-bond donor and acceptor are directly bound to the seven-membered ring, it is reasonable to expect that the enhanced strength of the IMHB in tropolone

(**1**) relative to **1s** may be due either to an enhanced basicity of the hydrogen-bond acceptor, or to an enhanced acidity of the hydrogen-bond donor or to both. To investigate if these effects are actually playing a role we have evaluated the intrinsic basicity of tropone and cycloheptanone and the acidity of cyclohepta-1,3,5-trienol and cycloheptanol by calculating the corresponding proton affinities and gas-phase acidity enthalpies.



The results obtained (which are in good agreement with the experimental values when available,[36] see Table 2) show that cyclohepta-1,3,5-trienol has an intrinsic acidity

Table 2. Proton affinities (PA) and gas-phase acidities ($\Delta_{acid}H$) of different model compounds. Available experimental values[a] are given within parentheses.

Compound	PA [kJ mol^{-1}]	$\Delta_{acid}H$ [kJ mol^{-1}]
tropone	925 (920.8)	–
cycloheptanone	851 (845.6)	–
acrylaldehyde	806 (797)	–
propionaldehyde	784 (786)	–
cyclohepta-2,4,6-trienimine	1019	–
cycloheptanimine	973	–
cyclohepta-1,3,5-trienol	755	1408
cycloheptanol	820	1563 (1559 ± 8.4)
prop-2-en-1-ol	–	1556 (1563 ± 12.0)
propan-1-ol	–	1573 (1572 ± 5.4)

[a] Values taken from ref. [36].

155 kJ mol^{-1} greater than that of cycloheptanol, whereas tropone is 74 kJ mol^{-1} more basic than cycloheptanone. We conclude that the enhanced IMHB in **1** reflects the fact that it has both a better hydrogen-bond donor and acceptor than **1s**. A further ratification of this conclusion is that the intermolecular hydrogen bond between tropone and cyclohepta-1,3,5-trienol (dimer **1** in Figure 1) is not only much stronger than the intermolecular hydrogen bond between cycloheptanol and cycloheptanone (dimer **2** in Figure 1), but is also stronger than the IMHB in tropolone (see Table 2), because in dimer **1** there are no ring constraints.

Similarly, the gas-phase basicity of cyclohepta-2,4,6-trienimine is 46 kJ mol^{-1} higher than that of its saturated counterpart cycloheptanimine (see Table 2), which explains why the IMHB in **2*b*** is stronger than that in **2s_*b***.

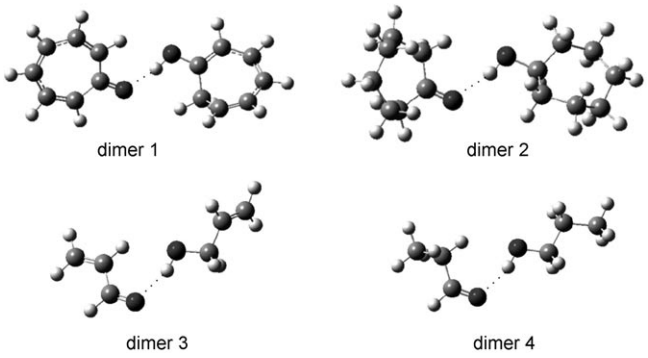
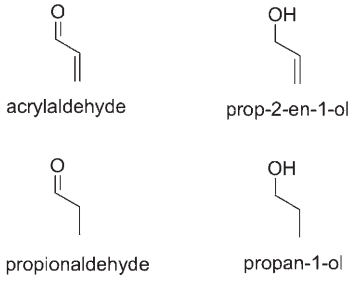


Figure 1. Structures of the dimers between tropone and cyclohepta-1,3,5-trienol (dimer **1**); cycloheptanol and cycloheptanone (dimer **2**); acrylaldehyde and prop-2-en-1-ol (dimer **3**); and propionaldehyde and propan-1-ol (dimer **4**).

The same arguments also explain why the situation is reversed for isomers **2_*c*** and **2s_*c*** in that the IMHB is stronger in the unsaturated one. In these isomers, the OH group behaves as a hydrogen-bond acceptor rather than as a hydrogen-bond donor, and, according to our previous basicity/acidity arguments it is a much poorer hydrogen-bond acceptor in the unsaturated derivative, as revealed by the calculated basicities of cyclohepta-1,3,5-trienol and cycloheptanol (see Table 2). It is also worth noting that species **2_*c*** and **2s_*c*** exhibit the weakest IMHB of all the systems investigated, but this is consistent with the trends discussed above, because these two compounds contain the weakest hydrogen-bond donor (NH) with the weakest hydrogen-bond acceptor (OH).

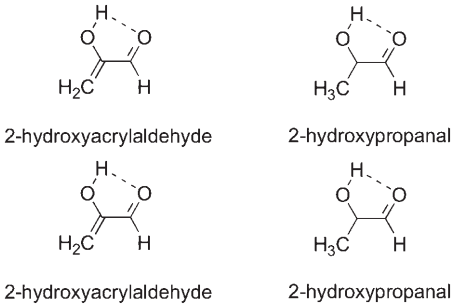
One question still needs to be answered: Does the acidity and basicity enhancement arise solely from the fact that tropone and cyclohepta-1,3,5-trienol are unsaturated compounds, whereas cycloheptanone and cycloheptanol are saturated, or is there also an effect associated with the fact that these are cyclic systems?

In an attempt to separate these effects, we have considered four noncyclic model compounds, namely, acrylaldehyde, prop-2-en-1-ol, propionaldehyde, and propan-1-ol, in which the environment of the basic and acidic sites are similar to those in tropolone and its saturated analogue, respectively.



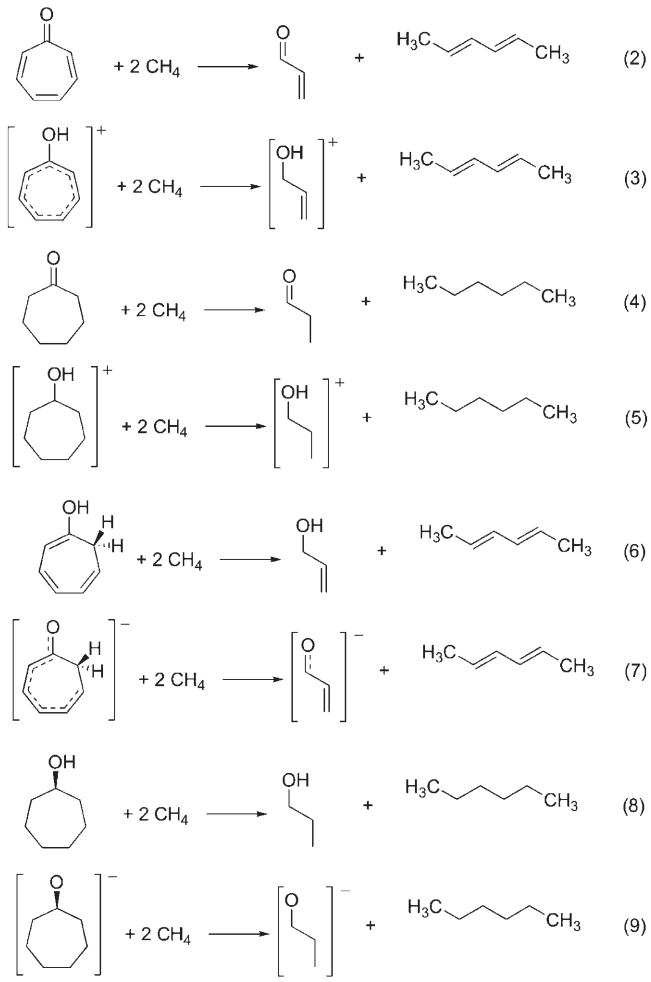
The calculated intrinsic basicities of acrylaldehyde and propionaldehyde and the intrinsic acidities of prop-2-en-1-ol and propan-1-ol are summarized in Table 2. The first conspicuous fact is that, similarly to what was found for the cyclic systems, the unsaturated compound (acrylaldehyde) is more basic than the saturated analogue (propionaldehyde), but the basicity gap (22 kJ mol^{-1}) is significantly smaller than that estimated for the couple tropone/cycloheptanone (74 kJ mol^{-1}). Similarly, the unsaturated alcohol (prop-2-en-1-ol) is a stronger acid than the saturated one (propan-1-ol), but again the gap between their acidities (17 kJ mol^{-1}) is much smaller than that between cyclohepta-1,3,5-trienol and cycloheptanol (155 kJ mol^{-1}). This clearly indicates that ring effects also play a significant role in the enhancement of the basicity and acidity of the hydrogen-bond donor and acceptor of tropolone with respect to its saturated counterpart. In other words, this enhancement is not only associated with the fact that the active sites are attached to an unsaturated moiety, because the enhancement effect is significantly amplified if the unsaturated moiety forms part of a seven-membered ring.

This is also consistent with the fact that the IMHBs in 2-hydroxyacrylaldehyde and 2-hydroxypropanal are much weaker than those in tropolone (**1**) and its saturated analogue (**1s**), respectively.



In 2-hydroxyacrylaldehyde both the heteroatomic distance and the length of the hydrogen bond are much greater than those in tropolone, the OH bond length is shorter, and the orbital interaction energies as well as the population of the σ^*_{OH} antibonding orbital are much smaller. Furthermore, no bcp point is found in the O···H region, which indicates that, strictly speaking, we cannot say that an IMHB actually exists. The same behavior was found when 2-hydroxypropanal was compared with **1s**, although in this case a bcp associated with the IMHB was located. Furthermore, the intermolecular hydrogen bond between acrylaldehyde and prop-2-en-1-ol (dimer **3** in Figure 1) is stronger than that between propionaldehyde and propan-1-ol (dimer **4** in Figure 1), but weaker than that between tropone and cyclohepta-1,3,5-trienol (dimer **1**).

It would be interesting to know whether these ring effects affect the saturated or the unsaturated compounds more. A possible way to answer this question is through the use of isodesmic reactions (2)–(9):



Isodesmic reactions (2) and (3) were used to measure the ring-stabilization effect on the neutral and protonated forms of unsaturated bases, respectively. These effects were measured by using reactions (4) and (5) for the saturated analogues. Reactions (6) to (9) were used to measure similar effects on the neutral and the deprotonated species of the corresponding acids. The calculated enthalpies for these reactions are presented in Table 3. Reactions (2) to (5) are all endothermic, which indicates that ring effects stabilize both the neutral and protonated forms, although the latter to a greater extent. It is also worth noting that these effects are much larger for the unsaturated than for the saturated compounds. These differences are even more dramatic as far as intrinsic acidities are concerned. Again, the stabilization is larger for the anion than for the neutral compound, but,

Table 3. Calculated enthalpies [kJ mol^{-1}] for isodesmic reactions (2)–(9).

Unsaturated		Saturated	
reaction 2	reaction 3	reaction 4	reaction 5
77	197	28	96
reaction 6	reaction 7	reaction 8	reaction 9
47	195	−17	−8

whereas reactions (6) and (7) are endothermic, reactions (8) and (9) are slightly exothermic. The most relevant finding is, however, that although the acidity enhancement due to cyclization is 148 kJ mol^{-1} for unsaturated compounds, it is very small (9 kJ mol^{-1}) for the saturated ones. It is also worth noting that whereas for the unsaturated compounds the acidity enhancement is about 20% larger than the basicity enhancement, for the saturated compounds it is the other way around and the basicity enhancement (87% larger) clearly dominates over the acidity enhancement. In other words, on going from open systems (like 2-hydroxyacrylaldehyde or 2-hydroxypropanal) to cyclic systems (like tropolone or **1s**) one should expect a reinforcement of the OH···O intramolecular hydrogen bond, because in the cyclic compound the hydrogen-bond donor and acceptor capacities both increase, with the former being dominant.

Conclusion

The properties of the intramolecular hydrogen bond in tropolone, aminotropone, and aminotroponimine have been compared with those in the corresponding saturated analogues at the B3LYP/6-311+G(3df,2p)//B3LYP/6-311+G(d,p) level of theory.

Aminotropone is predicted to be more stable than its isomer 2-iminocycloheptanol. Similar relative stabilities are predicted for the corresponding saturated analogues, although the energy gaps are almost half those found for the unsaturated derivatives. 2-Iminocycloheptanol and its saturated analogue present two conformers depending on the role (hydrogen-bond donor or acceptor) played by the OH and NH groups. The more stable corresponds to that in which the OH group is the donor and the NH group the acceptor. As a matter of fact, and as found before for other compounds, the IMHB strength follows the [donor, acceptor] trend: [OH, C=NH] > [OH, C=O] > [NH_2, C=NH] > [NH_2, C=O].

In general, all those compounds in which the seven-membered ring is unsaturated exhibit a stronger IMHB than their saturated counterparts. Nevertheless, this enhanced strength is not primarily due to resonance-assisted hydrogen-bond effects, but to the much higher intrinsic basicity and acidity of the hydrogen-bond acceptor and donor groups, respectively, in the unsaturated compounds. A more detailed analysis indicates that these basicity and acidity enhancements arise from two effects: 1) the higher basicity of the CO (or CNH) group and the higher acidity of an OH (NH_2) group when attached to an unsaturated moiety, and 2) to the amplification of these effects on going from open to cyclic systems, because in the cyclic compounds the necessary electron-density redistribution associated with the presence of a positive (or negative) charge in the system is favored, thus stabilizing the protonated and the deprotonated forms and therefore enhancing the intrinsic basicity and acidity of the corresponding active sites.

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