

# Cooperativity in Intramolecular Bifurcated Hydrogen Bonds: An Ab Initio Study

Rubén D. Parra\* and Jessica Ohlssen

Department of Chemistry, DePaul University, Chicago, Illinois 60614

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Molecular orbital and density functional theory calculations are performed on some di- and tetrasubstituted derivatives of anthraquinone, dihydrophenazine, and acridone to investigate cooperativity in a pair of bifurcated hydrogen bonds occurring in the same molecule. The various structures were selected as convenient model systems for three-center hydrogen bonding of both  $H\cdots A\cdots H$  and  $A\cdots H\cdots A$  types. In the former type, the  $C=O$  moieties in anthraquinone and acridone act as bifurcated hydrogen bond acceptors, and substituted OH groups act as hydrogen bond donors. In the latter type, the  $N-H$  moieties in dihydrophenazine, acridones act as bifurcated hydrogen bond donors, and the carbonyl oxygens of substituted CHO groups act as hydrogen bond acceptors. Different indicators of cooperativity reveal that two intramolecular bifurcated hydrogen bonds simultaneously present in the same molecule significantly reinforce each other.

## 1. Introduction

A typical hydrogen bond (H bond) is defined in terms of a proton donor  $D-H$  and a proton acceptor  $A$ . The H atom is bound covalently to an electronegative atom in  $D$ , and noncovalently to an electronegative atom in  $A$ . Such  $D-H\cdots A$  interaction is often termed a two-center H bond, and it may occur when both  $D-H$  and  $A$  groups are different molecules, or when both groups are part of the same molecule. Because of their long-range interactions, H bonds are also found between a proton donor and two acceptors, or between one acceptor and two donors. The former is usually known as a bifurcated or three-center donor, and the latter as a bifurcated or three-center acceptor.<sup>1</sup>

An important concept in the theory of hydrogen bonding is cooperativity, wherein each one of the individual H bonds making up a chain of inter-linked H bonds is more strongly bound than it would be in the absence of the others. Considerable attention has been given to the study of cooperativity in molecular clusters containing conventional two-center H bonds.<sup>1–6</sup> Cooperative effects in bifurcated H bonds, however, have been much less investigated. Recent studies have discussed cooperativity in terms of the two-center components of the bifurcated H bond. These studies support the notion that an intermolecular bifurcated H bond is energetically weaker (negative cooperativity) than the regular two-center H bonds.<sup>7–14</sup> For intramolecular bifurcated H bonds, examples of negative and positive cooperativity have been reported.<sup>7–9,13–15</sup> Interestingly, a recent study has shown that for some bifurcated H bonds, the strength of the interaction may be simply additive (neither positive nor negative cooperativity).<sup>16</sup> Even though a bifurcated H bond may be weaker than its two-center H bond components, it remains a fact that bifurcated H bonds occur frequently in nature.<sup>14,17–19</sup> It is, then, likely that bifurcated H bonds can benefit cooperatively from the existence of other bifurcated H bonds. However, relatively few studies have been reported that investigate the cooperative enhancement of a bifurcated H bond when it is part of an array of inter-linked bifurcated H bonds. Cooperative

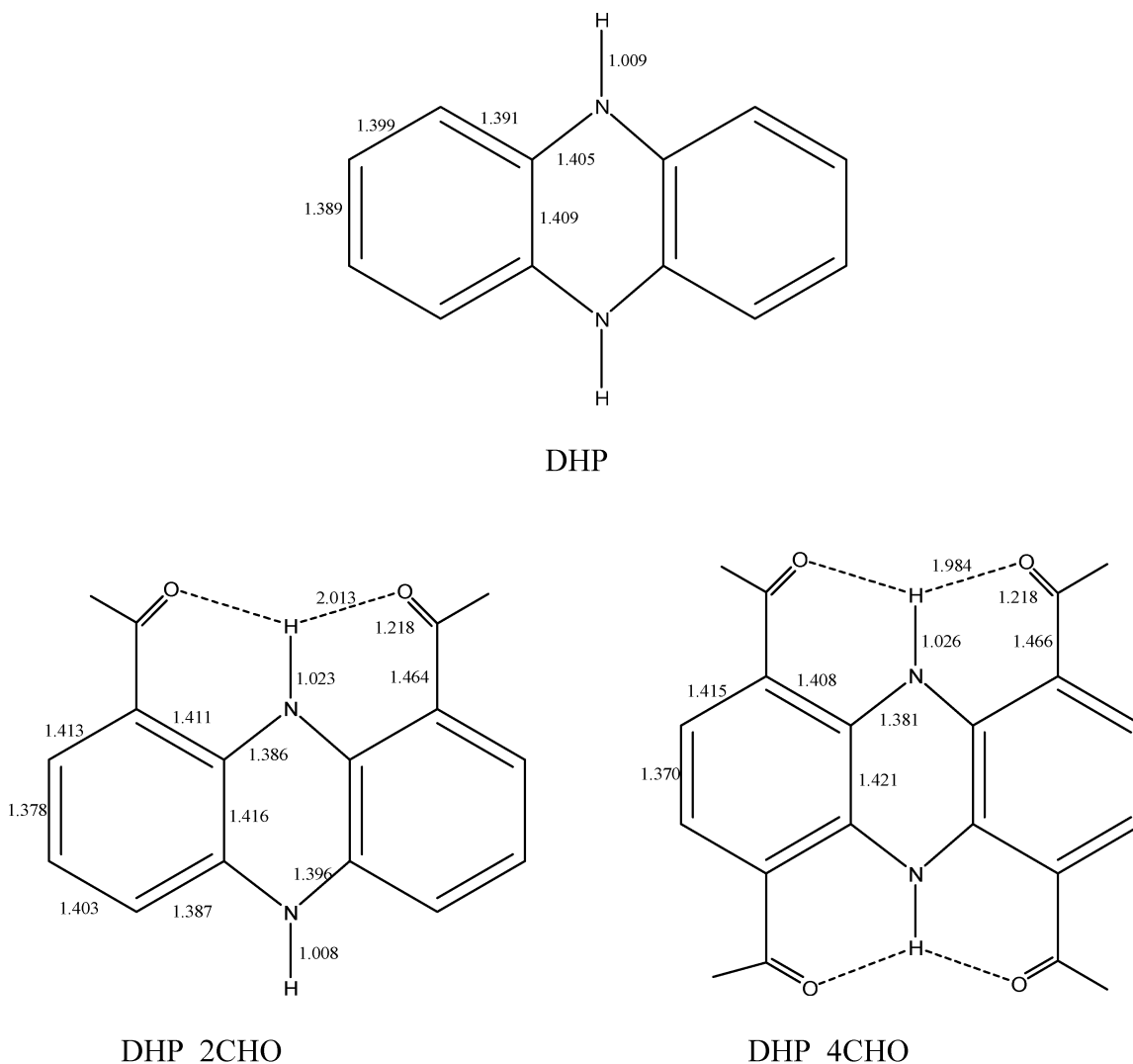
effects in one-dimensional aggregates of bifurcated acceptors have been studied, for example, on chains and ribbons of urea and thiourea using various ab initio and semiempirical methods.<sup>20,21</sup> It was found that the cooperative effects for the urea and thiourea chains are important and similar, and the cooperative effects for the corresponding ribbons are negligible. Ab initio studies have established the existence of significant cooperativity in two-dimensional ring-like networks of bifurcated acceptors consisting of up to nine molecules of carbonic acid in its *cis-cis* conformation.<sup>22</sup> Similarly, cooperative enhancement in one-dimensional chains of bifurcated donors was shown by means of ab initio calculations on a system containing up to twelve molecules of diformamide in its *trans-trans* conformation.<sup>23</sup>

In this paper, we expand our current knowledge of cooperativity in bifurcated H bonds by investigating the cooperative effects arising when two bifurcated H bonds are part of the same molecule. The model systems are conveniently chosen to represent bifurcated donors, bifurcated acceptors, and a mixture of both donors and acceptors. Moreover, the model systems are expected to exhibit resonance-assisted hydrogen bonding (RAHB).<sup>24–27</sup> The importance of resonance-assisted hydrogen bonding (RAHB) in bifurcated H bonds has been pointed out. In particular, it was found that although a bifurcated H bond is generally weak, the presence of intramolecular RAHB strengthens substantially the bifurcated H bond.<sup>26</sup>

## 2. Computational Details

All calculations were done with the GAUSSIAN 03 program.<sup>28</sup> The geometries of the different systems were optimized at the B3LYP/6-311++G(d,p) level using the opt=tight convergence criterion. The same level of theory was used to compute harmonic vibrational frequencies that in turn confirmed that each structure corresponded to a minimum on the potential energy surface. In this study, cooperative effects are highlighted using several indicators such as the hydrogen bond  $H\cdots O$  distance, the elongation of the  $N-H$  and  $C=O$  bond lengths, and the corresponding frequency shifts undergone by the  $N-H$  and  $C=O$  stretching modes. We employed the natural bond orbital (NBO) method and the B3LYP/6-311G(2d,2p) level for

\* To whom correspondence should be addressed. E-mail: rparra1@depaul.edu.



**Figure 1.** B3LYP/6-311++G(d,p) optimized geometries (Å) of the model systems used to investigate cooperativity in hydrogen bonds of two bifurcated donors present in the same molecule. DHP stands for dihydrophenazine, and CHO represents the proton acceptor group. The N–H units in DHP act as bifurcated donors.

analyzing wavefunctions of the optimized structures to estimate the energetic importance of the transfer of electron density from the lone pairs of the proton acceptor to the antibonding orbital of the D–H bond in the proton donor.<sup>29</sup> The theory of atoms in molecules (AIM) was also employed at the B3LYP/6-311G-(2d,2p) level to indicate both the existence and the relative strength of the various bifurcated hydrogen bonds considered in this study.<sup>30</sup> Furthermore, convenient isodesmic reactions were devised as an alternate tool for estimating the enthalpy change associated with the simultaneous formation of two intramolecular bifurcated H bonds.<sup>31</sup> For the isodesmic reactions, single-point energy calculations at the MP2/6-311++G(2d,2p) level were performed on the B3LYP/6-311++G(d,p) optimized structures.

### 3. Results and Discussion

**Geometries and Harmonic Vibrational Frequencies.** The mutual enhancement of two bifurcated H bonds, each having an N–H group as the proton donor in the same molecule, is investigated using dihydrophenazine substituted with CHO groups, as shown in Figure 1. To facilitate the discussion, we have conveniently labeled dihydrophenazine with two and four CHO groups as DHP\_2CHO and DHP\_4CHO, respectively. The parent molecule, with no CHO groups, will be referred to as

DHP. In agreement with other studies, the electronic ground state of the parent molecule exhibits a nonplanar structure.<sup>32–34</sup> The formation of a bifurcated donor brings the system closer to planarity, and the formation of the second bifurcated donor brings the system to complete planarity. The structural parameters in Figure 1 reveals that, in addition to bringing the system closer to planarity, the formation of a three-center H bond gives rise to a sizable lengthening of 0.014 Å of the N–H bond, accompanied by a shortening of 0.019 Å of the N–C bonds. The C–C bonds in the central ring are also lengthened by about 0.007 Å. The N–H unit not involved in the H bond has only a minor reduction in its bond length. However, the corresponding N–C bond lengths are reduced by about 0.009 Å. The presence of a second bifurcated donor triggers an additional lengthening of the N–H bonds, and of the C–C bonds in the central ring, tied in with an additional reduction of the N–C bonds. The H bond distance in the system with two bifurcated donors (1.984 Å) is also much shorter than that with just one bifurcated donor (2.013 Å).

Changes in geometrical parameters are mirrored in the corresponding vibrational frequency shifts. For example, the lengthening of the N–H bond upon formation of one bifurcated H bond results in a shift to lower frequencies of about 230 cm<sup>-1</sup> in the more intense N–H stretching mode, as shown in Table

**TABLE 1: N–H and C=O Stretching Frequencies (cm<sup>-1</sup>) for the Bifurcated Donor and Acceptor, Respectively<sup>a</sup>**

bifurcated donor	$\nu_{\text{N-H}}$	bifurcated acceptor	$\nu_{\text{C=O}}$
DHP	3612	ANT	1729
DHP_2CHO	3382	ANT_2OH	1661
DHP_4CHO	3341	ANT_4OH	1612
ACR	3624	ACR	1698
ACR_2CHO	3354	ACR_2CHO	1676
ACR_2CHO_2OH	3284	ACR_2CHO_2OH	1664

<sup>a</sup> B3LYP/6-311++G(d,p) harmonic frequencies.

1. Formation of the second bifurcated H bond causes an additional red shift of 41 cm<sup>-1</sup>. The mentioned geometric changes as well as the N–H stretching frequency changes are all consistent with stronger bifurcated H bonds resulting from the cooperative reinforcement of the individual bifurcated donors in the selected DHP model systems.

The cooperative enhancement of two three-center hydrogen bonding interactions, each having a C=O group as the proton acceptor in the same molecule, is investigated using anthraquinone substituted with OH groups, as shown in Figure 2. The anthraquinone systems with two and four OH groups are labeled ANT\_2OH and ANT\_4OH, respectively, and the parent molecule will be labeled ANT. All the optimized structures are found to be completely planar.<sup>35–39</sup> The formation of the first bifurcated H bond brings about a major elongation of 0.039 Å of the C=O bond length, along with a shortening of 0.031 Å of the bond lengths of the carbonyl carbon with the adjacent carbon atoms. Moreover, the C–C bonds in the central ring also present an important elongation of 0.011 Å. These changes are more substantial than the corresponding changes noted in DHP\_2CHO and thus show that the bifurcated H bond acceptor in ANT\_2OH is somewhat stronger than the bifurcated H bond donor in DHP\_2CHO. The C=O unit not involved in the bifurcated H bond presents no changes in its bond length. The second bifurcated H bond prompts an additional lengthening of the C=O bonds, and of the C–C bonds in the central ring. The H bond distance in the system with two bifurcated H bonds (1.688 Å) is also much shorter than that with only one such interaction (1.701 Å).

The vibrational frequencies in the anthraquinone models can also be used to gauge the cooperative nature of the pertinent bifurcated H bonds. The calculated harmonic frequencies listed in Table 1 were found, by visual inspection of the animated modes, to have a very significant contribution of the C=O stretching motion of both C=O units in the parent molecule. The selected mode corresponds to the simultaneous out of phase motion of the C=O units. The presence of a single bifurcated H bond induces a red shift of 68 cm<sup>-1</sup>, and the formation of the second bifurcated H bond causes an additional red shift of 49 cm<sup>-1</sup>. This additional red shift is evidence that the two bifurcated H bonds cooperatively reinforce each other.

The cooperative enhancement of two three-center hydrogen bonding interactions one having the C=O group as the proton acceptor (bifurcated acceptor), and the other having the N–H group as a proton donor (bifurcated donor) is investigated using conveniently substituted derivatives of acridone, as shown in Figure 3. All the optimized structures are found to be completely planar.<sup>40–42</sup> The structure with just two OH groups is labeled ACR\_2OH, the structure with just two CHO groups is labeled ACR\_2CHO, and the structure with two OH and two CHO groups is labeled ACR\_2CHO\_2OH. The parent molecule is labeled simply as ACR. The structural parameters displayed in Figure 3 reveal that the individual three-center H bonds appear stronger than their counterparts in the respective DHP (Figure

1) and ANT (Figure 2) disubstituted derivatives. For example, the N–H···O=C distances are decreased from 2.013 to 2.005 Å, and the relevant N–H bond length increases from 1.023 to 1.025 Å. Likewise, the C=O···H–O distances are decreased from 1.701 to 1.694 Å in passing from the anthraquinone to the acridone disubstituted derivatives. Thus, the N–H proton donor and the C=O proton acceptor abilities appear to improve when both groups are present in the same molecule. Accordingly, having both N–H and C=O groups simultaneously forming bifurcated H bonding interactions is expected to bolster each individual three-center H bond even more than was observed in the DHP\_2CHO and ANT\_2OH systems separately. A careful inspection of the geometric parameters displayed in Figure 3 confirms the expectation. For example, although the N–H···O=C distances in ACR\_2CHO\_2OH are comparable to those in DHP\_4CHO, the C=O···H–O distances are significantly shorter by 0.027 Å than they are in ANT\_4OH. Moreover, the N–H and C=O bond lengths are also longer in ACR\_2CHO\_2OH.

As seen in the other model systems, Table 1 shows that the N–H and C=O stretching frequencies exhibit the red shifts indicative of cooperativity in passing from the disubstituted (one bifurcated H bond) to the tetrasubstituted (two bifurcated H bonds) acridone.

**Atoms in Molecules Analysis.** The relative strength of the intramolecular N–H···O=C hydrogen bonds, as well as the C=O···H–O hydrogen bonds, was further evaluated using the theory of atoms in molecules (AIM)<sup>30</sup> as implemented in the Gaussian 03 program. In particular, the electron densities,  $\rho_c$ , and their Laplacians,  $\nabla^2\rho_c$ , evaluated at the H bond critical points are frequently used as indicators of H bond cooperativity. It should be noted that two symmetric H···O bond critical points are found in a given bifurcated H bond. Table 2 presents the calculated electron densities and Laplacians of each H···O bond making up a given bifurcated H bond. The values of  $\rho_c$  and  $\nabla^2\rho_c$  are in tandem with typical features of the H bond that have been pointed out by other studies.<sup>42–47</sup> An increase in both  $\rho_c$  and  $\nabla^2\rho_c$  correlates well with a decrease in the H···O distances, which in turn correlates with an increase in the strength of the hydrogen bond. The positive  $\nabla^2\rho_c$  values signal a depletion of charge between the atoms and indicate an interaction between closed-shell systems, such as a hydrogen bond interaction.<sup>5,43</sup>

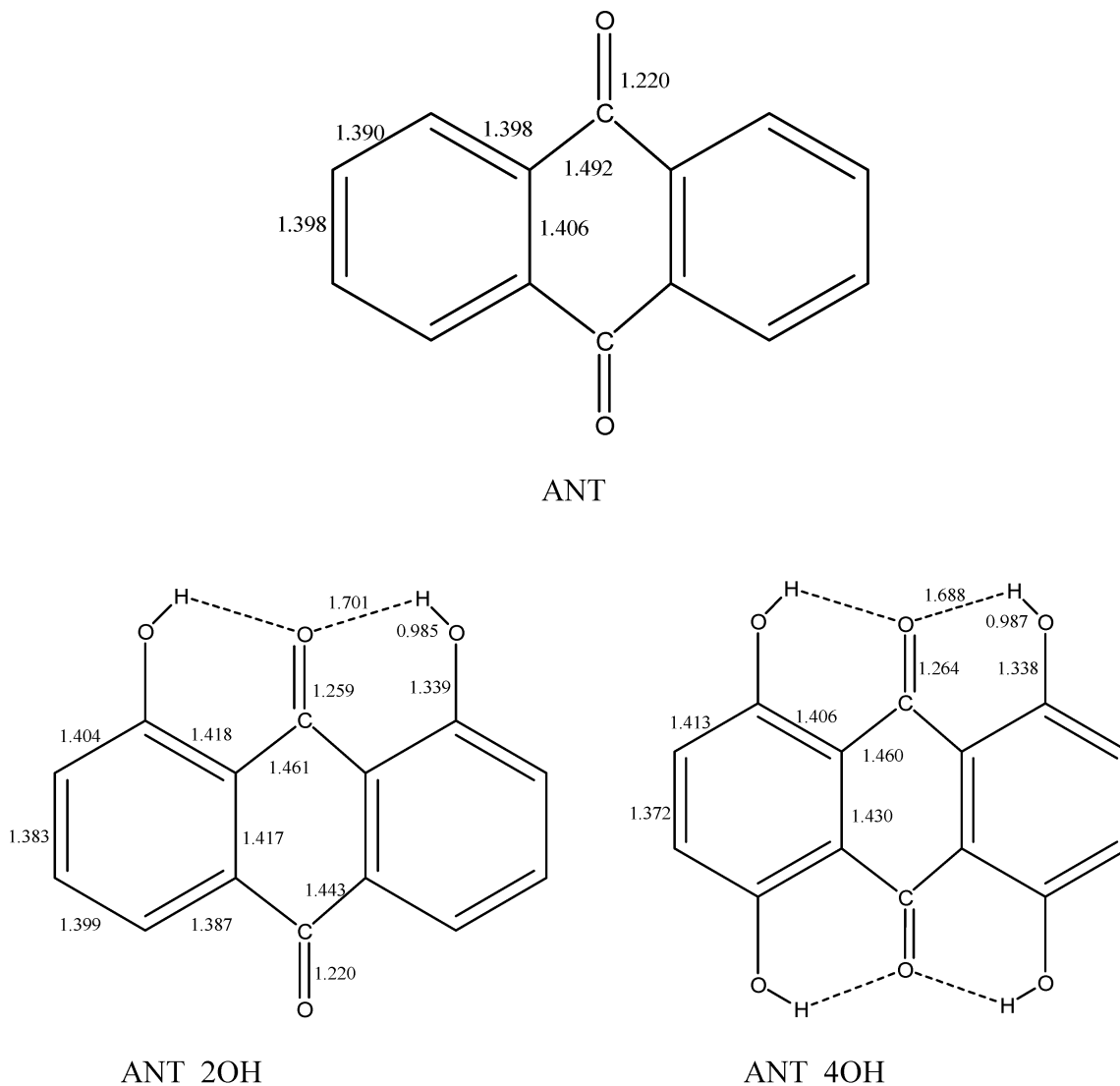
In addition to the electron densities and Laplacians, the electron energy density ( $H_c$ ) at the H bond critical point, as well as its components, the kinetic ( $G_c$ ) and potential ( $V_c$ ) electron energy densities, is often used to gain additional insight on the strength and nature of a given H bond.<sup>44–47</sup> The local kinetic electron energy density can be evaluated from the values of  $\rho_c$  and  $\nabla^2\rho_c$  as

$$G_c = \frac{3}{10}(3\pi^2)^{2/3}\rho_c^{5/3} + \frac{1}{6}\nabla^2\rho_c$$

whereas the local potential electron energy density can be obtained from the local form of the virial equation

$$V_c = \frac{1}{4}\nabla^2\rho_c - 2G_c$$

Previous studies have established that a partly covalent H bond can be said to exist if  $\nabla^2\rho_c$  is positive and  $H_c$  is negative.<sup>48,49</sup> An alternative tool for assessing the nature of H bond is the ratio  $-G_c/V_c$ . Accordingly, if  $-G_c/V_c > 1$ , then the H bond is noncovalent in nature. On the other hand, if  $0.5 < -G_c/V_c <$



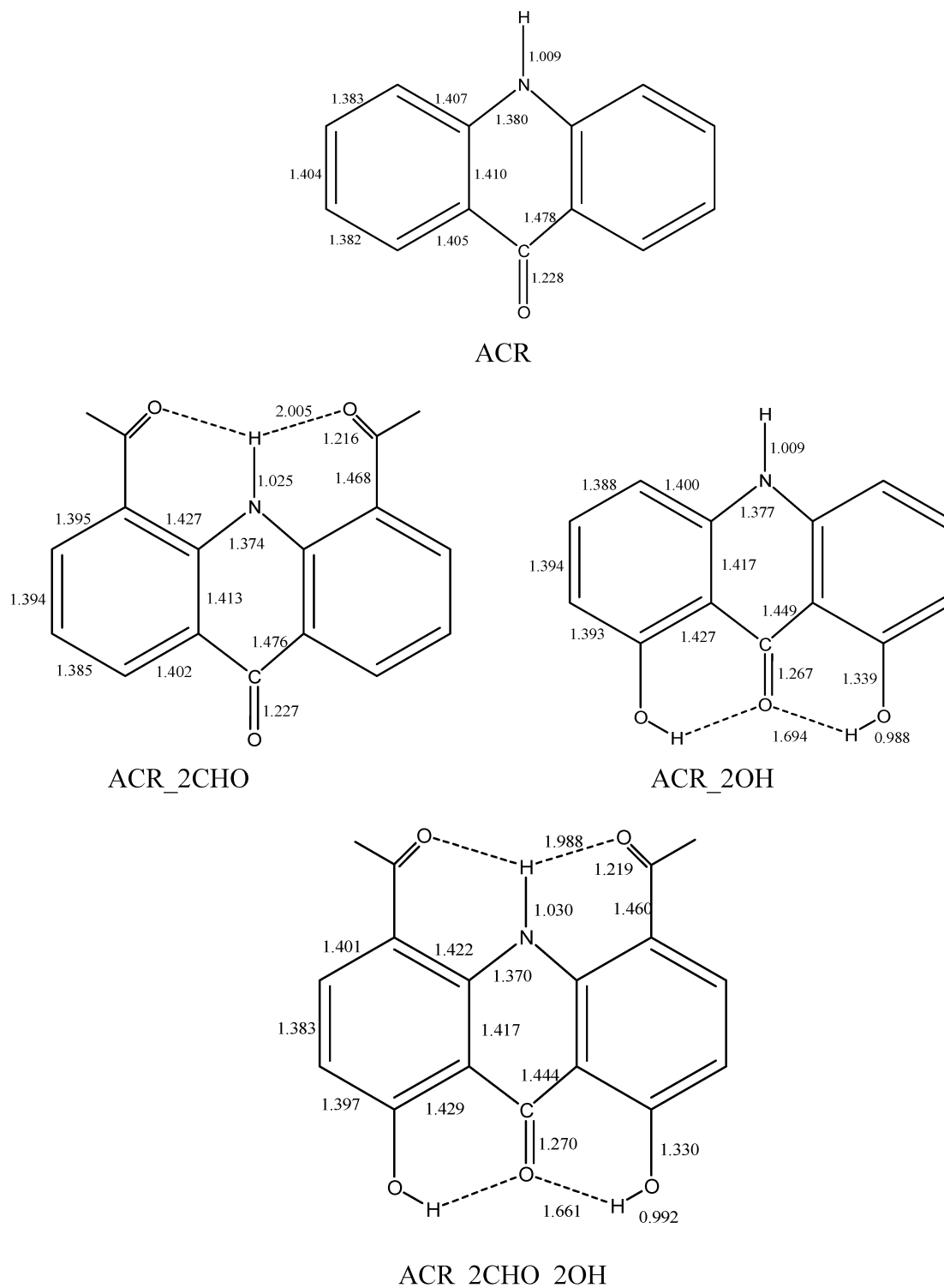
**Figure 2.** B3LYP/6-311++G(d,p) optimized geometries (Å) of the model systems used to investigate cooperativity in hydrogen bonds of two bifurcated acceptors present in the same molecule. ANT stands for anthraquinone, and OH represents the proton donor group. The C=O units in ANT act as bifurcated acceptors.

1, then the interaction is partly covalent.<sup>42</sup> Inspection of Table 2 reveals clearly that the H bonds in the bifurcated N-H...O=C bonds are all weaker than in the bifurcated C=O...H-O bonds. For example, the respective  $\rho_c$  and  $\nabla^2\rho_c$  values (in au) of 0.0241 and 0.0904 of the H bonds in DHP\_2CHO are much smaller than the corresponding values of 0.0472 and 0.1384 in ANT\_2OH. It can also be noted that the weaker H bonds exhibit a noncovalent nature, whereas the stronger interactions exhibit a partly covalent nature. For example, DHP\_2CHO has a  $-G_c/V_c$  ratio greater than one (1.0926), in contrast to the less than one (0.8687) ratio in ANT\_2OH. Moreover, the partly covalent nature in ANT\_2OH is further confirmed by the negative value of  $H_c$ .

Positive cooperativity is evident in the larger values of  $\rho_c$  and  $\nabla^2\rho_c$  calculated in the system with two bifurcated H bonds. Cooperativity is also evident in an increase of  $G_c$ , accompanied by a decrease in both  $V_c$  and  $H_c$ . As pointed out by Espinosa et al.,<sup>44-46</sup> the increase in magnitude of  $V_c$  with a decrease in the O...H distance reflects a greater capacity to accumulate electrons at the critical point. A greater accumulation of electrons implies a larger repulsion between them; this larger repulsion is manifested in an increase in the local kinetic electron energy density,  $G_c$ . In short, the various two three-center H bonds

examined here cannot be considered simply as the sum of the corresponding two independent three-center H bonds.

**NBO Analysis.** We employed the NBO method to examine, via second-order perturbation theory, the delocalization energies associated with the charge transfer from the acceptor oxygen lone pairs into the antibonding N-H orbitals,  $n_O \rightarrow \sigma^*_{N-H}$ , or into the O-H antibonding orbitals,  $n_O \rightarrow \sigma^*_{O-H}$ . The results displayed in Table 2 show an increase of about 15% in the delocalization energy upon formation of the second bifurcated H bond in the DHP derivatives. Also, the delocalization energy of the N-H...O=C interaction in ACR\_2CHO is about 8% larger than in DHP\_2CHO. An increase of about 6% of the delocalization energy upon formation of the second bifurcated H bond is likewise observed in the ANT derivatives. Furthermore, the C=O...H-O interaction in the ACR\_2OH is about 6% larger than in ANT\_2OH. These results substantiate the cooperative reinforcement of two intramolecular bifurcated H bonds. Furthermore, these results validate the superior strength of the N-H...O=C and C=O...H-O interactions in ACR\_2CHO, and ACR\_2OH compared with the same interactions in DHP\_2CHO and ANT\_2OH. The enhanced cooperativity in acridone is verified with the larger  $n_O \rightarrow \sigma^*_{N-H}$  and  $n_O \rightarrow \sigma^*_{O-H}$  stabilization energies relative



**Figure 3.** B3LYP/6-311++G(d,p) optimized geometries (Å) of the model systems used to investigate cooperativity in hydrogen bonds of two bifurcated H bonds. One of the H bonds is a bifurcated acceptor, and the other is a bifurcated donor. ACR stands for acridone, OH is a proton donor group, and CHO is a proton acceptor group. The C=O unit in ACR acts as the bifurcated acceptor, and the N-H unit as the bifurcated donor.

to the corresponding DHP\_4CHO and ANT\_4OH. In fact, the  $n_{\text{O}} \rightarrow \sigma_{\text{N-H}}^*$  stabilization energy in ACR\_2CHO\_2OH is 4% larger than in DHP\_4CHO. Similarly, the  $n_{\text{O}} \rightarrow \sigma_{\text{O-H}}^*$  stabilization energy is 14% larger in ACR\_2CHO\_2OH than that in ANT\_4OH.

The analysis of the strength of the bifurcated H bonds based on the NBO method and the AIM theory appears equivalent and renders essentially the same conclusions. In fact, the equivalence of these two methods in describing the H bond

strength has been established by other studies that show a linear relationship between the second-order stabilization energy and the local electronic potential energy density at the H bond critical point.<sup>5,6</sup> Such a linear relationship is found in the systems considered here, where the two quantities exhibit the linear relationship ( $r^2 = 0.998$ ).

$$V_{\text{c}} = -(3.146 + 1.290E_{n(\text{O}) \rightarrow \sigma^*})$$



TABLE 2: Topological Parameters and NBO Second-Order Stabilization Energies,  $E^2$ <sup>a</sup>

	$\rho_c$	$\nabla^2\rho_c$	$G_c$	$V_c$	$H_c$	$-G_c/V_c$	$E^2(n(O)\rightarrow\sigma^*)$
Bifurcated Donors							
N-H $\cdots$ O=C							
DHP_2CHO	0.0241	0.0904	0.0208	-0.0191	0.0018	1.0926	0.0105
DHP_4CHO	0.0257	0.0959	0.0224	-0.0208	0.0016	1.0756	0.0121
ACR_2CHO	0.0244	0.0909	0.0210	-0.0193	0.0017	1.0872	0.0113
ACR_2CHO_2OH	0.0254	0.0930	0.0218	-0.0204	0.0014	1.0708	0.0126
Bifurcated Acceptors							
C=O $\cdots$ H-O							
ANT_2OH	0.0472	0.1384	0.0408	-0.0469	-0.0062	0.8687	0.0316
ANT_4OH	0.0487	0.1384	0.0419	-0.0489	-0.0069	0.8581	0.0335
ACR_2OH	0.0481	0.1359	0.0409	-0.0478	-0.0069	0.8553	0.0336
ACR_2CHO_2OH	0.0520	0.1407	0.0442	-0.0533	-0.0091	0.8301	0.0382

<sup>a</sup> B3LYP/6-311G(2d,2p) derived topological parameters using the B3LYP/6-311++G(d,p) geometries. B3LYP/6-311G(2d,2p) NBO analysis on B3LYP/6-311++G(d,p) geometries.

A linear dependence is also found between the second-order stabilization energy and the  $-G_c/V_c$  ratio, as conveniently shown below ( $r^2 = 0.996$ ).

$$-G/V_c = (1.197 - 0.0160E_{n(O)\rightarrow\sigma^*2})$$

It must be added, however, that further studies in other systems including, for instance, changing the CO and NH groups by other functional groups are in order to test the generality of the above relationships in the context of intramolecular bifurcated H bonds.

**H-Bond Energetics.** It is instructive to estimate the energetics of the H-bonds, for example, by breaking the internal H bonds via 180° rotations of the relevant groups. We performed MP2/6-311++G(2d,2p) single-point energy calculations on the structures containing bifurcated H bonds and the corresponding structure without the bifurcated H bond, resulting from 180° rotation of the respective O-H bonds. The estimated rise in the energies of the systems upon breaking the bifurcated H-bond via 180° rotation of the pertinent groups are as follows:

DHP\_2CHO (no H bonds) - DHP\_2CHO = 14.31 kcal/mol  
 DHP\_4CHO (no H bonds) - DHP\_4CHO = 31.10 kcal/mol  
 ANT\_2OH (no H bonds) - ANT\_2OH = 27.29 kcal/mol  
 ANT\_4OH (no H bonds) - ANT\_4OH = 58.81 kcal/mol  
 ACR\_2CHO (no H bonds) - ACR\_2CHO = 15.32 kcal/mol  
 ACR\_2OH (no H bonds) - ACR\_2OH = 30.46 kcal/mol  
 ACR\_2CHO\_2OH (no H bonds) - ACR\_2CHO\_2OH = 47.30 kcal/mol

The above results show qualitative agreement with the results based on the more accurate results based on the geometries, frequencies, AIM, and NBO analyses. It is apparent, for example, that breaking two bifurcated H bonds simultaneously present in a molecule increases the energy by more than twice that of breaking one such interaction in the absence of the other. Also, a bifurcated H bond in ACR appears stronger than in either DHP or ANT in conformity with the analysis based on the other indicators of H bond strength.

We also devised relevant isodesmic reactions as an alternate tool for estimating the enthalpy change associated with the formation of two bifurcated H bonds in the same molecule from the component three-center H bonds. The B3LYP/6-311++G(d,p) optimized geometries were used to calculate MP2/6-311++G(2d,2p) energies. After zero-point corrections, the enthalpy values (at 0 K) are obtained for the following reactions.

reaction	$\Delta H_o$ (kcal/mol)
2 ANT_2OH $\rightarrow$ ANT + ANT_4OH	-0.17
2 DHP_2CHO $\rightarrow$ DHP + DHP_4CHO	-1.24
ACR_2OH + DHP_2CHO $\rightarrow$ DHP_2CHO_2OH + ACR	-3.90

The above reactions demonstrate that the formation of two bifurcated H bonds from their individual components is a thermodynamically favorable process, with the reaction involving the ACR systems being by far the most exothermic.

#### 4. Summary

The cooperative enhancement of the strength of intramolecular bifurcated H bonds was investigated for model systems containing either bifurcated donors or bifurcated acceptors. A model system containing both a bifurcated donor and a bifurcated acceptor was also examined. Different indicators of H bond strength consistently show the existence of cooperative effects in all the systems considered. Thus, two bifurcated H bonds simultaneously present in the same molecule cooperatively reinforce each other. This is confirmed, for example, by geometrical, energetic and topological analysis. The H $\cdots$ O distances in a bifurcated H bond are decreased upon formation of the second bifurcated H bond. A reduction in a given H $\cdots$ O distance signals an increase in the corresponding H bond strength. The enhancement of the H bond is reflected in an increase in the electron density and the Laplacian evaluated at the bond critical point. Of the systems examined, the bifurcated donors contain H bonds that are noncovalent in nature, and the bifurcated acceptors contain H bonds that are partly covalent, as indicated, for example, by the ratio of the local kinetic and potential electron energy densities,  $-G_c/V_c$ . Cooperativity is also corroborated in the increase in stabilization energy ( $E^2(n(O)\rightarrow\sigma^*)$ ) resulting from the transfer of electron density from the lone pairs of the acceptor oxygen atom into the antibonding orbital of the proton donor,  $\sigma^*_{N-H}$  (in bifurcated donors) or  $\sigma^*_{O-H}$  (in bifurcated acceptors). Estimates of H bond energetics, via 180° rotation of the pertinent H bonds, also lead us to conclude that H bond cooperativity is playing a role in the systems investigated. Isodesmic reactions also support the existence of cooperativity, and indicate that the formation of two bifurcated H bonds from their individual components is a thermodynamically favorable process. Although the results of this study show that positive cooperative effects exist in the model systems, more studies are needed to assess the generality of the results.

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