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# Energetics and cooperativity in three-center hydrogen bonding interactions. I. Diacetamide-X dimers (X=HCN, CH<sub>3</sub>OH)

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High level *ab initio* calculations are carried out on diacetamide-X (DA-X) dimers, X=HCN, CH<sub>3</sub>OH. The dimers are used as model systems to investigate the energetics and cooperative phenomena in *intermolecular three-center* hydrogen-bond (H-bond) interactions relative to two-center H-bond interactions. The *trans-trans* conformer of diacetamide is chosen as a suitable model for intermolecular three-center H bonding where one H atom is interacting with two acceptor atoms. The proton-acceptor atoms are rigidly held in the same molecule. For both model systems, it is found that the calculated interaction energy per H bond is appreciably smaller in the three-center than in the two-center H-bond dimers, suggesting possibly a general characteristic of intermolecular three-center H bonds, namely, a negative cooperativity. More importantly, it is found that frequency shifts, intensity factors, bond lengths, and <sup>1</sup>H nuclear magnetic resonance chemical shifts all support the energetic calculations in that the intermolecular three-center H-bond dimers exhibit marked negative cooperative effects. Despite the negative cooperativity, the three-center DA-HCN dimer is actually energetically favorable over the two-center counterpart, whereas the three-center DA-CH<sub>3</sub>OH dimer is energetically unfavorable over the two-center counterpart. © 2001 American Institute of Physics. [DOI: 10.1063/1.1400141]

## I. INTRODUCTION

Three-center or bifurcated hydrogen bonds are often found in the solid state of many compounds,<sup>1</sup> and in the crystal structures of a number of biologically relevant systems.<sup>2</sup> The existence of three-center H-bond interactions in solution has also been experimentally demonstrated.<sup>3</sup> Two types of three-center H-bond interaction can be distinguished: (a) one that involves an H atom and two acceptor atoms (denoted A<sub>1</sub>HA<sub>2</sub>), and (b) one that involves an acceptor atom and two H atoms (denoted H<sub>1</sub>AH<sub>2</sub>).<sup>4</sup> These two possibilities are depicted in Fig. 1. Although a vast number of examples are known in the solid state, three-center H bonds have been used mainly to account for the observed experimental facts. Compared to the tremendous amount of data available on two-center H bonds, relatively few model systems that provide insights on the strength of three-center H bonds have appeared. Gellman *et al.* recently reported intramolecular H-bond systems that experimentally probed the relative energetic merits of two-center versus three-center H bonds.<sup>5</sup> By designing depsipeptides containing either excess H-bond donors or acceptors, it was found that there were negative cooperativity effects between the two-center components of the three-center H-bonding interactions. Rozas

*et al.* applied the theory of atoms in molecules (AIM) to show that three-center interactions do exist and that they are energetically weaker than two-center hydrogen bonds.<sup>6</sup> The systematic studies by Jorgensen *et al.*,<sup>7(a),7(b)</sup> Gellman *et al.*,<sup>7(c),7(d)</sup> and Zimmerman *et al.*,<sup>7(e),7(f)</sup> have led to the finding that A<sub>1</sub>HA<sub>2</sub> three-center interactions would become favorable if both acceptors occurred in the same molecule and were rigidly held in the proper arrangement. Additional model studies are needed to further substantiate these findings.

The purpose of this paper is to study the energetics and cooperativity of three-center H-bond interactions in diacetamide-X dimer model systems (X=HCN, CH<sub>3</sub>OH). The cooperative effects will be highlighted using several indications. The energy per hydrogen bond, defined as the interaction energy divided by the number of H bonds present in the dimer, will provide insight into the stabilizing or destabilizing effects of having a three center as opposed to a two center H bond, namely, to assess the relative stability of a three-center over a two-center H-bond configuration. We will examine the generality of the prediction that A<sub>1</sub>HA<sub>2</sub> three-center interactions would become favorable if both acceptors occurred in the same molecule and were rigidly held in the proper arrangement. Besides energetics, attention is also given to other indicators of cooperativity such as the stretching and bending frequencies of the X-H group, the X-H

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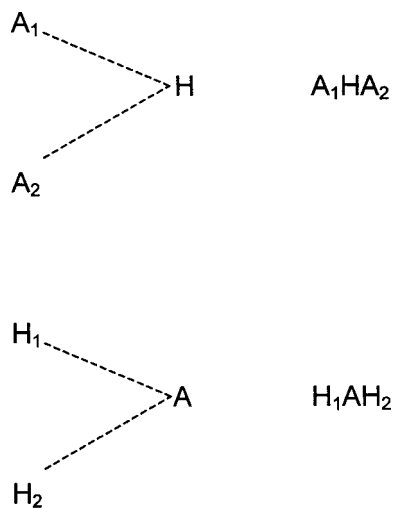


FIG. 1. Two types of three-center interactions, one involving one proton donor and two acceptors, designated  $A_1HA_2$ , and one involving two donors and one acceptor, designated  $H_1AH_2$ .

bond length, the intensity change of the X–H stretching mode, and the X–H proton chemical shifts.

## II. COMPUTATIONAL DETAILS

All the computations were carried out using the GAUSSIAN 98 program.<sup>8</sup> The geometries of the different systems were optimized at the MP2/6-31+G(d,p) level. The same level of theory was used to compute harmonic vibrational frequencies and zero-point energy corrections to the electronic energies. The optimized geometries were used to compute single point energy calculations at the MP2/6-311++G(2d,2p) level, and  $^1\text{H}$ -NMR chemical shielding constants at the B3LYP/6-311+G(2d,p) level. Interaction energies were corrected for basis set superposition error (BSSE) using the standard counterpoise method.<sup>9</sup>

## III. MODEL SYSTEMS

The imide group is considered as an amino group flanked by two carbonyl groups. This functional group may occur in acyclic diacylamines or in 4-, 5-, 6-membered ring compounds.<sup>10(a)</sup> The free imide group can adopt three different conformations that are shown in Fig. 2. Because of resonance, the free imide group is essentially planar. The *cis-cis* conformer has the highest energy due to steric overcrowding between  $R$  and  $R'$ . This conformer has not been observed in solution or in the solid state for any known acyclic imides. The *cis-trans* conformer is the most stable form and is ob-

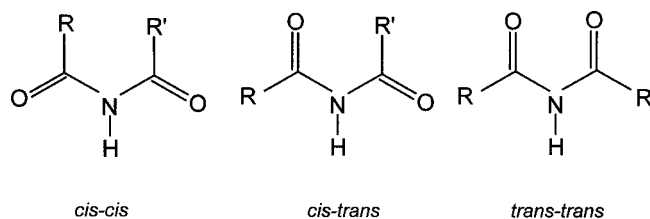


FIG. 2. Three different conformations of the imide group.

served in solutions for all simple acyclic imides except dipivalamide.<sup>10(d)</sup> The *trans-trans* conformer is destabilized relative to the *cis-trans* by the electrostatic repulsion between the two imide carbonyl groups; nevertheless, it is frequently observed in the solid state.<sup>10(b),10(c)</sup>

We have chosen the diacetamide (DA) molecule in the *trans-trans* conformation as a model system to investigate both the energetics and the cooperativity effects in three-center H-bond interactions of the type  $A_1HA_2$ . Because the acceptor atoms are part of the same molecule, this sort of interactions is often called three-center chelated hydrogen bonding.<sup>4(a)</sup> For single proton donors we have chosen hydrogen cyanide (HCN), and methanol ( $\text{CH}_3\text{OH}$ ). Unlike most C–H bonds, the triple  $\text{N}\equiv\text{C}$  bond makes HCN a very effective proton donor molecule.<sup>11</sup> The proton donor ability of methanol is also well recognized.<sup>12</sup>

## IV. RESULTS AND DISCUSSION

*Cooperative effects.* An array of interlinked hydrogen bonds can exhibit positive cooperativity, defined as the enhancement of the first H bond between a donor and an acceptor when a second H bond is formed between one of these two species and a third partner. The sum of the nonadditive, many-body energies has been considered as the energetic contribution of the cooperativity to the stability.<sup>13</sup> This energy-based definition of cooperativity has been traditionally used in the discussion of cooperative phenomena in intermolecular H-bonded systems.<sup>14</sup> Other definitions for the cooperativity have been used in the literature<sup>15</sup> because the effects of cooperativity can be manifested in properties other than the energetics. For instance, several groups have shown that a quantitative treatment of cooperativity effects in intermolecular and intramolecular H bonds can be achieved in terms of the relative vibrational frequency shifts undergone by the X–H group involved in the hydrogen bonding.<sup>16</sup> Evidence of positive-cooperativity behavior has been seen also in measurements of geometries, dipole moments, vibrational spectra, vibrational mode intensities, and quadrupole coupling constants,<sup>17</sup> suggesting a close correlation between these properties with the energetics as far as the cooperative effects are concerned.

### A. Diacetamide–HCN dimers

(a) Energetics. The mean H-bond interaction energies, defined as the interaction energy per hydrogen bond, for the DA–HCN dimers are shown in Table I. The two-center H-bond interaction ( $-3.78$  kcal/mol) appears energetically superior to the mean three-center H-bond interaction ( $-3.04$  kcal/mol). This result is consistent with the fact that multiple H bonds do not always reinforce each other. This sort of weakening of an existing H bond by adding another acceptor/donor to the interaction is sometimes referred to as *negative cooperativity*.<sup>17(a)</sup>

To quantify the cooperativity effects in multicenter H-bond systems we proposed to use a coefficient analog to the  $C_1$  coefficient proposed by Koehler *et al.*<sup>18</sup>

$$C_1 = (\Delta E_{av} - \Delta E) / (\Delta E).$$

TABLE I. MP2/6-311++G(2d,2p) interaction and relative energies (kcal/mol).

	Two-center H-bond dimers		
	$\Delta E$	$\Delta E/\text{H-bond}$	
DA-HCN	-3.78	-3.78	
DA-CH <sub>3</sub> OH	-5.32	-5.32	
	Three-center H-bond dimers		$E_{\text{three}} - E_{\text{two}}$
	$\Delta E$	$\Delta E/\text{H-bond}$	
DA-HCN	-6.09	-3.04	-2.50
DA-CH <sub>3</sub> OH	-4.91	-2.45	0.18

Here,  $\Delta E_{\text{av}}$  is the mean hydrogen-bond energy in the multi-center system and  $\Delta E$  is the hydrogen-bond energy in the two-center system. A positive value of  $C_1$ , which defines the *positive cooperativity*, means that the H-bond energy of an array of  $n$ -center hydrogen bonds is greater than the sum of  $n$  isolated hydrogen bonds. Naturally, a negative value of  $C_1$  will define the *negative cooperativity*. For the DA-HCN dimers,  $C_1 = -0.20$ , namely, a 20% reduction of the strength of the two-center H bond upon formation of the three-center H bond.

It should be noted that even in the case of negative cooperativity, formation of a second H bond is overall energetically favorable when compared to the case without the presence of a second H bond. In other words, two H bonds together are usually more favored than one. As shown in Table I, the interaction energy of the three-center H-bond dimer is  $-6.09$  kcal/mol, that is, 2.31 kcal/mol lower than that of the two-center H-bond dimer. Including zero-point energy corrections, the three-center H-bond dimer is still 2.50 kcal/mol more stable. This result confirms the prediction that  $A_1HA_2$  three-center interactions become favorable if both acceptors occurred in the same molecule and were rigidly held in the proper arrangement.<sup>7</sup>

(b) Geometries. Geometry of a three-center hydrogen bond can be described by the distances  $r$ ,  $d_1$ ,  $d_2$ , and the

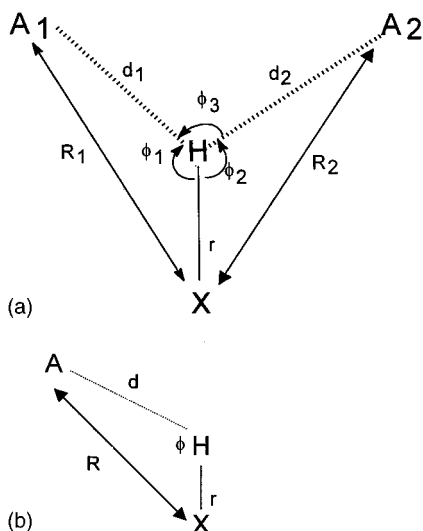


FIG. 3. (a) Geometrical parameters used to describe three-center H-bond interactions. (b) Geometrical parameters used to describe two-center H-bond interactions.

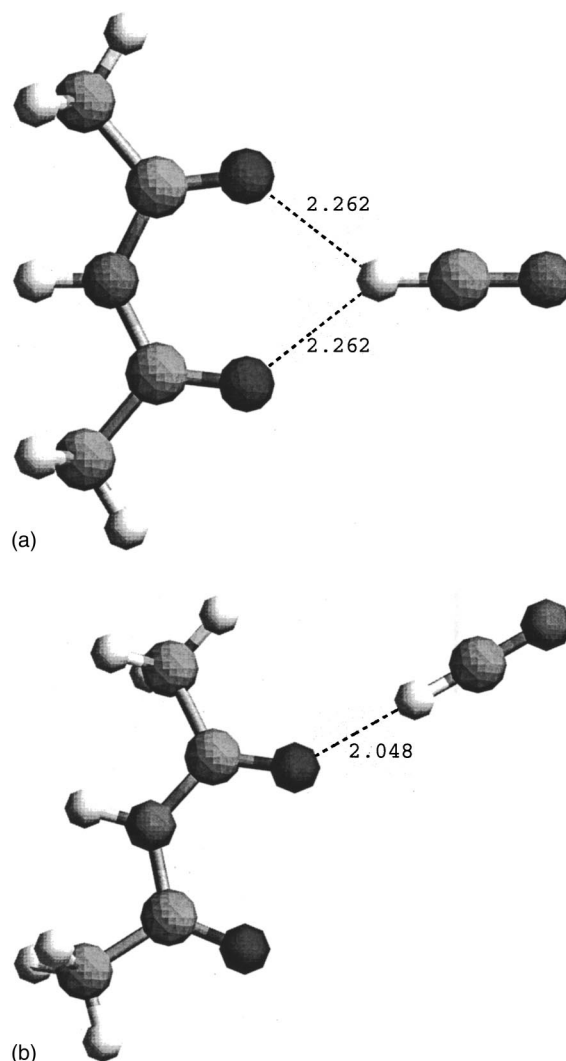


FIG. 4. (a) Optimized three-center DA-HCN dimer. Distances given in Å. (b) Optimized two-center DA-HCN dimer. Distances given in Å.

angles  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  [see Fig. 3(a)]. A more stringent description should include the distances between the heavy atoms,  $R_1$ ,  $R_2$ . The deviation of the H atom from the plane formed by the three heavy atoms, as measured by the sum  $\phi_1 + \phi_2 + \phi_3$ , is commonly used to characterize the three-center H bond. The geometric parameters used to describe the conventional two-center hydrogen bond are shown in Fig. 3(b).

The Optimized DA-HCN dimers are shown in Fig. 4. Table II displays relevant geometric parameters for the dimers. The three-center DA-HCN dimer is symmetric with  $d_1 = d_2 = 2.262$  Å, and  $R_1 = R_2 = 3.175$  Å. The O...O distance ( $R_3$ ) is calculated to be 2.802 Å. The H atom lies in the same plane of the three heavy atoms involved in the H bond ( $\phi_1 + \phi_2 + \phi_3 = 360^\circ$ ). The HCN molecule is in the plane of the diacetamide molecule. The two-center H bond appears stronger than the three-center interaction as indicated by the geometric parameters. For instance, the donor C-H distance is shortened by 0.001 Å upon bifurcation. The weaker character of the three-center interaction is also reflected in longer H...O ( $d_1$ ) and C...O ( $R_1$  and  $R_2$ ) distances. In other words, adding a second acceptor to the two-center H bond gives rise to negative cooperative effects.

TABLE II. Relevant structural parameters.<sup>a</sup>

	Two-center H-bond dimers				Three-center H-bond dimers									
	<i>r</i>	<i>d</i>	<i>R</i>	$\phi$	<i>r</i>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>R</i> <sub>1</sub>	<i>R</i> <sub>2</sub>	<i>R</i> <sub>3</sub>	$\phi_1$	$\phi_2$	$\phi_3$	$\Sigma \phi_1$
DA–HCN	1.075	2.048	3.123	179.7										
DA–CH <sub>3</sub> OH	0.972	1.921	2.860	161.6										
DA–HCN	1.074	2.262	2.262	3.175	3.175	2.802	141.7	141.7	76.6	360.0				
DA–CH <sub>3</sub> OH	0.969	2.404	2.111	3.113	3.010	2.809	129.6	153.6	76.7	359.9				

<sup>a</sup>Bond lengths in Å; bond angles in degrees.

(c) Vibrational frequencies and <sup>1</sup>H chemical shifts. Frequency calculations at the MP2/6-31+G(d,p) show that both the two-center and the three-center DA–HCN dimers are local minima. Some relevant harmonic vibrational frequencies for the dimers are listed in Table III. The negative cooperative effects seen in the energetics, and in the geometric parameters are also reflected in the vibrational stretching and bending modes of the proton donor C–H bond. There is a sizeable blueshift, relative to the two-center dimer, in the C–H stretching mode of HCN accompanied by a redshift in the C–H bending modes upon formation of the three-center dimer. The intensity behavior of the C–H stretching mode can be examined using the intensity factor (*A*). This intensity factor is defined as the ratio of the intensity of the stretching X–H bond in the three-center dimer divided by the intensity of this mode in the two-center dimer. Positive cooperativity would be indicated by *A* > 1.0, whereas negative cooperativity would be indicated by *A* < 1.0. Intensity factors are often used in intermolecular H-bond systems to gauge the strength of the H bond and to assess cooperative phenomena.<sup>17(a)</sup> Table III shows that the intensity factor for DA–HCN dimer is 0.81. This decrease in the intensity of the C–H stretching mode is a clear indicator of negative cooperativity and thus is consistent with the energy per H-bond results.

Table III also lists the <sup>1</sup>H–NMR chemical shifts of the HCN molecule. As a rule, H-bonding interaction leads to a downfield shift of the NMR resonance of the hydrogen atom.<sup>19</sup> The strength of H-bond interactions correlates with the proton NMR chemical shifts. Accordingly, the two-center

DA–HCN dimer is stronger than the three-center dimer in agreement with the energetics, geometry, and frequency-shift data.

## B. Diacetamide–CH<sub>3</sub>OH dimers

(a) Energetics. Table I shows that the calculated H-bond interaction energy for the two-center dimer (–5.32 kcal/mol) is energetically superior to the average three-center H-bond interaction (–2.45 kcal/mol). The calculated *C*<sub>1</sub> coefficient (–0.54) demonstrates marked negative cooperative effects in the three-center H-bond dimer, that is, a 54% reduction in the strength of the two-center H-bond interaction. Moreover the two-center dimer is 0.18 kcal/mol more stable than the three-center dimer. Thus, energy data demonstrates that the preferred conformation for the DA–CH<sub>3</sub>OH dimer is the one with a two-center H-bond rather than that with a three-center H bond. This result contrasts with the energetics of the DA–HCN dimers discussed previously.

(b) Geometries. The optimized structural parameters of the three-center and two-center DA–CH<sub>3</sub>OH dimers are displayed in Table II. The optimized dimers are shown in Fig. 5. Table II shows that the bifurcated dimer has two different hydrogen-bond distances, *d*<sub>1</sub> = 2.404 Å and *d*<sub>2</sub> = 2.111 Å. The atoms directly involved in the bifurcated H bond are all in the same plane ( $\phi_1 + \phi_2 + \phi_3 = 359.9^\circ$ ).

Table II also shows that, relative to the three-center dimer, the O–H bond length is longer and the H-bond distance shorter in the two-center dimer. That is, adding a second acceptor to the two-center H-bond interaction gives rise to negative cooperative effects that are apparent in the structural parameters.

(c) Vibrational frequencies and <sup>1</sup>H chemical shifts. Frequency calculations at the MP2/6-31+G(d,p) indicate that the two-center DA–CH<sub>3</sub>OH is a local minimum; however, the corresponding three-center dimer is a first-order saddle point with a small negative frequency (–8.8 cm<sup>–1</sup>). Table III shows that the harmonic O–H stretching mode in the two-center dimer is found at 3745 cm<sup>–1</sup>. This mode is shifted upward 84 cm<sup>–1</sup> in the three-center H-bond dimer. The O–H bending mode in the three-center dimer is redshifted by 27 cm<sup>–1</sup>, compared to the two-center dimer. The increase in the O–H stretching frequency along with the decrease in the O–H bending frequency is another manifestation of the negative cooperative effects that occur in the three-center dimer. The intensity factor calculated for the three-center

TABLE III. Relevant vibrational and NMR data.<sup>a</sup>

	Diacetamide–HCN dimers				<sup>1</sup> H–NMR
	$\nu_{(\text{CH})}$	<i>A</i>	<i>b</i> <sub>out(CH)</sub>	<i>b</i> <sub>in(CH)</sub>	
Two-center	3401	1.00	841	833	5.38
Three-center	3425	0.81	836	747	5.14
	Diacetamide–CH <sub>3</sub> OH dimers			H–NMR	
	$\nu_{(\text{OH})}$	<i>A</i>	<i>b</i> <sub>(OH)</sub>		
Two-center	3745	1.00	1435	3.28	
Three-center	3829	0.61	1408	2.55	

<sup>a</sup>Stretching ( $\nu$ ) and bending (*b*) modes in units of cm<sup>–1</sup>; proton chemical shifts in ppm. Intensity factors (*A*) are dimensionless.

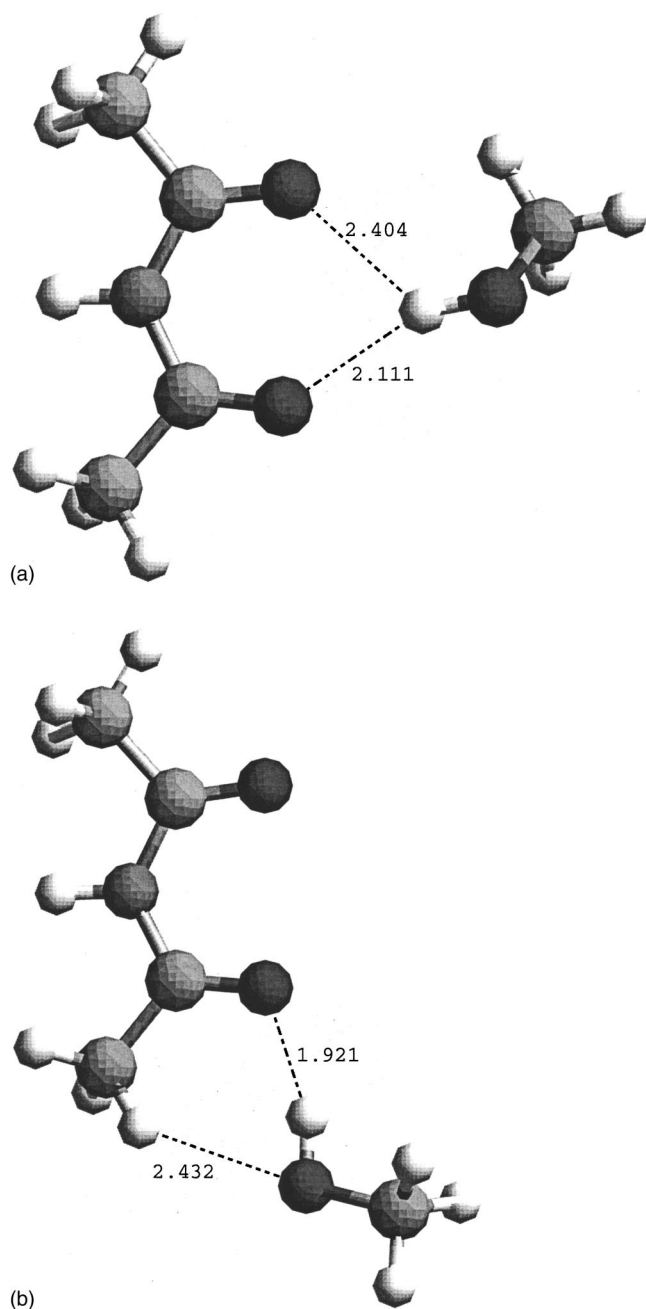


FIG. 5. (a) Optimized two-center DA-CH<sub>3</sub>OH dimer. Distances given in Å. (b) Optimized three-center DA-CH<sub>3</sub>OH dimer. Distances given in Å.

dimer is 0.61. This reduction in the O-H mode intensity further demonstrates the destabilizing effects of adding a second acceptor to the two-center interaction.

Table III also lists the <sup>1</sup>H-NMR chemical shifts of the methanol molecule. The stronger H-bond interaction in the two-center DA-CH<sub>3</sub>OH is clearly indicated by its relatively larger proton chemical downfield shift.

## V. CONCLUSIONS

Intermolecular three-center H-bond interactions of the type A<sub>1</sub>HA<sub>2</sub>, where A<sub>1</sub> and A<sub>2</sub> belong to the same molecule, have been studied using *ab initio* molecular orbital and density functional theory. The diacetamide-X dimers (X=HCN,

CH<sub>3</sub>OH) were used as model systems. The *trans-trans* conformer of diacetamide was chosen as a suitable model for a system having two proton acceptor atoms held in the proper arrangement to form a three-center H bond.

For both model systems, we found that the calculated interaction energy per H bond is appreciably lower in magnitude in the three-center than in the two-center H-bond dimers. This suggests possibly a general characteristic of intermolecular three-center H bonds, namely, a negative cooperativity. More importantly, we found that frequency shifts, intensity factors, bond lengths, and <sup>1</sup>H-NMR chemical shifts all correlate well with the energetic calculations in that the intermolecular three-center H-bond dimers exhibit marked negative cooperative effects. Despite the negative cooperativity, interestingly, the three-center DA-HCN dimer is actually *preferred energetically* over the two-center counterpart, whereas the three-center DA-CH<sub>3</sub>OH dimer is less preferred energetically than the two-center counterpart. Additional secondary electrostatic interactions may be responsible for the relative stability found in the DA-CH<sub>3</sub>OH dimers. For instance, the secondary attractive interaction between the oxygen of methanol and one of the hydrogen atoms of diacetamide (separated by 2.432 Å) provides additional stability to the two-center dimer. On the other hand, the secondary repulsive interaction between the CH<sub>3</sub> group of methanol and one of the oxygen atoms of diacetamide increases the energy of the three-center dimer compared with that of the two-center counterpart. Indeed, the orientation of the proton-donor molecule can be another important factor in predicting the energetic merits of three-center H-bond interaction.

This study and previous studies by other researchers<sup>5,6</sup> support the notion that intermolecular three-center H-bond formation is a process that gives rise to negative cooperative effects. However, the issue of cooperativity in intramolecular three-center H bonding is still open to further research. In paper II of this work, we will turn our attention to a number of systems containing intramolecular three-center H bonding of the type A<sub>1</sub>HA<sub>2</sub>.

## ACKNOWLEDGMENTS

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