Ab Initio Study of Interactions in Hydrazine Clusters of One To Four Molecules: Cooperativity in the Interaction

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Computations on systems consisting of up to four hydrazine molecules were performed by using the HF, DFT/B3LYP, and MP2 methods with the 6-31+G* basis set. The dimer was found to exhibit two minima with very similar interaction energies (ca. 20−22 kJ/mol). The overall minimum at the MP2 level corresponds to a structure of C_1 symmetry involving a hydrogen bond at about 2.2 Å in addition to several other N···H contacts at longer distances. The other minimum found possesses C_2 symmetry and involves two hydrogen bonds, also at ca. 2.2 Å. A transition state about 4−6 kJ/mol less stable than the previous minima was also found. The trimer occurs in several structures that correspond to minima with slight energy differences among them; hydrogen bond distances are shorter than those in the dimer as a result of the stronger interactions between molecules. The contribution of cooperative phenomena to the interaction energy is quite significant (it amounts to as much as 12% of the overall interaction energy). The two minima of the tetramer behave similarly to those of the trimer; the contribution of nonadditive terms accounts for 10% of the overall interaction energy.

1. Introduction

Molecules in clusters are usually bound via weak van der Waals interactions or stronger, hydrogen-bonding interactions.[1,2] The properties of molecular clusters in general and those involving hydrogen bonding in particular are especially significant with a view to understanding a variety of chemical and biochemical processes. The behavior of molecular clusters is usually between two extremes (viz. the gas phase and the crystal solid phase); consequently, by examining the properties of clusters of increasing size, one can acquire valuable knowledge about the transition between both extremes. Clusters containing more than two molecules exhibit so-called cooperative effects,[3−5] which is reflected in changes in some properties with increase in cluster size. Thus, the strength of hydrogen bonds in the clusters usually increases as further molecules are added; also, the frequencies of some vibrational modes are shifted by effect of the incorporation of new molecules—in some hydrogen-bonded clusters, the shift can amount to several hundred reciprocal centimeters. Properly characterizing these phenomena is thus crucial with a view to understanding the behavior of some chemical and biochemical systems.

Clusters consisting of several hydrazine molecules exhibit some interesting properties; shifts in the frequencies of some vibrational modes with an increase in the number of cluster molecules have been determined.[6] Hydrazine is a polar molecule that can form hydrogen bonds; as such, it must exhibit marked cooperativity in its molecular interactions. Because experimental measurements provide no detailed structural information about the structure of the clusters involved or the characteristics of the interaction, one must use theoretical methods to derive it. So far, hydrazine clusters have seemingly been the subject of only two theoretical studies,[7,8] where a semiempirical potential function was used to locate the minima on the potential surface for the clusters and to reproduce shifts in the experimental frequencies.

This paper reports a theoretical study of clusters consisting of up to four hydrazine molecules based on ab initio calculations. Various structures corresponding to minima on the potential surface for the clusters were located by using the HF, DFT/B3LYP, and MP2 methods, and the frequencies at the corresponding computational levels were calculated. One other aim of this work was to determine the magnitude of nonadditivity in the interaction of clusters of more than two molecules; this was estimated basically from the pairwise interaction energy. All calculations were carried out by using the program Gaussian 94.[9]

2. Computational Details

As stated above, we used three different computational methods (viz., HF, DFT/B3LYP, and MP2) to fully optimize the geometries of clusters formed by two, three, and four hydrazine molecules. After stationary points were located, vibrational frequencies were calculated in order to ascertain that each structure found corresponded to a minimum. We initially used the HF method to identify stationary points on the potential surface, using previously reported geometries[7] as starting points; alternative geometries were also tested in order to search for additional stationary points however. The stationary points found at the HF level were used as the starting points for optimization with methods including electron correlation (viz. DFT/B3LYP and MP2).

At each minimum found, the interaction energy was calculated by using the supermolecule method,[1,2,10] which determines the interaction energy of a cluster as the energy difference between the cluster and its constituent molecules in isolation. The binding energies thus obtained are subject to the basis set superposition error (BSSE)[11,12] and thus are overestimated. This shortcoming can usually be circumvented by using the counterpoise method of Boys and Bernardi,[12,13] where the interaction energy is calculated as

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$$\Delta E_{ABC}^{\mathrm{CP}} = E_{ABC}(ABC) - E_A(ABC) - E_B(ABC) - E_C(ABC) \quad (1)$$

Terms in parentheses in the equation indicate that the whole cluster basis set is used in the computations; the molecules are at the geometry they adopt in the cluster. Finally, one must consider the energy changes associated with structural changes in the molecules on forming the cluster.[12,14] To this end, the deformation energy is defined as the energy change undergone by an isolated molecule in adopting the geometry it possesses in the cluster,

$$E_{\mathrm{def}} = \sum_i (E_i^{\mathrm{complex}} - E_i^{\mathrm{isolated}}) \quad (2)$$

where superscripts denote the particular geometry to be used. The overall interaction energy will thus be a combination of the following two quantities:

$$\Delta E = \Delta E^{\mathrm{CP}} + E_{\mathrm{def}} \quad (3)$$

The contributions of cooperativity in the interaction were estimated from various parameters. In a number of hydrogen-bonded clusters, the interaction increases the dipole moment of the complex relative to the value obtained from the vector addition of the dipoles for the isolated molecules in the geometries they possess in the cluster, so this quantity can be used to estimate the significance of cooperativity in the interaction.[2,15,16] The significance of cooperativity can also be estimated from the structural changes undergone by the molecules as cluster size is increased, as well as from the shifts in some vibrational frequencies (particularly those associated with stretching vibrations of the protons involved in hydrogen bonds). Finally, a more direct measure of the significance of cooperativity in this context can be obtained by comparing the interaction energy of the complex with the pairwise interaction energies calculated employing the whole basis set for the complex in order to exclude BSSE.[5,14] Thus, for the trimer,

$$E_{\mathrm{nopair}} = \Delta E_{ABC} - \Delta E_{AB} - \Delta E_{AC} - \Delta E_{BC} \quad (4)$$

One important aspect of any study of this type is the use of an appropriate basis set. Obtaining an accurate description of hydrogen-bonded clusters is known to require the use of sets of substantial size.[10] However, the size of the clusters studied in this work precluded the use of large sets; we thus chose to employ the 6-31+G* basis set, which had previously been successfully applied to other clusters,[10,16] and compared its results for hydrazine monomer and dimer to those provided by the 6-311++G(2d,2p) set. As shown later on, and except for slight numerical differences, the results obtained with both sets were quite similar.

3. Results

This section presents and discusses the results obtained in this theoretical study of the hydrazine molecule and its dimer, trimer, and tetramer. The results for hydrazine monomer and dimer are discussed first and used to assess the quality of the basis set used. In a subsequent section are presented the results for the trimer and tetramer. Finally, the calculated frequency shifts are examined and compared with reported experimental values.

3.1. Hydrazine Monomer. Table 1 lists the geometric results for hydrazine monomer provided by the three computational methods as used with the 6-31+G* basis set, in addition to those provided by the 6-311++G(2d,2p) set, which were employed to estimate the effects on the results of using an extended set.

TABLE 1: Geometry of Hydrazine Monomer As Optimized at Different Computational Levels ($H_3 = H_4$; $H_5 = H_6$; See Figure 1 for Numbering)

	6-31+G*			6-311++G(2d,2p)			
	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl[a]
r_{NN}	1.412	1.434	1.438	1.412	1.437	1.439	1.449
r_{NH3}	0.999	1.016	1.016	0.995	1.011	1.008	1.021
r_{NH5}	1.002	1.020	1.020	0.998	1.015	1.011	1.021
θ_{NNH3}	108.3	107.7	107.1	108.5	107.6	107.2	106
θ_{NNH5}	112.5	112.6	112.1	112.4	112.1	111.7	112
θ_{H3NH5}	108.7	108.4	108.4	108.7	108.1	107.6	
$\varphi_{\mathrm{H6NNH3}}$	91.0	91.4	91.5	90.1	90.8	90.5	91
$\mu(D)$	2.22	2.19	2.29	2.02	1.97	2.03	1.88[b]

[a] Reference 17. [b] References 18 and 19.

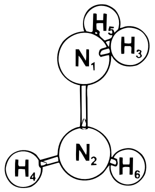


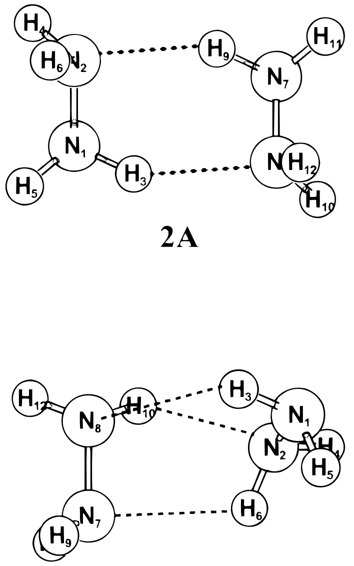
Figure 1. Hydrazine monomer.

The optimized geometry possessed C_2 symmetry in all instances, and the results were similar to those obtained from experiment.[17] The main differences are in the values provided by the HF method, which gave too short N−N distances. The methods including electron correlation provided longer distances that were more consistent with their experimental counterparts. Also, the two basis sets provided essentially identical results.

Table 1 also gives the dipole moments obtained at the different computational levels tested. The results were very similar whichever the method, HF included, which usually overestimates dipole moments. The values provided by the 6-31+G* basis set were all large relative to their experimental counterparts;[18,19] the results obtained with the larger set, 6-311++G(2d,2p), were closer to the experimental values but still slightly overestimated, though virtually identical with those obtained at the MP2/6-311+G(3df,2p) level elsewhere.[20] Overall, the data in Table 1 suggest that the 6-31+G* set provides quite an accurate description of hydrazine monomer, even though it overestimates its dipole moment. However, ensuring an accurate estimate of this quantity entails using a large basis set and makes computations on larger hydrazine clusters impractical. For this reason, and based on the results for the dimer discussed in the following section, we chose to adopt the 6-31+G* basis set for computations on the larger hydrazine clusters.

3.2. Hydrazine Dimer. Hydrazine dimer has so far been the subject of relatively few theoretical studies. The only available results in this respect were obtained by using a semiempirical potential function[7] that revealed the occurrence of three minima, the most attractive of which possesses C_2 symmetry and an interaction energy of −24 kJ/mol (i.e., about 2 kJ/mol lower than that of the following minimum in the stability sequence). All three structures form hydrogen bonds, the shortest being those in the most stable minimum.

Our computational methods and basis sets only revealed the two structures shown in Figure 2. Their features are summarized in Table 2. These structures are the same as those for the two most attractive minima identified in previous work,[7] and possess very similar interaction energies which differ by less than 1.0 kJ/mol. The most stable minimum located by the HF and MP2



2A

2B

Figure 2. Minima of hydrazine dimer.

TABLE 2: Properties of the Minima for Hydrazine Dimer As Determined by Using the 6-31+G* and 6-311++G(2d,2p) Basis Sets (Distances in Å, Energies in kJ/mol)

	6-31+G*			6-311++G(2d,2p)		
	HF	B3LYP	MP2	HF	B3LYP	MP2
			Structure **2A**			
$R_{N\cdots H}$	2.421	2.221	2.208	2.502	2.280	2.217
$R_{m-m}^{(a)}$	3.266	3.102	3.077	3.349	3.159	3.076
ΔE	−14.2	−20.5	−21.4	−12.2	−18.0	−23.3
E_{def}	0.3	0.6	0.6	0.2	0.4	0.5
A (GHz)	12.557	12.150	12.184	12.588	12.186	12.262
B (GHz)	2.694	2.977	2.990	2.574	2.878	2.987
C (GHz)	2.399	2.572	2.620	2.300	2.497	2.627
$\mu(D)$	3.48	3.46	3.56	3.14	3.10	3.15
$\mu'(D)^b$	3.57	3.54	3.64	3.19	3.15	3.17
			Structure **2B**			
R_{N2H10}	2.377	2.189	2.198	2.464	2.292	2.198
R_{N7H6}	2.695	2.615	2.572	2.711	2.399	2.579
R_{N8H3}	2.837	2.614	2.484	3.027	3.172	2.445
R_{m-m}^a	3.263	3.105	3.020	3.377	3.292	3.003
ΔE	−14.5	−19.9	−22.2	−12.3	−17.0	−23.8
E_{def}	0.6	1.2	1.2	0.4	0.5	1.1
A (GHz)	13.032	12.720	12.506	13.178	13.257	12.524
B (GHz)	2.602	2.821	2.959	2.454	2.558	2.988
C (GHz)	2.523	2.727	2.860	2.375	2.464	2.893
$\mu(D)$	3.15	3.01	3.28	2.87	2.83	2.95
$\mu'(D)^b$	3.13	3.09	3.25	2.82	2.74	2.88

[a] R_{m-m} is the distance between centers in the N−N bond. [b] Dipole moment obtained as the vector addition of the molecular dipoles. [c] The interaction energy at the MP4/6-31+G*//MP2/6-31G* levels is −20.6 kJ/mol for **2A** and −21.6 kJ/mol for **2B**.

TABLE 3: Selected Thermodynamic Properties of Hydrazine Dimer Calculated with the 6-31+G* Basis Set (Energies in kJ/mol)

	HF		B3LYP		MP2	
	2A	**2B**	**2A**	**2B**	**2A**	**2B**
D_0	−7.9	−8.3	−13.3	−13.1	−14.3	−15.5
ΔH_{dim}^{298}	−7.6	−7.6	−13.9	−13.0	−15.0	−15.8
ΔG_{dim}^{298}	28.3	25.9	25.4	22.3	24.6	22.5

methods is a structure of C_1 symmetry (**2B**) that involves up to three N···H contacts, some at quite long distances however. On the other hand, the most stable minimum identified by the DFT/B3LYP method is a structure of C_2 symmetry (**2A**) consistent with the results provided by the above-mentioned potential function.[7] The DFT/B3LYP and MP2 methods give similar interaction energies with the smaller basis set, energies that are much greater than those provided by the HF method; this reflects the prominent role of electron correlation in this system, which contributes nearly 35% of the overall interaction energy. The interaction energies at the MP4 level obtained from an MP2 optimized geometry for structures **2A** and **2B** were −20.6 and −21.6 kJ/mol, respectively, and differed by less than 1 kJ/mol from the MP2 results. The use of a larger basis set has no significant influence on these results, which are similar to those obtained with the 6-31+G* set. The interaction energies at the MP2 level are about 1−2 kJ/mol more negative than those found with the 6-31+G* set; on the other hand, the use of the larger basis set with the other methods leads to less negative interaction energies. As a result, use of the 6-311++G(2d,2p) basis set increases the contribution of electron correlation up to about 50% of the interaction energy with the MP2 method. Table 2 also gives the deformation energy associated with the formation of each minimum. As can be seen, its contribution to the interaction energy is very small (barely 1 kJ/mol). If the deformation energy is excluded, then the energy difference between minima is greater as structure **2B** is more strongly distorted.

As regards the geometries of the minima, all methods lead to similar results; however, HF provides longer intermolecular distances than does MP2, and DFT/B3LYP gives results between the two. Structure **2A** involves two N···H contacts, at about 2.2 Å, whereas structure **2B** establishes a single one, also at 2.2 Å, accompanied by another two at longer distances. Consequently, a balance between the number of contacts and their strength is reached that results in the observed stability sequence. Unlike in the previous study,[7] there seems to be no direct relationship between the interaction strength and the average distance of the hydrogen bonds.

The interaction distorts the geometry of the molecule, as reflected in its deformation energy. In hydrogen-bonded clusters, cooperativity is usually estimated from the lengthening in the X−H bonds involved in hydrogen bonding interactions. In our case, N−H bond distances increased by up to 0.006 Å with the correlated methods; this value is similar to that obtained for the N−N bond and also to reported data for other hydrogen-bonded systems.[21,22] Polar molecules frequently exhibit an increased dipole moment relative to the vector addition of the dipole moments for the monomers. The electric field created by each molecule induces a dipole moment in its neighbor that can modify the net dipole moment of the cluster.[2,15] Table 2 compares the dipole moment for the cluster with the result of the vector addition of the values obtained for the individual molecules. As can be seen, the differences are negligible (3%), so the presence of a significant induced dipole moment in the cluster can be safely discarded. Also, the dipole moment decreases slightly at **2A**, and the opposite is true at **2B**. The results provided by the larger basis set are quite similar; while it gives smaller values for the total dipole moment, consistent with the results for hydrazine monomer, the values exhibit the same trend as those obtained with the smaller basis set (6-31+G*), which suggests that this one is quite appropriate for studying larger clusters.

Table 3 gives the values of selected thermodynamic properties for the minima of hydrazine dimer as determined by using the 6-31+G* basis set. The dimerization enthalpy change is about −15 kJ/mol for both structures with the MP2 method. The stability sequence is the same as that reached by comparing

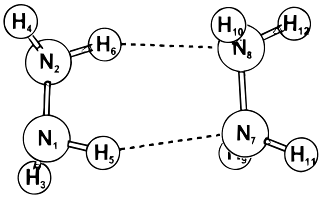


Figure 3. Transition state of hydrazine dimer.

TABLE 4: Characteristics of the Transition State of Hydrazine Dimer As Determined by Using the 6-31+G* and 6-311++G(2d,2p) Basis Sets (Distances in Å, Energies in kJ/mol)

	6-31+G*			6-311++G(2d,2p)		
	HF	B3LYP	MP2	HF	B3LYP	MP2
$R_{N\cdots H}$	2.657	2.645	2.394	2.699	2.526	2.428
R_{m-m}[a]	3.508	3.335	3.287	3.624	3.405	3.309
ΔE	−10.7	−13.6	−15.2	−9.0	−11.6	−16.4
E_{def}	1.1	1.9	2.3	0.7	1.3	1.6
A (GHz)	12.466	12.083	12.070	12.485	12.087	12.103
B (GHz)	2.461	2.703	2.774	2.314	2.604	2.747
C (GHz)	2.131	2.302	2.358	2.020	2.224	2.332
$\mu(D)$	4.95	5.11	5.25	4.51	4.63	4.75
$\mu'(D)$[b]	4.49	4.43	4.58	4.06	3.97	4.07

[a] R_{m-m} is the distance between centers in the N−N bond. [b] Dipole moment obtained as the vector addition of the molecular dipoles.

the interaction energies; therefore, although the vibrational factor accounts for more than 30% of the interaction, it is similar in both structures. As can be seen from the ΔG values, the entropic contribution to the dimerization process destabilizes structure **2A** with respect to the other minimum, reflecting the more orderer structure that the molecules adopt in the former.

So far, we have made no mention of a stationary point located in previous work,[7] the structure and characteristics of which are shown in Figure 3 and Table 4. At all computational levels tested, this structure was found to be a transition state with an interaction energy 4−6 kJ/mol less negative than that of the global minimum. The structure, of C_2 symmetry, exhibits two hydrogen-bonding contacts; the distances of the hydrogen bonds, however, are much longer, and the interaction energy is lower than that in **2A**. As can be seen, the deformation energy for this structure exceeds those at the minima, which suggests that the structure is more distorted and that the hydrazine molecules cannot adopt a relaxed arrangement. Also, its dipole moment is up to 15% greater than the vector addition of those for the individual molecules in isolation, in contrast with the small increments at the minima.

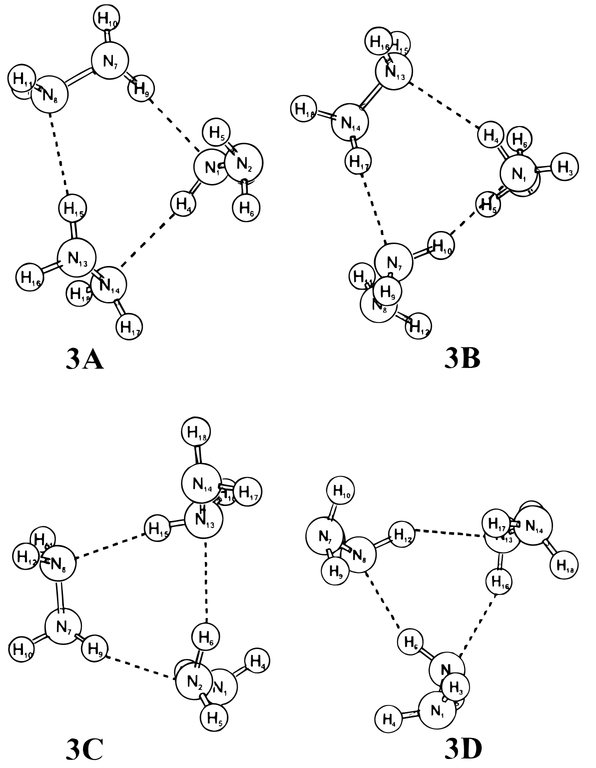


Figure 4. Minima of hydrazine trimer.

TABLE 5: Calculated Properties of Hydrazine Trimer with the 6-31+G* Basis Set (Distances in Å, Energies in kJ/mol)

		ΔE	E_{def}	E_{nopair}	$R_{N\cdots H}$[a]	R_{m-m}[a]	$\mu(D)$	$\mu'(D)$[b]
HF	**3A**	−32.7	1.8	−2.3	2.361	3.685	4.44	4.37
	3B	−32.8	1.6	−2.8	2.349	3.744	3.19	3.09
	3C	−31.7	1.5	−2.2	2.325	3.869	3.50	3.49
	3D	−29.3	0.5	−3.0	2.411	4.153	0.56	0.71
B3LYP	**3A**	−46.3	2.9	−4.8	2.125	3.545	5.01	4.31
	3B	−44.6	7.0	−6.6	2.226	3.480	3.55	3.61
	3C	−45.5	2.6	−4.8	2.122	3.709	3.47	3.43
	3D	−40.7	1.1	−5.9	2.201	3.950	0.51	0.72
MP2	**3A**	−48.0 (−45.0)	5.2	−4.2 (−3.9)	2.137	3.411	5.06	5.00
	3B	−48.4 (−45.5)	7.6	−5.6 (−5.2)	2.195	3.354	4.08	4.05
	3C	−46.9 (−44.0)	3.0	−3.2 (−3.0)	2.129	3.584	3.98	4.03
	3D	−41.0 (−39.3)	1.3	−5.1 (−4.9)	2.204	3.694	0.11	0.24

[a] R_{m-m} is the distance between centers in the N−N bond, and $R_{N\cdots H}$ is the average N···H distance. [b] Dipole moment obtained as the vector addition of the molecular dipoles. [c] Values in parentheses were obtained at the MP4/6-31+G*//MP2/6-31+G* level.

3.3. Hydrazine Trimer. Figure 4 shows the minima located for hydrazine trimer. Their most salient features are summarized in Table 5. As with the dimer, the minima of the trimer have seemingly been the subject of only one theoretical study, based on the use of a potential function.[7] The structures of Figure 4 are similar to those found in such a study. We identified an additional structure corresponding to a minimum and exhibiting a cyclic configuration; taking into account the increasing complexity of the potential surface for clusters of this size, there might exist other, unidentified minima. The four structures of Figure 4 differ from one another in the type of contact established by each hydrazine molecule. At minimum **3A**, two of the molecules form two hydrogen bonds each via two different amino groups. In structures **3B** and **3C**, only one molecule in the cluster interacts via its two amino groups. Finally, in structure **3D**, all three hydrazine molecules interact via a single amino group. The position of the free amino group is the essential difference between structures **3B** and **3C**; thus, in **3B**, both amino groups are on the same side of the ring, whereas in **3C** the two are on opposite sides. The stability sequence observed depends on the particular method. Thus, with HF and MP2, **3A** and **3B** are virtually isoenergetic, the latter being slightly more stable; with DFT/B3LYP, both **3A** and **3C** are more stable than **3B**, consistent with the results provided by a potential function. Structure **3D** is the least stable with any of the methods used. In any case, the energy differences among the most stable structures are so small (about 1−2 kJ/mol) that the effect of BSSE in the position of the minimum may change the actual stability sequence. Table 5 also gives the deformation energy for each structure. As can be seen, this factor is more significant than in the dimer; in some cases, its contribution exceeds the energy difference between minima and

TABLE 6: Selected Thermodynamic Properties of Hydrazine Trimer Calculated with the 6-31+G* Basis Set (Energies in kJ/mol)

		3A	3B	3C	3D
HF	D_0	−20.0	−20.7	−19.1	−18.5
	$\Delta H^{298}_{\text{trim}}$	−18.7	−18.7	−17.6	−15.6
	$\Delta G^{298}_{\text{trim}}$	53.5	47.8	52.4	48.0
B3LYP	D_0	−31.8	−30.9	−31.6	−28.0
	$\Delta H^{298}_{\text{trim}}$	−32.3	−30.7	−31.6	−26.7
	$\Delta G^{298}_{\text{trim}}$	46.6	46.5	44.7	47.6
MP2	D_0	−33.9	−35.3	−33.5	−28.9
	$\Delta H^{298}_{\text{trim}}$	−34.5	−35.4	−33.6	−27.7
	$\Delta G^{298}_{\text{trim}}$	45.8	43.8	42.0	44.1

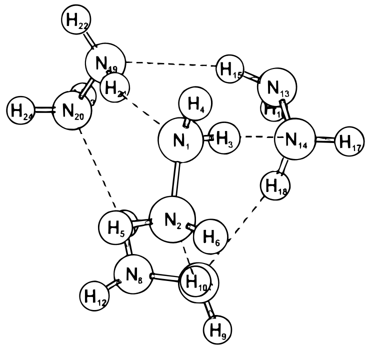
amounts to 15% of the total interaction energy, so its inclusion may alter the stability sequence. Also, such a contribution is greater with the methods that include electron correlation than with HF.

Table 5 also lists the contribution of nonadditive terms to the interaction energy, calculated as the difference between the combined interaction energy of molecular pairs and the interaction energy of the complex (eq 4). As can be seen, nonadditive terms contribute significantly to the interaction, particularly in the methods that include electron correlation, where they account for 10−12% of the overall interaction energy. For a polar molecule such as hydrazine, this contribution is likely to arise from inductive phenomena; however, as with the dimer, the dipole moments for the trimer are scarcely different from the vector addition of the molecular dipoles, thereby reflecting the presence of a small net induced moment. It is interesting to note that both the interaction energies at the MP4 level and the contributions of nonadditive terms to the interaction are almost identical—slightly less negative however—with those obtained at the MP2 level and exhibit the same trend as in the dimer.

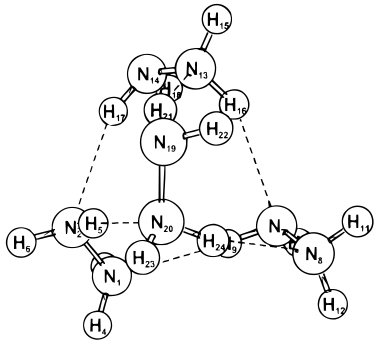
As regards geometries, hydrogen bond distances are generally shorter than those in the dimer by virtue of the stronger interaction. Also, N−H and N−N distances are about 0.010 Å longer than those in the isolated molecule by the effect of cooperativity in the interaction.

Table 6 gives the values of selected thermodynamic properties of the minima for hydrazine trimer. The trimerization enthalpy for the most stable structure is about −35 kJ/mol with the MP2 method. Therefore, the formation of the dimer involves an enthalpy change of ca. −16 kJ/mol, whereas the transition from the dimer to the trimer involves a change of ca. −20 kJ/mol, which again reflects the influence of cooperativity in the interaction. Contrary to that found for the dimer, the entropic contribution to the trimerization process has a significant effect, changing the order of stability of the minima. As a consequence, the structure with smaller binding energy (**3D**) is more stable than some other minima when free energies are considered.

3.4. Hydrazine Tetramer. After the characteristics of hydrazine dimer and trimer were examined, the study was extended to a cluster consisting of four molecules. On the basis of the results for the trimer, the tetramer should exhibit a number of minima with similar interaction energies. Figure 5 shows the structures of the two most attractive minima identified, which form six hydrogen bonds; their features are summarized in Table 7. Structure **4A** is the more stable with the three methods tested; the difference, however, is barely 2 kJ/mol. Again, we should emphasize the importance of including the deformation energy in calculating the interaction energy as the magnitude of the former is large enough to reverse the stability sequence of the minima, particularly with the methods that include electron correlation. The contribution of nonadditive terms is again significant and similar to that in the trimer (about 10%). However, N···H distances in the hydrogen bonds of the tetramer minima are slightly longer than those in the trimer, which suggests that the net effect of cooperativity here is not as strong as in the cluster formed by three molecules. This same trend is observed in the N−H and N−N distances, which are similar to or even shorter than those for the trimer minima. However, based on the enthalpy changes observed upon addition of a new molecule to a cluster, the transition from the trimer to the tetramer involves slightly larger stabilization (about 1 kJ/mol more) than that from the dimer to the trimer.



4A



4B

Figure 5. Most stable structures of hydrazine tetramer.

3.5. Frequency Shifts. Interactions between molecules usually shift some vibrational frequencies corresponding to modes closely involved in the interaction. Thus, the hydrogen stretching vibration is frequently shifted in clusters involving hydrogen bonding. For hydrazine, shifts in the asymmetric $-NH_2$ wagging (ν_{12}) and the symmetric N−N stretching (ν_5) vibrations have been experimentally measured.[6] The former mode undergoes a blue shift and the latter a, less marked, red shift. Table 8 gives the calculated frequency shifts for both normal modes at the most stable minima for each cluster, in addition to their experimental values. As can be seen, the shifts in the asymmetric $-NH_2$ wagging mode are qualitatively consistent with their experimental counterparts. All methods predict large blue shifts in a range similar to that observed in the experiment. The HF and MP2 methods provide very similar results that differ by only a few wavenumbers compared to the experimental measurements. The DFT/B3LYP method also predicts large blue shifts, but they are somewhat overestimated with respect to the experimental values. The qualitative agreement between calculated and experimental results is improved if a new experimental shift[8] of 64 cm^{-1} is considered. As indicated in ref 8, this result suggests that there are contributions from more than one isomer, thus increasing the complexity of the spectrum. The errors in the N−N stretching mode are even greater; most are even of the opposite sign to the experimental values. Only the

TABLE 7: Characteristics of the Minima of Hydrazine Tetramer As Determined by Using the 6-31+G* Basis Set (Energies in kJ/mol, Distances in Å)

		ΔE	E_{def}	E_{nopair}	$R_{N\cdots H}$[a]	R_{m-m}[a]	D_0	ΔH^{298}_{tetr}	ΔG^{298}_{tetr}
HF	**4A**	−52.5	2.7	−3.8	2.395	3.924	−32.21	−30.71	85.91
	4B	−50.9	3.8	−4.1	2.402	3.877	−31.00	−29.47	87.49
B3LYP	**4A**	−75.3	5.3	−8.4	2.181	3.742	−51.96	−53.61	74.12
	4B	−73.0	7.3	−9.2	2.185	3.688	−50.42	−51.87	76.13
MP2	**4A**	−76.9	4.4	−6.6	2.167	3.717	−54.40	−56.09	70.10
	4B	−75.3	7.4	−7.8	2.166	3.663	−53.65	−55.04	72.19

[a] R_{m-m} is the distance between centers in the N−N bond, and $R_{N\cdots H}$ the average N···H distance.

HF method predicts a small negative shift in the dimer. Experimental measurements[23] indicate that the frequency of the N−N stretching mode undergoes a blue shift in condensed phases with respect to the gas-phase value. All methods qualitatively reproduce this behavior, giving larger shifts as the size of the cluster growths. The observed behavior is similar to that obtained by using a potential function in previous work; the function provided acceptably accurate shifts in the wagging frequency but failed as regards the N−N stretching frequency. In any case, one should bear in mind that both the harmonic approximation used in calculating the frequencies and changes in the potential surface due to BSSE might be partly responsible for the discrepancies.

As regards the N−H stretching motion, no experimental information is available. Hydrazine presents four N−H stretching modes, which are grouped by pairs, corresponding to symmetric and asymmetric motions of the hydrogen atoms belonging to the same NH_2 group. As a guidance for further experiments, the calculated shifts for stretching modes ν_1 and ν_9 are also presented in Table 8. Both modes show similar patterns; as expected, frequencies are red-shifted with respect to the values obtained for the isolated molecule. However, the magnitude of the shifts is somewhat smaller than that observed in other hydrogen-bonded systems. The DFT/B3LYP and MP2 methods provide larger shifts than does the HF method, as a consequence of the poor description of the hydrogen-bonding interaction provided by the latter. The largest shift in the dimer corresponds to the hydrogen atoms closest to the nitrogen atom of the other molecule, thus revealing the relation between the strength of the hydrogen bond and the observed frequency shift. As the size of the cluster growths, the shifts are larger, reaching more than 100 cm^{-1} in the cluster of four molecules.

4. Conclusions

We used the HF, DFT/B3LYP, and MP2 methods in combination with the 6-31+G* basis set to perform calculations on hydrazine clusters consisting of up to four molecules. All three methods predict the occurrence of two minima with very similar binding energies (ca. 20−22 kJ/mol with the methods including electron correlation) for hydrazine dimer. The DFT results are similar in quality to those provided by MP2; the stability sequences they establish, however, are different. The results for the dimer are essentially similar to those provided by the 6-311++G(2d,2p) basis set and by a more powerful method such as MP4. The geometries and interaction energies obtained seemingly reveal the lack of clear-cut correlation between the stability sequence and the hydrogen bond distances. Clustering induces changes in the molecular structure of hydrazine, basically in the form of lengthened N−H and N−N bond distances. Also, contrary to the expectations for a molecule with a substantial dipole moment, this changes very little (less than 3%) by effect of the interaction. A transition state of C_2 symmetry, 4−6 kJ/mol less stable than the minima, was also located.

TABLE 8: Calculated Frequency Shifts (cm^{-1}) in the Asymmetric NH_2 Wagging (ν_{12}), the Symmetric N−N Stretching (ν_5), and the N−H Stretching (ν_1 and ν_9) Modes for the Most Stable Minima of Hydrazine Clusters (6-31+G* Basis Set)

	NH_2 wagging (ν_{12})				N−N stretching (ν_5)			
n	exptl[a]	HF	B3LYP	MP2	exptl[a]	HF	B3LYP	MP2
2	42	41	57	39	−16	−2	0	3
	48	43	61	51		8	3	19
	64[b]							
3	55	46	81	59	−10	1	9	17
	88	62	96	68		11	12	31
		73	96	79		22	40	50
4	88	54	79	62		−1	6	6
	109	78	104	86		11	27	33
		89	116	98		16	42	47
		94	121	102		22	50	55

	N−H stretching (ν_1)			N−H stretching (ν_9)		
	HF	B3LYP	MP2	HF	B3LYP	MP2
2	−10	−46	−47	−7	−28	−32
	−4	−14	−14	1	−13	−14
3	−27	−73	−89	−19	−96	−90
	−12	−28	−33	−11	−56	−40
	−4	−21	−23	1	−23	−27
4	−50	−98	−104	−36	−163	−139
	−20	−70	−62	−17	−68	−63
	−12	−25	−40	−10	−43	−43
	−9	−16	−27	−8	−15	−25

[a] Reference 6. [b] Reference 8.

The trimer occurs as several structures that correspond to minima with scarcely different interaction energies. The structures are relatively similar, and differ basically in the role played by the amino groups of each molecule in the hydrogen bonds. In general, hydrogen bond distances are shorter than those in the dimer by effect of the stronger interaction. The contribution of nonadditive terms to the interaction energy is significant (up to 12%).

The tetramer possesses two minima of also very similar interaction energy that involve six hydrogen bonds. The trends observed in this cluster are similar to those in the trimer; cooperativity accounts for up to 10% of the overall interaction energy. However, hydrogen bonds are longer than in the trimer, which suggests that the effect of cooperativity in the interactions is less significant in the cluster of four molecules.

Finally, the calculated shifts in the asymmetric $-NH_2$ wagging and N−N stretching frequencies reproduce their experimental counterparts, in a qualitative manner the former and with substantial errors the latter; the differences, however, may have arisen from the approximations used in computing the frequencies. Also, large frequency shifts are predicted for the N−H stretching modes as a consequence of hydrogen bonding interaction.

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