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Six Structures of the Hydrazine Dimer

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All possible structures of the hydrazine dimer have been investigated in a systematic way for all combinations of the two hydrazine conformers. Three structures with two hydrogen bonds, three with three hydrogen bonds and no structure with only a single hydrogen bond have been found. Two structures with four hydrogen bonds are saddle points of the potential energy surface. In the first step, the geometries of all investigated structures were optimized at the MP2/aug-cc-pVDZ level of theory. In the second step, the intermolecular parameters of all stable structures were determined at the CCSD(T)/aug-cc-pVTZ level. The binding energies of the six stable conformations include the BSSE correction. The frequency shifts of the antisymmetric wagging mode and the NH-stretching modes were calculated with the MP2/6-31++(2df,2p) method. The barrier heights of three rearrangement reactions were determined at the CCSD(T)/aug-cc-pVTZ level.

Introduction

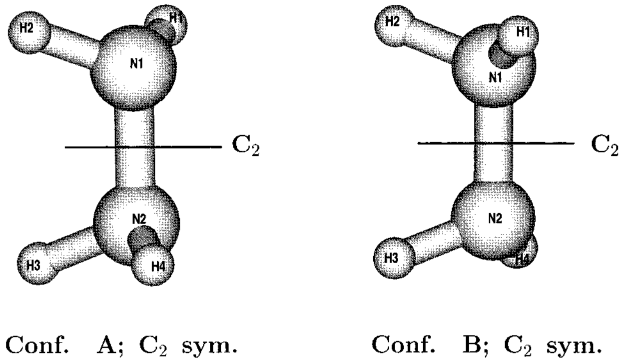
The hydrogen bond[1,2] is very important in nearly every field of chemistry and biology. Hydrogen bonds result from attractive interactions between a hydrogen atom and an electronegative atom such as oxygen, a halogen, or to a lesser extent nitrogen. Electronic structure theory has proven to be an invaluable tool in the quest for understanding of these intermolecular interactions.

Encouraged by the experimental work of Buck et al.,[3−5] we are especially interested in the dimer structures and the shift of the antisymmetric NH_2 wagging mode with respect to the monomer. Beu et al.[6,7] determined the binding energies, and the wavenumbers of the antisymmetric NH_2 wagging modes for three dimer structures of hydrazine, making use of their intermolecular potential model. The model potential included the multipolar electrostatic energy, dipole polarizabilities and dipole−dipole dispersion energy coefficients, located only on the nitrogen atoms, and simple atom−atom isotropic repulsion and penetration contributions. So far, there exists only one ab initio study from Cabaleiro-Lago and Ríos[8] on the interactions in hydrazine clusters of one to four molecules. They found two stable conformations and one saddle point for the dimer.

Since the hydrazine molecule has two lone pairs, four H atoms and two conformations, a large number of possible dimer structures is expected. An extensive search for all stable conformations of dihydrazine is indispensable.

Computational Details

Full geometry optimization of all analyzed structures of the hydrazine dimer were performed at the MP2/basis 1 and MP2/6-31++G(2df,2p) level. Here, basis 1 consists of the aug-cc-pVDZ basis of Dunning[9] for N atoms; the same basis set was used for the s functions of the H atoms; yet for the p functions the smaller cc-pVDZ basis set was employed. In the second step, all intermolecular parameters were optimized at the CCSD(T)/basis 2 level. Basis 2 consists of the aug-cc-pVTZ basis of Dunning[9] for the s,p,d functions of the N atoms, with f functions from the cc−pVTZ basis set; the s functions of the H atoms originate from the aug-cc-pVTZ basis, while the p functions are from the cc−pVTZ basis set. All MP2,[10] DFT[11] and harmonic frequency calculations were carried out with the GAUSSIAN-94 program.[12] The DFT variant B3LYP was used, which is a HF/DFT hybrid functional constructed from Becke's three parameter exchange functional[13] and the Lee, Yang, Parr correlation functional.[14] CCSD(T) calculations[15−17] were performed with the MOLPRO98 suite of programs[18] on workstations of the Abteilung für Theoretische Chemie at Göttingen.



Conf. A; C_2 sym.   Conf. B; C_2 sym.

Figure 1. Two equivalent conformations of hydrazine.

Hydrazine Molecule

For hydrazine, two equivalent monomer structures with C_2 symmetry, A and B (see Figure 1), exist. They are related by an inversion operation, wherby the center of mass is the center of inversion. Hydrazine has two groups of H atoms: the two inner H atoms, i (in Figure 1, the atoms H2 and H3) and the two outer H atoms, o (H1 and H4).

The structure of hydrazine has been determined experimentally by Kohata et al.,[19] using electron diffraction and the first ab initio calculation of the geometry, force field and vibrational frequencies were carried out by Tanaka et al.[20]

In this work the equilibrium structure, the dipole moment and the two rotation barrier heights were determined (see Tables 1 and 2). The equilibrium structure was calculated with the

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TABLE 1: Geometry of Hydrazine[a]

conf	method	R(NN)	R(NH)$_i$[e]	R(NH)$_o$[e]	∠NNH$_i$[e]	∠NNH$_o$[e]	∠HNH	HNNH[f]
equilibrium	ref 20[b]	1.448	1.021	1.018	110.82	105.94	106.64	90.05
	ref 8[c]	1.439	1.011	1.008	111.7	107.6	107.6	90.5
	MP2/basis 1	1.4442	1.0222	1.0191	111.37	106.68	107.37	90.40
	B3LYP/basis 1	1.4365	1.0206	1.0175	112.11	107.55	107.66	90.80
	MP2/avtz	1.4345	1.0136	1.0105	111.68	107.13	107.65	89.94
	CCSD(T)/vtz	1.4448	1.0154	1.0120	110.79	106.21	106.57	89.86
	CCSD(T)/basis 2	1.4438	1.0158	1.0127	111.17	106.64	107.11	90.05
	CCSD(T)/avtz	1.4449	1.0161	1.0130	111.11	106.61	107.11	90.07
	exp[d]	1.449	1.021	1.021	112.	106.		91
SAT 1 (C_{2v})	CCSD(T)/avtz	1.4852	1.0177	1.0177	107.51	107.51	111.308	0
SAT 2 (C_{2h})	CCSD(T)/avtz	1.4860	1.0187	1.0187	103.68	103.68	106.89	0.

[a] Bond lengths in ångstroms and angles in degrees. [b] CISD/6-31* calculation with a Davidson correction by Tanaka et al.[20] [c] MP2/6-311++G(2d,2p) calculation of Cabaleiro-Lago and Ríos.[8] [d] Reference 19. [e] The inner bonds and angles, denoted with i, are (see Figure 1, conformation A) the N1−H2 and N2−H3 bonds and the ∠H2−N1−N2 and ∠H3−N2−N1 angles. All other outer N−H bonds and ∠H−N−N's are denoted with o. [f] The dihedral angle H2−N1−N2−H4 in Figure 1 conformation A.

TABLE 2: Rotation Barriers (kJ mol^{-1}) and the Dipole Moment of Hydrazine

method	trans barrier	cis barrier	μ (D)
ref 21[a]	13.69	37.51	2.022
ref 21[b]	12.83	36.72	
MP2/vtz	10.39	35.46	2.0042
CCSD(T)/vtz	8.95	33.91	2.0045
CCSD(T)/avtz	10.15	34.27	1.9809
CCSD(T)/vqz[c])	10.53	34.54	1.9801

[a] MP2/6-311+G(3df,2p) results. [b] QCISD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) results. [c] With the CCSD(T)/avtz optimized geometry.

following methods: MP2/basis 1, MP2/631++(2df,2p), MP2/aug-cc-pVTZ, B3LYP/basis 1, CCSD(T)/cc-pVTZ, CCSD(T)/basis 2, CCSD(T)/aug-cc-pVTZ. In Table 1, the most reliable parameters are those of the CCSD(T)/aug-cc-pVTZ calculation. Taking this into account, the MP2/basis 1 results are better than the MP2/6-311++G(2d,2p) results of Cabaleiro-Lago and Ríos.[8] The reason for this is a better compensation of the errors due to the MP2 method (see the MP2/aug-cc-pVTZ results) for basis 1. Surprisingly, the dihedral angle H2−N1−N2−H4 (see Figure 1 conformation A) varies for all calculations by less than 1 degree.

The population analysis from MP2/basis 1 level yields an interesting result; the inner and the outer H atoms have different Mulliken atomic charges. The inner H atoms have a charge of 0.085 and the outer ones of 0.111; with other basis sets, similar results are obtained. This difference is one important feature for the relative stability of the dimers.

Two barriers of rotation about the central NN bond exist. The corresponding saddle points have C_{2h} and C_{2v} symmetry for the trans and cis forms, respectively. The rotation barrier heights for different methods are listed in Table 2. Also included are the previously reported barriers on the MP2/6-311+G(3df,2p) and QCISD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p) level of Chung-Phillips and Jebber.[21] Most reliable are the CCSD(T)/vqz values: 10.53 kJ mol^{-1} for the trans-barrier and 34.54 kJ mol^{-1} for the cis barrier. Thus, the two conformations of hydrazine are stable at room temperature.

The polarizability of hydrazine at the CCSD(T)/avtz level in the direction of its C_2 axis is 21.50 (au) and its isotropic polarizability is 22.84 (au).

Systematic Search for All Stable Dimer Structures

All dimer structures resulting from the two equal monomers A, A or B, B (see Figure 1), are in the following denoted by **a**, and all structures resulting from two different monomer structures A and B are denoted by **b**.

It is assumed for all dimer structures that at least one normal hydrogen bond exists. Taking this into account, only the following dimer structures are possible:

(a) Two plausible structures with only one hydrogen bond were analyzed, but neither was stable: geometry optimization yielded structures with two hydrogen bonds.

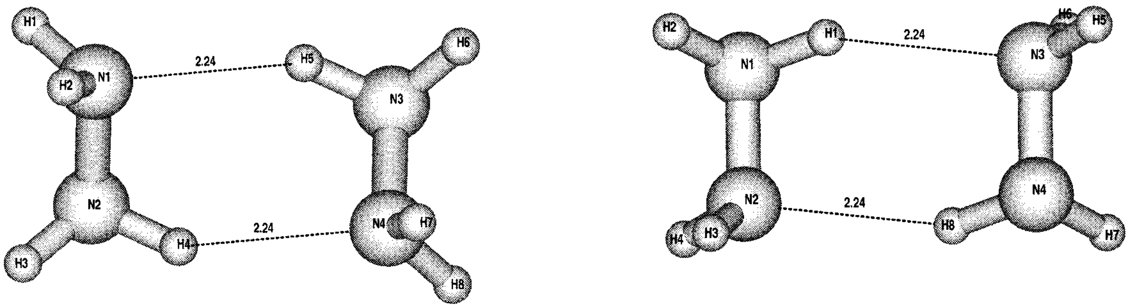
(b) Each hydrazine molecule participates with one H atom in the two hydrogen bonds; further, for each monomer, the H atom and the lone pair participating in the hydrogen bonds are located at different N atoms. Four possible situations arise: AA, BB, AB, BA. The conformations AA and BB are related by an inversion operation. Also, the conformations AB and BA are equivalent. So only the two conformations AA and AB were investigated; in the following, the structures resulting from AA and AB are denoted as conformation **1a** and **1b**, respectively. According to MP2 calculations with three different basis sets, the geometry optimization, and the analysis of the harmonic wavenumbers, both structures are minima on the Potential Energy Surface (PES). Conformation **1a** (see Figure 2) has C_2 symmetry (the C_2 axis is perpendicular to the midpoint of the connection line through the midpoints of the N−N bonds and perpendicular to the plane of projection). Conformation **1b** has a center of inversion (see Figure 2).

(c) The two H atoms participating in the hydrogen bonds are both located on one monomer structure and here on different N atoms. Again, four structures are possible: AA and BB, which are denoted in the following with **2a**, and AB and BA which we denote with **2b**. For conformation **2a** no minimum on the PES was found, yet for conformation **2b** a stable conformation exists. Conformation **2b** (see Figure 3) has C_2 symmetry whereby the C_2 axis connects the midpoints of the two N−N bonds.

(d) Each hydrazine molecule participates with one H atom in the two hydrogen bonds; further, for one monomer, only one N atom with its lone pair and one of its H atoms is involved in the hydrogen bonds. The structure resulting from AA and the structure resulting from BB are equivalent. In Figure 4 the structure resulting from the BB combination is shown: conformation **3a**. The combination of the monomers A and B gives the conformation **3b1** and also the conformation **3b2** (see Figure 4). All three structures are minima on the PES.

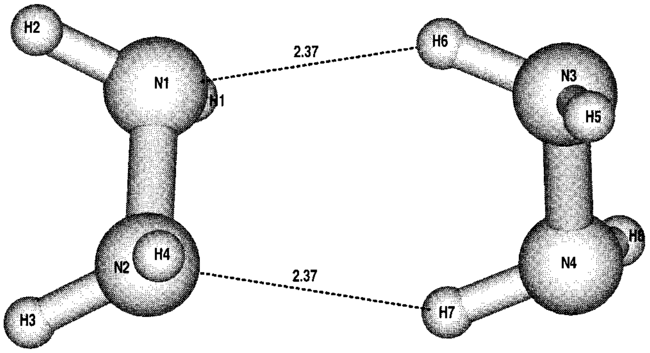
(e) One monomer participates with two H atoms in the hydrogen bonds, whereby the H atoms are bound to only one N atom. No minimum for the two possible structures was found on the PES.

(f) Each hydrazine molecule participates with one H atom in the two hydrogen bonds, and the H atoms and lone pairs are located at only one N atom for both monomers. For these



Conf. 1a; C_2 Sym. **Conf. 1b; C_i Sym.**

Figure 2. Conformation **1a** (C_2 axis is perpendicular to the plane of projection) and the conformation **1b**.



Conf. 2b; C_2 Sym.

Figure 3. Conformation **2b**. The C_2 axis connects the midpoints of the two NN bonds.

structures no minimum was found on the PES. This seems reasonable since the two lone pairs are too close together.

(g) Two possible structures with four hydrogen bonds exist. One conformation **4a**, has D_2 symmetry, the other, **4b**, has S_4 symmetry (see Figure 5). For both structures it holds that the NN bonds are perpendicular to the connection line between the middle points of the NN bonds. Calculations at the MP2 level with different basis sets show that both structures are saddle points. Conformation **4a** has one imaginary frequency and conformation **4b** has two imaginary frequencies.

In the paper of Cabaleiro–Lago and Ríos,[8] only the three dimer structures of the paper of Beu et al.[6] (**b** type dimers are absent) were investigated by the SCF, DFT/B3LYP and MP2 methods with the 6-31+G* and 6-311++G(2d,2p) basis sets: conformation **1a**, conformation **3a** and conformation **2a**. In agreement with our calculations, they found minima on the PES for the configurations **1a** and **3a**, while structure **2a** was determined to be a saddle point.

Stable Dimer Structures

All stable structures of hydrazine have two hydrogen bonds, yet for the conformations **3a**, **3b1**, and **3b2** additionally a third weak hydrogen bond exists (see the dotted lines in Figure 4. The existence of a third weak bond ("near contact") was already found for the conformation **3a** by Cabaleiro-Lago and Ríos.[8]

In Table 3 the binding energies are listed for all stable conformations and the two investigated saddle points. At each minimum found, the MP2/basis 1 and MP2/631++(2df,2p) energies were calculated. The geometry used for the CCSD(T)/basis 2 calculations were determined in the following way: Starting from the MP2/basis 1 optimized geometry parameters, all intermolecular parameters were optimized at the CCSD(T)/basis 2 level. At this level the length of the hydrogen bonds are longer between 0.014 and 0.043 Å with an average value of 0.029 Å than at the MP2/basis 1 level.

The energetic sequences of the MP2/basis 1, MP2/6-31++(2df,2p), and the CCSD(T)/basis 2 levels are the same. It is not changed by the inclusion of the counterpoise correction (CPC) of Boys and Bernadi.[22] The BSSE corrected binding energies for conformation **1a** and conformation **3a** calculated by Cabaleiro-Lago and Ríos at the MP2/6-311++-(2d,2p) level are 23.3 and 23.8 kJ mol^{-1} and at the MP4/6-31+G*//MP2/6-31G* level 20.6 and 21.6 kJ mol^{-1}, respectively. This is in good agreement with our results (see Table 3). With their semiempirical "systematic potential", Beu et al.[6] obtained 23.99 kJ mol^{-1} for conformation **1a** and 22.08 kJ mol^{-1} for conformation **3a**, which are qualitative good binding energies.

The energetic sequence correlates with the length of the hydrogen bonds. According to the BSSE corrected CCSD(T)/basis 2 results, the most stable conformations with two hydrogen bonds are **1a** and **1b**, having significantly shorter N···H bonds than the weakly bound conformation **2b** (see Table 4). The dipole moments vectors of the monomers of conformation **2b** are parallel and both are in the direction of the C_2 axis (see Figure 3). The dipole moment of the weakly bound conformation **2b** is larger than the vector sum of its monomers by a factor of 1.17. In contrast to this, the most stable conformation, **1b**, has a zero dipole moment; the monomer moments are antiparallel. So it is evident that an increased dipole moment relative to the vector sum of the monomer dipole moments is no good measure for the stability of the dimers. In conformation **2b** the dipole moment vectors have the optimal orientation in contrast to the most stable conformation **1b**; on this account no clear correlation between the orientation of the dimer dipoles and the binding energies exists. It is more realistic to consider the dipole moments of the NH_2 groups separately.

The conformation **3a** has the shortest N···H bond of all (N3···H4 in Figure 4 and in Table 4); additionally two weak N···H bonds exist; one of them has one of the largest N···H distances (see Table 4 and Figure 4). In this conformation, the highest deformation energy of all dimers with 1.073 kJ mol^{-1} exists, showing that three hydrogen bonds exist due only to bent bonds. It can be seen in Table 4 that the three listed $N_jH_i\cdots N_k$ values for **3a** are smaller than for each value of the other stable conformations. Conformation **3a** has the greatest charge transfer of all dimers (0.024 au on the MP2/6-31++G(2df,2p) level), yet this has no significant influence on the binding energy.

In the conformations **3b1** and **3b2**, an unusual bonding situation exists (see Figure 4): one H atom is involved in two hydrogen bonds. In both conformations their exists one strong bond and one weak bond with an H···N distance of about 2.63 Å. By the third hydrogen bond the total binding energy is enlarged and has for conformation **3b1** roughly the same value

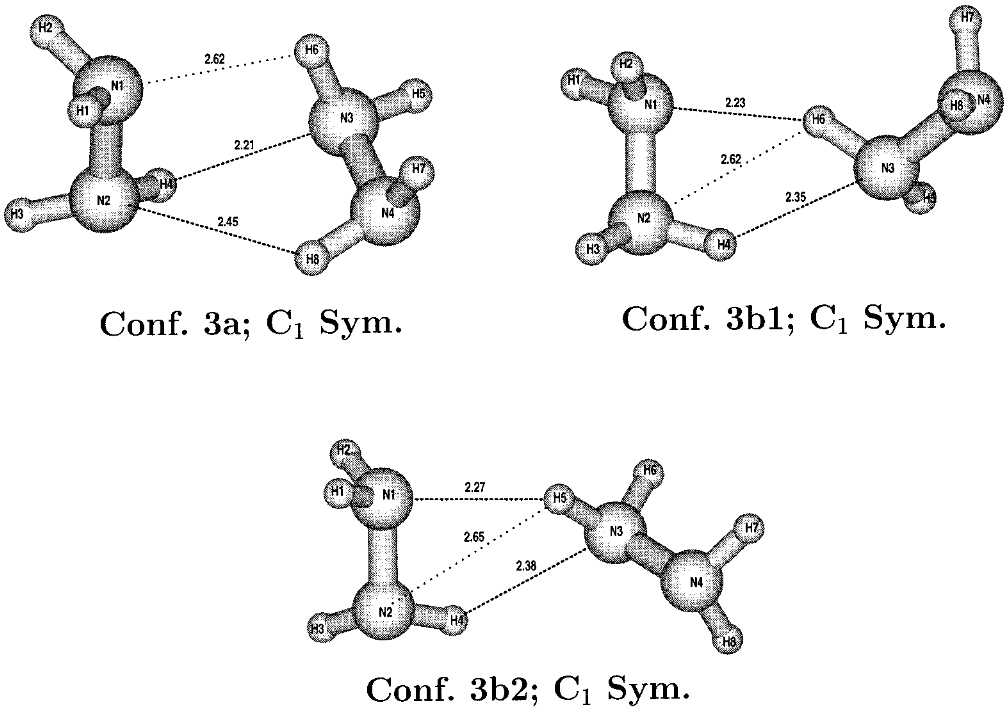


Figure 4. Conformations **3a**, **3b1**, and **3b2**.

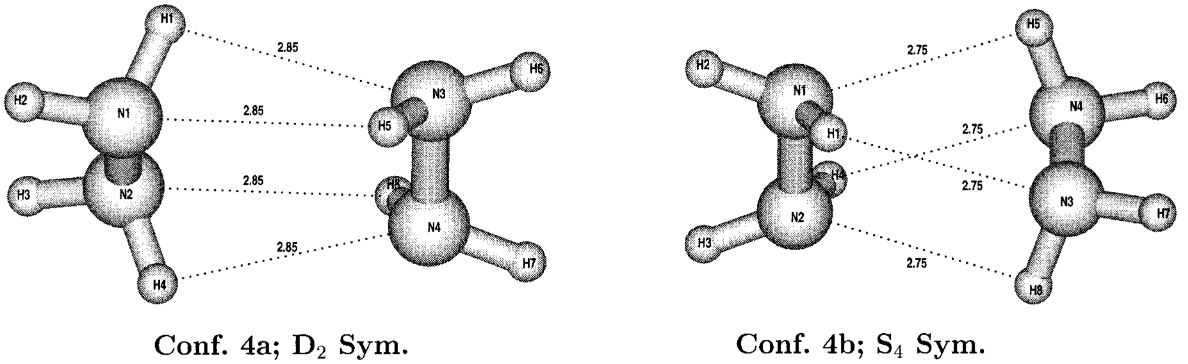


Figure 5. Saddle point structures **4a** and **4b**.

TABLE 3: Binding Energies of the Six Stable Conformations and of Two Saddle Points (Conformation 4a and 4b) for Dihydrazine in kJ mol^{-1}

conf	MP2/basis 1		MP2/6-31++(2df,2p)		CCSD(T)/basis 2		
		with CPC[a]		with CPC[a]		with CPC[a]	$\Delta H(298)$[b]
1a	−28.56	−22.80	−28.47	−23.41	−26.53	−23.77	−17.70
1b	−30.44	−24.95	−30.64	−25.63	−28.69	−26.03	−19.72
2b	−23.17	−18.32	−23.18	−18.99	−22.14	−19.62	−13.61
3a	−28.90	−22.97	−28.81	−24.61	−27.17	−24.13	−17.96
3b1	−24.21	−19.63	−24.51	−20.30	−23.02	−20.70	−14.40
3b2	−21.50	−17.27	−21.62	−17.56	−20.23	−17.89	−11.95
4a	−9.65	−6.53	−8.02	−6.61	−8.36	−7.77	
4b	−14.02	−10.78	−12.50	−11.68	−11.48	−10.94	

[a] With the counterpoise correction. [b] The enthalpy correction is calculated at the MP2/6-31++(2d,2p) level by use of harmonic frequencies.

as that of conformation **3a**. In conformation **3b2** the same situation exists yet the electrostatic interaction differs: while the two lone pairs, which do not participate in the hydrogen bonds, are far away from each other in conformation **3b1** (see Figure 4), they are closer in conformation **3b2**. Because of this the binding energy of conformation **3b2** is 3 kJ mol^{-1} smaller than for conformation **3b1** (see Table 3).

The intramolecular N−H distances increase for all hydrogen bonds with respect to the monomer structure. It is of interest that those hydrogen bonds, where the outer N−H bonds are involved, have shorter hydrogen bonds than the those where the inner N−H bonds are involved. The only exception is the inner H6 atom of conformation **3b1**, yet here we have the special case that the atom H6 is involved in two hydrogen bonds. The reason the outer H atoms participate in hydrogen bonds more readily and with greater bond strength in comparison to the inner H atoms is their higher Mulliken[23] atomic charges (see Table 4). High atomic charges also exist for the H atoms incorporated in the strong hydrogen bonds of conformation **1a** and **1b**. In the conformation **3b1** and **3b2**, one H atom is connected to two lone pairs of the other monomer; the Mulliken charges here are both very large at 0.167. So strong hydrogen bonds are

TABLE 4: CCSD(T)/Basis 2 Geometry Parameters of the Hydrogen Bonds of the Hydrazine Dimers[a] and Deformation Energies E_d (kJ mol^{-1}) (Bond Lengths in Å and Angles in Degrees)

conf	i,j,k,l	H_iN_j	type	$\angle H_iN_jN_l$	$H_i\cdots N_k$	$\angle N_jH_i\cdots N_k$	Δq[c]	E_d
a[b]	1,1,-,2	1.0191	o	106.68			0.111	
	2,1,-,2	1.0222	i	111.37			0.085	
1a	5,3,1,4	1.0242	o	105.78	2.239	149.07	0.158	0.700
	4,2,4,1	1.0242	o	105.78	2.239	149.07	0.158	
1b	1,1,3,2	1.0241	o	106.13	2.240	150.33	0.168	0.785
	8,4,2,3	1.0241	o	106.13	2.240	150.33	0.168	
2b	6,3,1,4	1.0242	i	109.79	2.365	145.94	0.127	1.065
	7,4,2,3	1.0242	i	109.79	2.365	145.94	0.127	
3a	4,2,3,1	1.0242	o	105.77	2.211	128.75	0.141	1.073
	8,4,2,3	1.0219	o	105.59	2.451	127.04	0.132	
	6,3,1,4	1.0237	i	110.59	2.623	110.49	0.129	
3b1	6,3,1,4	1.0251	i	110.75	2.234	137.24	0.167	0.477
	4,2,3,1	1.0228	o	106.13	2.348	131.47	0.145	
	6,3,2,4	1.0225	i	110.75	2.616	110.15		
3b2	5,3,1,4	1.0237	o	107.40	2.269	138.82	0.167	0.547
	4,2,3,1	1.0228	o	106.02	2.376	132.05	0.139	
	5,3,2,4	1.0237	o	107.40	2.650	110.21		
4a[d]	5,3,1,4	1.0135	o	110.73	2.852	94.37	0.112	1.943
4b[d]	5,4,1,3	1.0213	o	110.40	2.748	98.74	0.121	1.783

[a] The intramolecular parameters were optimized at the MP2/basis 1 level and all intermolecular parameters at the CCSD(T)/basis 2 level. [b] The momomer structure. [c] Mulliken charges,[23] MP2/basis 1 results. [d] Saddle points with four equivalent hydrogen bonds.

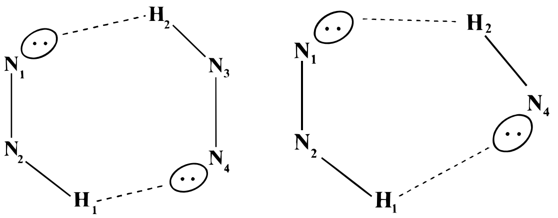


Figure 6. Cooperative effect enhancing the binding energies of the conformations **1a** and **1b** (see left diagram) and of the conformations **3a**, **3b1**, and **3b2** (right diagram).

strengthened by induced charges. In general, there is a clear relationship between the strength of a hydrogen bond and the Mulliken charges (see Table 4). There is also a qualitative correlation between the enlargement of the N−H bonds and the binding energies (see Tables 3 and 4). Further, with only one exception, the HNN angles decrease upon dimerization.

Stability by Means of Cooperative Effects

There exist two types of conformations:

(1) Conformations with cooperative effects: These are the stable conformations **1a**, **1b**, **3a**, **3b1**, and **3b2**. Their binding schemes are shown in Figure 6 (left conformation **1a**, **1b** and right conformation **3a**, **3b1**, and **3b2**). The negative charge of the atom N1 induces an additional dipole moment on the right monomer. By this, the negative charge of the N4 atom is enlarged. The N4 atom induces a dipole moment on the left monomer, by which the charge of the N1 atom is enlarged. So there exists a cyclic strengthening of the electrostatic interaction. This mechanism is important for most stable systems with two hydrogen bonds, e.g., the hydrogen bonds in the AT base pair of the DNA.

(2) Systems with noncooperative effects (see Figure 7): Here, the negative charge of the N1 atom induces an dipole on the right monomer by which the positive charge of the H2 atom is reduced and the N2···H2 bond is weakened. In the same way the negative charge of N2 weakens the N1···H1 bond. In principle, four systems of this kind exist for dihydrazine: conformation **2a**, **2b** (left diagram in Figure 7) and the two possible conformations mentioned above, where the two H atoms of two hydrogen bonds are located on only one N atom while on the other monomer the two lone pairs exist. From these four systems, only the weakly bound conformation **2b** is a minimum on the PES. Its small Mulliken charges (see Table 4) is evidence of a noncooperative effect for conformation **2b**.

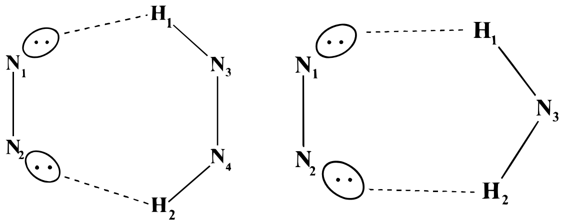


Figure 7. Noncooperative effect reducing the binding energies of the conformations **2a** and **2b** (see left diagram) and of two unstable conformations (right diagram).

Saddle Points

For the two saddle points **4a** and **4b** the dipole moments of the monomers are exactly antiparallel and are in the direction of the connection line of the midpoints of the two N−N bonds (see Figure 5). All four lone pairs are close together. This is surely the main reason no stable dimer structure with four hydrogen bonds exists. Both conformations have large deformation energies of the monomers (see Table 4). Further, the long hydrogen bridges, the short HN distances and the small Mulliken Charges indicate weakly bonded systems.

At room temperature, transition between any two of the 6 stable conformations is only possible if the two conformations both belong either to class **a** (conformation **1a**, **3a**) or both to class **b** (conformation **1b**, **2b**, **3b1**, **3b2**). For each transition, at least one transition state exists. Since most conformations have two equivalent structures, a transformation between them is also possible. Three examples are given here:

(1) If the left monomer of conformation **1a** (see Figure 2) is turned clockwise on the N1−N2 axis, and the right one clockwise on the N3−N4 axis, the molecule passes through the saddle point **2a** and proceeds to the other equivalent structure, **1a**.

(2) If the left monomer of conformation **1a** (see Figure 2) is turned clockwise, and the right monomer counterclockwise by about 120°, the other equivalent structure of conformation **1a** is obtained; the saddle point is conformation **4a** (see Figure 5).

(3) Conformation **4b** is a 2-fold transition state between two equivalent structures of conformation **3b2**.

In the following, more interesting rearrangement reactions are investigated. Since the PES's near the corresponding saddle points are extremely flat, their location was laborious. Therefore, they were only searched for at the MP2/basis 1 level. The investigated rearrangement reactions were

(I) Between conformations **2b** and **1b**. The calculated saddle point has only one hydrogen bond and is shown in Figure 8. Hydrogen bonds N1···H6 and N2···H7 in Figure 8 correspond to conformation **2b** and hydrogen bonds N1···H5 and N4···H4 correspond to conformation **1b**. The counterpoise corrected CCSD(T)/basis 2//MP2/basis 1 value for the barrier height of this reaction is 6.72 kJ mol^{-1}. This relatively high barrier results from both hydrogen bonds of conformation **2b** being broken off in this rearrangement reaction.

(II) Between conformations **3b2** and **1b**. The corresponding transition state, also with one hydrogen bond, is shown in Figure 8. Here H−bonds between N3···H1 and N1···H8 correspond to conformation **3b2**, and between N3···H1 and N2···H8 correspond to conformation **1b**. The value of the barrier height

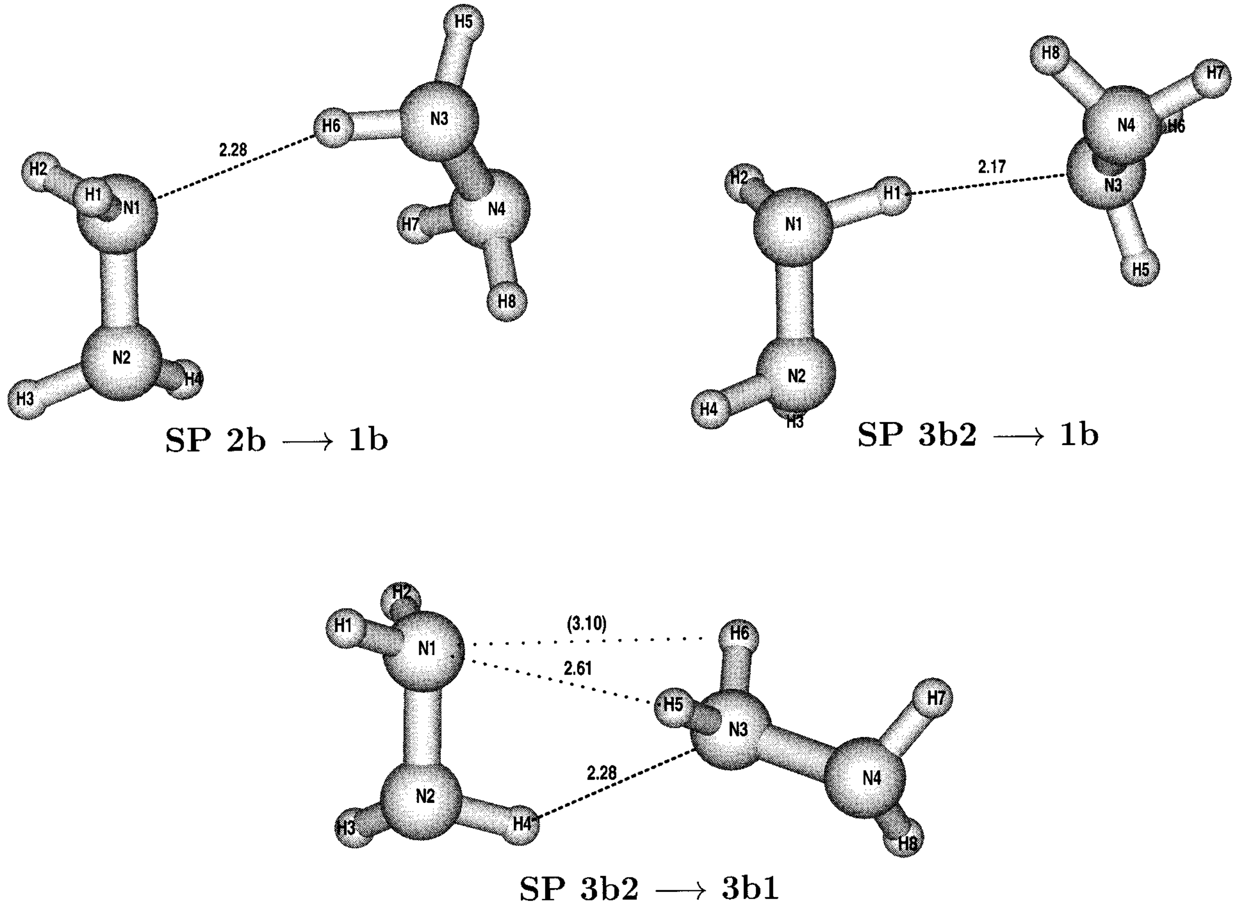


Figure 8. Saddle points of the rearrangement reactions conformation **2b** → conformation **1b**, conformation **3b2** → conformation **1b**, and conformation **3b2** → conformation **3b1**.

on the CCSD(T)/basis 2//MP2/basis 1 level is 5.95 kJ mol^{-1}. Two reaction paths exist (see Figure 8): the right monomer can turn clockwise or counterclockwise around the N3⋯H1 bond.

(III) Between conformations **3b2** and **3b1**. The corresponding barrier height, again from CCSD(T)/basis 1//MP2/basis 1, is small (0.94 kJ mol^{-1}), since, in addition to the normal N3⋯H4 bond, two weak hydrogen bonds, (see Figure 8) N1⋯H5 (corresponds to conformation **3b2**) and N1⋯H6 (corresponds to conformation **3b1**) exist. This suggests that conformation **3b2** is not thermodynamically stable at room temperature.

Frequency Shifts of the Antisymmetric Wagging and the NH-Stretching Modes

Frequency shifts for the antisymmetric wagging, the NN stretching and the NH-stretching frequencies of the stable structures of each hydrazine cluster with two to four molecules were already reported by Cabaleiro-Lago and Ríos.[8] For the dimers, they calculated only the conformation **1a** and **3a** with the MP2/6-31+G* method. In this work, the modes are determined with larger basis sets for all six dimer structures. We will see that the application of larger basis sets as well as the inclusion of all dimers are necessary for the interpretation of the antisymmetric wagging spectrum.

In Table 5 the calculated harmonic frequency shifts of the antisymmetric wagging mode are summarized. They were calculated at the MP2/basis 1, the B3LYP/basis 1, the MP2/6-31++G(2d,2p) and the MP2/6-31++G(2df,2p) level. From Beu et al.,[7] the experimental frequency of the antisymmetric NH_2 wagging mode is ν_{12} = 937 cm^{-1}. The measured photodissoziation spectrum of Beu et al.[7] for dihydrazine cannot be compared with our calculations since the abundances of the six stable conformeres are not known. What can be seen from the measured spectrum is the following (numbers in parentheses indicate the shift from the monomer value): nonvanishing intensities are between 945 (10) and 1010 (75) cm^{-1} with two very pronounced peaks at 979.7 (42.7) and 985.6 (48.6) cm^{-1} and a smaller peak at 1002 (64) cm^{-1}. A minimum exists at about 995 (58) cm^{-1}. Looking at the frequency shift of the MP2/basis 1 calculations (see Table 5) it can be seen, that most shifts are too small.

TABLE 5: Frequency Shifts of the Antisymmetric Wagging Vibrations (cm^{-1})[a]

conf	sym	MP2/basis 1	B3LYP/basis 1	MP2/basis 3[c]	MP2/basis 4[d]	exp[b]
1a	C_2	47.5 (143.6)	46.5 (162.1)	46.4 (156.8)	49.1 (155.4)	48.6
		44.4 (57.6)	48.3 (63.4)	47.4 (67.6)	52.1 (83.5)	48.6
1b	C_i	30.6 (0.0)	43.6 (0.0)	41.8 (0.0)	46.4 (0.0)	
		51.3 (189.3)	63.1 (201.8)	61.9 (206.8)	66.1 (218.6)	64.
2b	C_2	9.6 (28.2)	15.7 (46.4)	10.4 (29.5)	12.3 (33.2)	
		36.3 (169.8)	43.5 (163.3)	36.7 (197.2)	39.6 (204.4)	42.7
3a	C_1	36.8 (124.7)	37.9 (126.8)	37.2 (140.1)	40.2 (148.5)	42.7
		44.1 (88.7)	48.2 (97.1)	48.8 (98.6)	52.7 (105.7)	48.6
3b1	C_1	23.1 (79.54)	28.3 (81.4)	26.6 (81.7)	30.7 (68.8)	
		32.3 (166.2)	35.2 (186.3)	35.8 (184.4)	39.0 (215.6)	42.7
3b2	C_1	27.1 (119.2)	28.3 (147.4)	29.2 (132.6)	31.0 (143.0)	
		33.1 (94.2)	33.0 (92.8)	36.5 (104.0)	41.5 (111.1)	42.7

[a] The IR intensities (km mol^{-1}) are added in parentheses. [b] Reference 7. [c] Basis 3 is the 6-31++G(2d,2p) basis. [d] Basis 4 is the 6-31++G(2df,2p) basis.

The B3LYP/basis 1 results are better. For the first peak of the photodissoziation spectrum the B3LYP/basis 1 calculations yield shifts of 37.9 and 43.5 cm^{-1} (conformation **3a** and **2b**),

TABLE 6: Frequency Shifts of the NH-Stretching Vibrations ν_1 and ν_9 of Hydrazine (cm^{-1}) Calculated with the MP2/631++(2df,2p) Method[a]

conf	shifts of ν_1		shifts of ν_9	
1a	−46.7 (165.9)		−48.2 (126.9)	
1b	−46.7 (188.6)		−51.3 (131.8)	
2b	−27.4 (47.8)		−19.8 (37.6)	
3a	−46.8 (41.3)	−47.5 (30.6)	−33.3 (28.8)	
3b1	−50.2 (28.4)	−25.7 (45.2)	−32.5 (38.2)	−15.9 (35.4)
3b2	−44.9 (27.9)	−20.2 (35.8)	−51.7 (40.5)	−26.6 (57.8)

[a] The IR intensities (km mol^{-1}) are added in parantheses.

respectively. For the second peak at 48.7 cm^{-1}, two lines from conformation **1a** at 46.5 and 48.3 cm^{-1} and one from conformation **3a** at 48.2 cm^{-1} exist. For the last peak we get a line at 63.1 cm^{-1} from conformation **1b**. Because there are no lines between 48.3 and 63.1 cm^{-1} the minimum of the photodissociation curve near 58 cm^{-1} is reproduced.

The MP2/6-31++G(2d,2p) results are similar to those from B3LYP/basis 1, yet the coordination to the peak at 42.7 cm^{-1} is poor. Since f functions are of some importance for the antisymmetric wagging mode, they were added to in the basis set. The results for dihydrazine with this basis set is shown in Table 5. Here, for those frequencies which correspond to the experimental frequencies 48.6 and 64 cm^{-1}, better values for the harmonic frequencies were calculated. The four calculated lines of conformation **2b** (39.6 cm^{-1}), conformation **3a** (40.2 cm^{-1}), conformation **3b1** (39.0 cm^{-1}) and conformation **3b2** (41.5 cm^{-1}) are close together. All of them have large intensities. Therefore, it is expected that the spectrum has an absolute maximum near 40 cm^{-1}; this is in agreement with the photodissoziation spectrum of cold hydrazine dimers measured by Beu et al.[7] If one takes into account that the superposition of the broadened lines near 40 and 50 cm^{-1} shifts their maxima together, then excellent qualitative agreement between the calculated frequencies and the measured spectrum exists.

The shifts of the hydrogen stretching vibrations are listed in Table 6. No experimental information is available. The four NH-stretching modes of hydrazine are grouped by pairs, corresponding to the symmetric and asymmetric vibrations. The calculated shifts are given from the asymmetric stretching mode ν_1 and the symmetric stretching mode ν_9 of hydrazine. A clear correspondence can be seen between the lengthening of the NH distances relative to the monomer (see Table 4), the strength of the hydrogen bonds and the red shift of the NH-stretching modes.

Conclusions

The structures of mono− and dihydrazine were determined at different levels of theory. The CCSD(T)/vqz values of the two rotation barriers of hydrazine are 10.53 and 34.54 kJ mol^{-1}.

By a systematic procedure all stable conformations of dihydrazine were found. In conformation **1a**, **1b**, and **2a** only two hydrogen bonds exist. In conformation **3a**, one additional weak hydrogen bond exists. For both conformations **3b1** and **3b2**, one H atom is incorporated in a normal hydrogen bond, and this H atom has an additional strong electrostatic interaction with another nearby lone pair 2.62 Å away. The attraction between H atoms and lone pairs as well as the repulsion of the lone pairs with each other are important for understanding the binding energies of the hydrazine cluster.

Cooperative effects stabilize the conformations **1a**, **1b**, **3a**, **3b1**, and **3b2** in contrast to conformation **2b**. A clear relation between the orientation of the dipoles of the monomers and the binding energies of the stable conformations does not exist.

There is a clear correspondence between the strength of the hydrogen bonds, the length of the hydrogen bonds, the lengthening of the NH distances, the blue shifts of the antisymmetric wagging modes, the red shifts of the NH-stretching modes and the increase in the partial charges of the H atoms.

For the interpretation of the measured photodissociation spectrum of the antisymmetric wagging mode of dihydrazine the knowledge of all stable conformations is necessary. The calculated shifts of the antisymmetric wagging mode with the MP2/6-31++G(2df,2p) are in a good qualitative agreement with the measured spectrum.

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