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The Trimer Structures of Hydrazine

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Twenty-eight structures of the hydrazine trimer have been investigated. Two new types of stable conformations were found. Geometry optimizations were carried out by B3LYP and MP2 methods with the aug-cc-pVDZ basis set. Two stable trimer structures were obtained with one monomer having a saddle-point structure. Three rearrangement reactions were investigated, and several tunneling processes were discussed. The frequency shifts of the antisymmetric wagging and the NH stretching modes were calculated with the MP2/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ methods. With one fitted parameter, the calculated wagging spectrum is in a good accordance with the experimental one.

Introduction

Clusters of stable molecules are usually bound by van der Waals forces or hydrogen bonds. Their properties are often different from those of the two limiting cases, the dimer and the solid crystal. By examining these properties with increasing cluster size, one can acquire valuable information, for example, about the change of the structural parameters and the shifts of spectral lines. Encouraged by the experimental work of Buck et al.,[1−4] we have recently calculated the six structures of the hydrazine dimer and have theoretically investigated the shift of the antisymmetric NH_2 wagging vibration with respect to the monomer.[6] Beu et al.,[4,5,7] making use of their intermolecular potential model, determined the binding energies and the wavenumbers of the antisymmetric NH_2 wagging modes for three dimer and six trimer structures of hydrazine. Up to now, there has only been one ab initio study by Cabalerio-Lago and Ríos[8] on the interactions in hydrazine clusters of one to four molecules. They investigated two stable conformations and one saddle point for the dimer; only four minima could be found for the hydrazine trimer. They state that other trimer structures might exist. It is our intention to obtain as many of the most stable trimer conformations as possible because reliable information about the properties of $(N_2H_4)_3$ can only be achieved with a large number of these trimer structures.

Normally only clusters with more than two molecules exhibit cooperative effects.[9] Hydrazine has two polar NH_2 groups, which can act both as a proton acceptor and as a proton donor. Therefore, the situation is here more complex. In the case of hydrazine, already the dimers show both cooperative and noncooperative effects.[6]

Because the hydrazine molecule has two lone pairs, four H atoms, and two conformations, a large number of possible trimer structures is expected. For the dimers, all six stable structures were found by a systematic search.[6] That does not seem to be possible for the trimers of hydrazine. The determination of all particularly stable trimer conformations is a challenge for the global geometry optimization (see Hartke[10]).

1. Computational Details

Geometry optimization of all intermolecular and intramolecular parameters was performed for all analyzed conformations of the hydrazine trimer at the MP2/basis 1 and B3LYP/basis 1 level. Here, basis 1 is the aug-cc-pVDZ basis of Dunning,[11] exclusive the diffuse p-functions at the H atoms. With this basis, the same energetic sequence of the six dimer conformations was obtained as in more extended calculations (CCSD(T)/avtz); also, the monomer geometry was in excellent agreement with the CCSD(T)/avtz results. B3LYP is a HF/DFT hybrid functional constructed from Becke's three-parameter exchange functional[12] and the Lee−Yang−Parr correlation functional.[13] All MP2[14] and B3LYP calculations were carried out with the Gaussian 98 program.[15]

2. The Search for Stable Trimer Structures

Hydrazine is a chiral molecule. Therefore, two enantiomer structures, **A** and **B**, exist (see Figure 1). Hydrazine has two groups of H atoms: the inner H atoms, i (in Figure 1, the atoms H2 and H3), and the two outer H atoms, o (H1 and H4). The inner and outer H atoms have different Mulliken atomic charges.[17] According to MP2/basis 1 calculations, the inner H atoms have a charge of 0.085 au and the outer ones 0.111 au. Consequently, the outer H atoms are expected to be involved in hydrogen bonds more often. For hydrazine, the barriers of inversion of a NH_2 group and to rotation about the NN axis are 24.39 and 10.53 kJ mol^{-1}, respectively, on the CCSD(T)/vqz level. These barriers are alike or smaller than the inversion barrier of NH_3 (21.14 kJ mol^{-1} from extrapolated coupled-cluster pair energies[16]); tunneling therefore takes place between the two structures **A** and **B** of hydrazine.

Because there are two enantiomeric structures **A** and **B**, the following classification appears to be useful: (1) those structures resulting from three equal monomer structures, that is, **AAA** or **BBB**, which are denoted in the following with **A** (see Figure 3) and (2) those structures resulting from different monomer structures, that is, **AAB** or **ABB**, which are denoted in the following with **B** (see Figure 4). It is noted that the **AAB** and the **ABA** structures are not identical at least for noncyclic conformations. Consequently, a larger number of conformations of the **B** type will exist. So far, only these two types of structures have been known. A third group of stable conformations are those structures for which one monomer has a saddle point structure (see in Figure 5, conformations **C1** and **C2**). A fourth group of trimer structures, which result from the combination of two dimer structures, is listed in Figure 2. If one takes into

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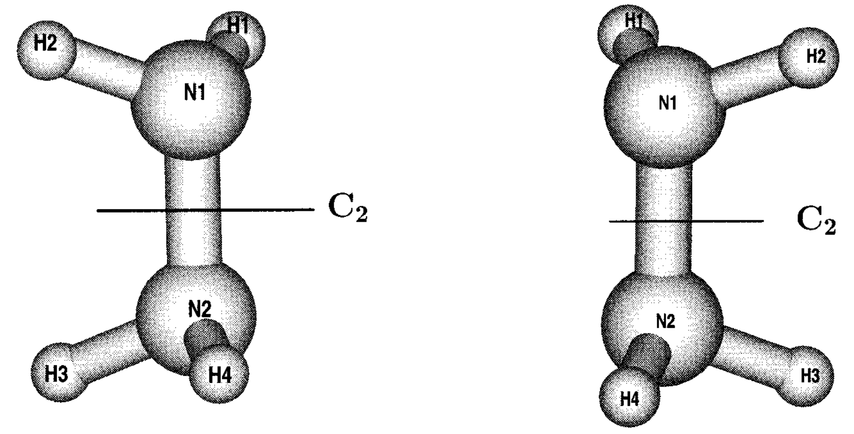
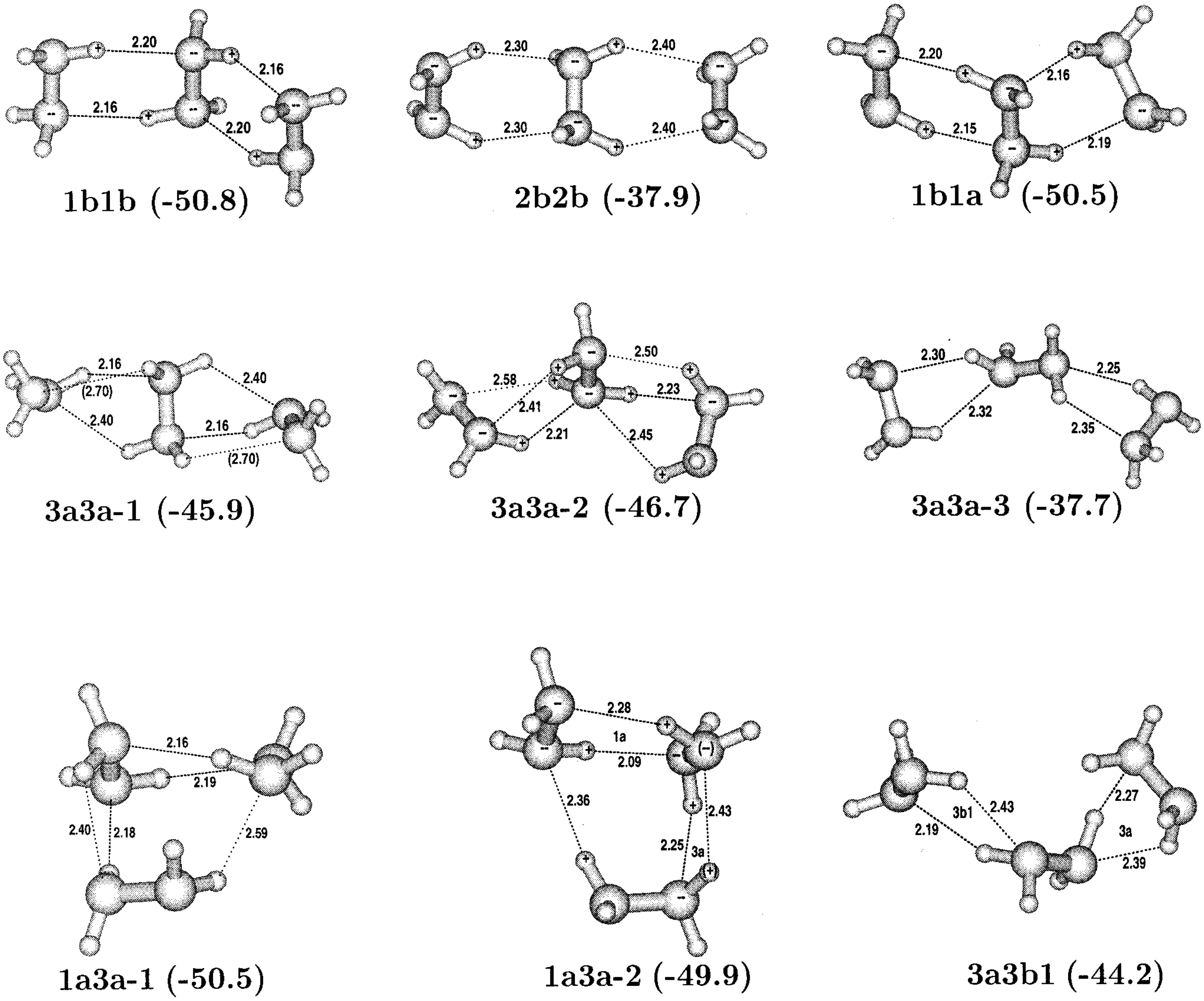


Struct. A; C_2 sym. Struct. B; C_2 sym.

Figure 1. The two equivalent conformations of hydrazine.



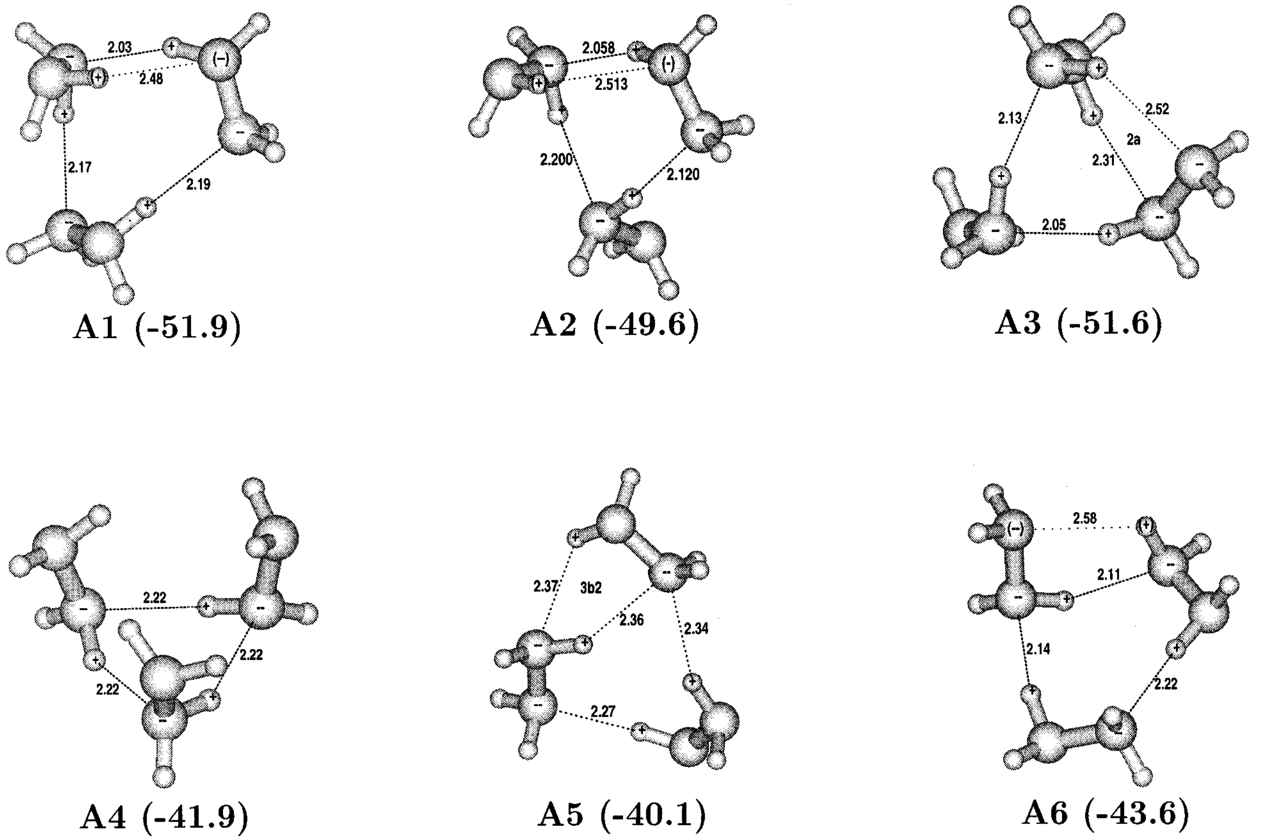
1b1b (-50.8) 2b2b (-37.9) 1b1a (-50.5)

3a3a-1 (-45.9) 3a3a-2 (-46.7) 3a3a-3 (-37.7)

1a3a-1 (-50.5) 1a3a-2 (-49.9) 3a3b1 (-44.2)

Figure 2. The trimer conformations resulting from the combination of two dimer conformations. Distances are given in Å. The CP-corrected MP2/basis 1 binding energies in kJ mol^{-1} are added in parentheses.

consideration that six dimer structures exist, then there are 6 × (6+1)/2 = 21 combinations. Not all of these combinations correspond to stable conformations. For instance, the hypothetical structure 1b2b is only a "shoulder" on the PES (potential energy surface); after 120 iterations of the geometry optimization procedure, it converges to the most stable conformation **B1** (see Figure 3). On the other hand, there are some combinations, that is, **3a3a** or **1a3a** (see Figure 2), for which several stable conformers exist. In case of conformation **1a3a**, up to five different structures exist. It is concluded from this that the total



A1 (-51.9) A2 (-49.6) A3 (-51.6)

A4 (-41.9) A5 (-40.1) A6 (-43.6)

Figure 3. The cyclic trimer conformations resulting from equal hydrazine monomer conformations. Distances are given in Å. The CP-corrected MP2/basis 1 binding energies in kJ mol^{-1} are added in parentheses.

number of structures formed by the combination of two dimer structures is about 30. For each dimer and trimer structure, an enantiomer structure exists.

Two strategies were used for finding the trimer structures: (1) A special structure was created and optimized. This strategy was sufficient to find all dimer structures. Because a thorough search for all trimer structures is too tedious, a second strategy is necessary. Otherwise, one might only obtain a special selection of conformations, and many of the most stable conformers are missing. (2) The stable structures were searched by a statistical procedure. Here, plausible structures of several types were generated in a first step; for instance, the center of mass of the three monomers forming a triangle and three orientation angles were randomly chosen. For another variant, the angle between two connection lines between the centers of mass of the hydrazine monomers was chosen to be 170°, and once again three orientation angles were randomly selected. Fifty-five structures of this kind were generated and initially optimized with the MP2/6-31G(d) method. Often a serious problem appeared: in many cases, the geometry optimization ended up in structures that are "near" a saddle-point structure on the PES. For 14 such structures, 100 additional geometry iteration steps did not considerably change the situation either.

With the statistical search, we obtained 20 new structures. Five new structures belong to the type that results from the combination of two dimer structures. The total number of this type was estimated to be about 30. We therefore obtained $(30/5) \times 20 = 120$ for the total number of trimer structures with this rough estimate.

Cabaleiro-Lago and Ríos[8] only investigated four trimer structures of the **A** type (three of them were taken over from the paper of Beu et al.[5]) by the SCF, B3LYP, and MP2 methods with a 6-31+G* basis set. In the paper of Beu and Buck,[4] three structures of the **B** type are also included. It is identical to the most stable structure **B1** (see Figure 4).

3. The Stable Trimer Structures

In Table 1, the binding energies and enthalpies of all investigated trimer structures are listed. They are determined at the B3LYP/basis 1 and further at the MP2/basis 1 level with and without the counterpoise correction (CPC) of Boys and Bernardi.[18] The present author[6] has shown that for the six stable dimer structures, the CP-corrected MP2/basis 1 results for the binding energies are only 1.03 ± 0.27 kJ mol^{-1} smaller than the corresponding CCSD(T)/avtz results. So it is also expected for the trimers that the energies calculated with the CP-corrected MP2/basis 1 are too small by roughly 2 kJ mol^{-1}. Taking this into account, the binding energies calculated with the B3LYP/basis 1 method are expected to be too small by about 7 kJ mol^{-1} on the average. So it is plausible that more optimized structures exist at the MP2/basis 1 level (**A5**, **B6**, **C1**) than at the B3LYP level.

The enthalpy values with respect to the monomers are listed in Table 1. Hereby, the harmonic approximation is used. The enthalpy is obtained from

$$\Delta H = E_{\mathrm{b}} + \Delta E_{\mathrm{vib}}^{\mathrm{T}} - 8RT \quad \text{with} \quad E_{\mathrm{vib}}^{\mathrm{T}} = \sum_i h\nu_i/2 + \sum_i h\nu_i/(\mathrm{e}^{h\nu_i/(RT)} - 1)$$

whereby E_{b} is the CP-corrected binding energy from Table 1, the ν_i parameters are the harmonic frequencies, and $\Delta E_{\mathrm{vib}}^{\mathrm{T}}$ is the change in the vibrational energies between the trimer and the three monomers. The energetic sequence of E_{b} and ΔH is the same.

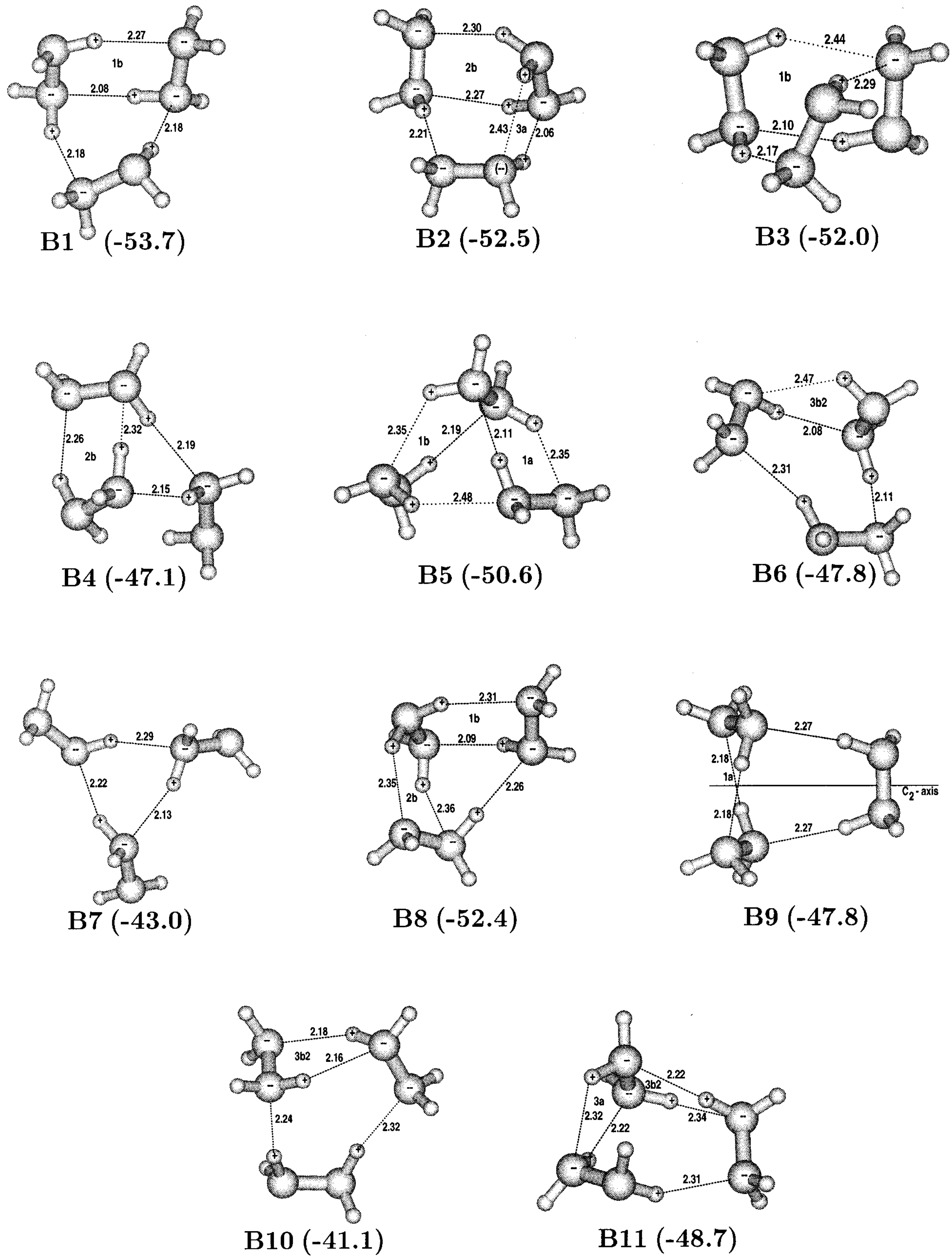
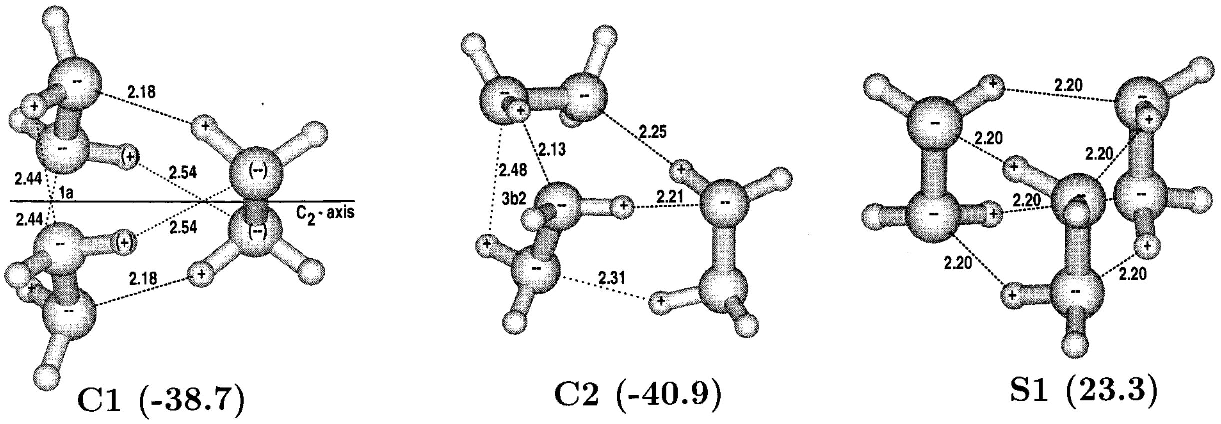


Figure 4. The cyclic trimer conformations resulting from different hydrazine monomer structures. Distances are given in Å. The CP-corrected MP2/basis 1 binding energies in kJ mol^{-1} are added in parentheses.

The first nine structures of Table 1 are the structures that are composed of two dimer structures (see Figure 2). Because the structure **1b** is the most stable dimer structure, it is plausible that the structure **1b1b** is one of the most stable trimer structures. In contrast to this, conformation **2b2b** was calculated to be the structure with the lowest binding energy. Here, one has the same situation as with the dimer structures **1b** and **2b**: In the case of conformation **1b1b**, the components of the dipole moment in the plane of projection (see Figure 2) are zero. In contrast to this, a large dipole moment (7.95 D at the MP2/basis 1 level)



C1 (-38.7) **C2 (-40.9)** **S1 (23.3)**

Figure 5. The two trimer conformations **C1** and **C2** with one monomer having a trans saddle-point structure. **S1** is a saddle-point structure in which all monomers have a cis saddle-point structure. Distances are given in Å. The CP-corrected MP2/basis 1 binding energies in kJ mol^{-1} are added in parentheses.

TABLE 1: Binding Energies, Deformation Energies (E_d), and Enthalpies of the Stable Conformations for Trihydrazine in kJ mol^{-1}

	N		B3LYP/	MP2/basis 1			
conf	o[a]	i[a]	basis 1		with CPC[b]	E_d	Δ*H* (298 K)[c]
1b1b	4	0	−45.53	−62.18	−50.75	4.48	−57.76
2b2b	0	4	−31.26	−47.82	−37.90	1.98	−45.28
1b1a	4	0	−45.12	−62.89	−50.47	1.30	−57.57
3a3a-1	4	0	−36.91	−58.00	−45.90	2.38	−53.18
3a3a-2	4	2	−37.37	−58.30	−46.68	2.37	−53.95
3a3a-3	3	1	−33.63	−46.72	−37.66	0.53	−45.28
1a3a-1	3	2	−41.85	−63.50	−50.50	2.25	−57.50
1a3a-2	4	1	−42.60	−63.41	−49.86	2.84	−57.38
3a3b1	3	2	−39.85	−61.38	−48.68	2.08	−55.75
A1	3	1	−46.32	−65.55	−51.86	2.84	−58.67
A2	3	1	−44.65	−61.92	−49.62	2.38	−56.69
A3	2	1	−44.80	−65.53	−51.58	6.65	−58.91
A4	0	3	−38.38	−52.42	−41.92	1.27	−49.53
A5	2	2		−50.52	−40.30	1.10	−47.53
A6	3	1	−41.38	−55.82	−43.64	1.13	−50.93
B1	3	1	−46.89	−66.88	−53.67	2.08	−60.66
B2	3	2	−45.08	−65.96	−52.53	3.81	−59.27
B3	3	1	−45.47	−65.32	−51.98	4.02	−59.16
B4	1	3	−39.69	−59.42	−47.14	4.34	−54.33
B5	4	1	−42.32	−63.86	−50.58	2.84	−58.00
B6	4	0		−61.20	−47.86	2.38	−55.51
B7	0	3	−38.85	−53.90	−42.97	1.90	−50.57
B8	3	2	−42.99	−65.63	−52.43	4.16	−59.35
B9	2	2	−41.93	−60.58	−47.78	1.61	−54.64
B10	2	2	−36.03	−52.75	−41.14	1.77	−48.31
B11	3	2	−34.41	−57.87	−44.19	4.01	−51.53
C1	4	0		−52.32	−38.65	13.98	−47.25
C2	3	0	−33.68	−54.57	−40.94	12.62	−48.83
S1			21.22	−6.86	23.33	109.66	

[a] Number of inner (i) and outer (o) H-atoms involved in the hydrogen bonds. [b] Including counterpoise correction. [c] The enthalpy correction is calculated at the MP2/basis 1 level by use of harmonic frequencies.

in the direction of the C_2 axis exists for conformation **2b2b**; here, the dipole moment is larger than the vector sum of its monomers by a factor of 1.26. As in the case of the dimers, an increased dipole moment relative to the vector sum of the monomers is not a good measure for the stability of the trimers.

In Table 1, the number of inner and outer hydrogen atoms involved in the hydrogen bonds are also listed. As expected (see section 2), the number of those outer H atoms, *N*(o) = 77, is significantly larger than the number of the inner H atoms, *N*(i) = 40. Only hydrogen bonds with a bond length up to 2.6 Å are considered here.

One remarkable result is the following: nearly all trimer structures contain at least one dimer structure. There are only three exceptions: conformations **A3, A4**, and **B7**.

Those trimer structures that contain only the weakly bonded dimer structures **2b** and **3b2** are generally also weakly bonded (see in Figures 2−5 the conformations **2b2b**, **B4**, **B6**, **B10**, and **C2**); in contrast to this, the more stable dimer structures **1a** and **3a** are included in more conformations (conformations **3a3a-1**, **3a3a-2**, **3a3a-3**, **1a3a-1**, **1a3a-2**, **A1**, **A2**, **A5**, **B9**, and **C1**). The conformations **1b1b**, **B1**, **B3**, and **B8**, which contain the most stable dimer conformation **1b**, belong to the most stable trimer structures.

In Figure 3, the structures **A1** and **A3** were taken from Beu et al.[5] together with the most stable structure **B1** (see Beu and Buck[4]). The second trimer structure of Beu et al.[5] was also taken in principle, yet the geometry optimization procedure turned it into structure **A2**. In this work, four hydrogen bonds were found for conformation **B1**, while Beu and Buck only drew three hydrogen bonds in their figure.

The first three structures of Cabaleiro-Lago and Ríos[8] are the enantiomers to those of Beu et al.,[5] while their fourth structure is the enantiomer of the conformation **A4** of this work. Conformation **A4** has the smallest harmonic frequency, ν_1 = 6.5 cm^{-1}, of all trimers (see Table 3).

The trimer structures of Cabaleiro-Lago and Ríos[8] are not at all typical for the trimers of hydrazine: (1) They are all of the type **A**, whereas in our results, only 12 of 27 stable structures are of this type. (2) In their Figure 4, only three hydrogen bonds were drawn, whereas we found only two conformations of that type altogether.

Conformations **A5** and **B3** are the only conformations of all calculated dimers and trimers in which only one N atom is incorporated in two hydrogen bonds.

The structures **C1** and **C2** (see Figure 5) both have one monomer with a trans saddle-point structure. The deformation energies therefore have to be higher than the trans barrier of the monomer, which is 10.7 kJ mol^{-1} at the MP2/basis 1 level. For the conformations **C1** and **C2**, they are 13.98 and 12.72 kJ mol^{-1}, respectively (see Table 1). The conformation **C1** is only a shoulder structure at the B3LYP level; here, the conformation **B9** is the corresponding minimum. On the other hand at 71.4 cm^{-1}, conformation **C1** has by far the greatest value for the lowest harmonic frequency (see Table 3) at the MP2/basis 1 level. This indicates a stable conformation.

The conformation **S1** is a saddle-point structure with three imaginary frequencies. All of its three monomers have cis saddle-point structures (see Dyczmons[6]). If one takes these three monomer saddle-point structures as a reference, then the binding energy of this structure **S1** amounts to 97.46 kJ mol^{-1} at the CP-corrected MP2/basis 1. This is nearly twice as large as for the most stable trimer conformations.

All stable trimer structures of hydrazine have at least three hydrogen bonds each. The average number of hydrogen bonds is 2.00 for the dimers and 4.37 for the trimers (only hydrogen bonds up to 2.6 Å are taken into account here). At the CP-corrected MP2/basis 1 level, the average binding energy of all investigated stable trimer structures $E_{\mathrm{av}}(\mathrm{trimer}) = 46.8$ kJ mol^{-1} and the corresponding dimer binding energy is $E_{\mathrm{av}}(\mathrm{dimer}) = 21.75$ kJ mol^{-1}. The ratio $E_{\mathrm{av}}(\mathrm{trimer})/E_{\mathrm{av}}(\mathrm{dimer}) = 2.15$ means that the cooperative effects are enhanced with increasing cluster size.

4. Stability by means of Cooperative Effects

Two types of conformations exist.

(1) Trimer Conformations with Cooperative Effects. The most simple situation for a cooperative system is the following: each of the three monomers is attached by the other two monomers in such a way that a chain of three dipoles are formed that enhance each other. This situation exists for most cyclic structures. We can see this in all cyclic conformations that contain two dimer structures (conformation **1a3a-1, 1a3a-2, B2, B5**, and **B8**). The sum of their CP-corrected binding energies is $E_1 = 255.9$ kJ mol^{-1}. On the other hand, if one adds up the CP-corrected energies of all of the dimers (see ref 6) incorporated in those five cyclic trimers, one will only obtain $E_2 = 229.8$ kJ mol^{-1}. The ratio is $E_1/E_2 = 1.11$. This cooperative effect is in full agreement with that of linear $(\mathrm{HCN})_n$ (see Buckingham[22]). Here, the formation of each hydrogen bond increases both the polarity of the NH bond and the basicity of the N atoms. The dissociation energy of $(\mathrm{HCN})_3$ to form monomers here is also 10% higher than that of two dimers.

In conformation **1b1b** and **1b1a**, an effective cooperative effect also exists on the periphery of these trimers, whereby four dipoles are included in a chain (see Figure 2). However, these trimers also have an anticooperative effect for the monomer in the middle in which the two negative charges of the N atoms are increased due to the cooperative effect of the periphery.

The most stable conformation **B1** has two efficient cooperative effects: on one hand, the cooperative effect of the conformation **1b** and furthermore a chain with three dipoles that enhance each other (see lower part of **B1** in Figure 4). In principle, the same situation also exists for the conformation **B3**.

(2) Systems with a Noncooperative Effect. All noncyclic conformations (**1b1b, 2b2b, 1b1a, 3a3a-1, 3a3a-2, 3a3a-3**, and **3a3b1**) have a noncooperative effect. This can easily be seen. Once again, we denote the sum of the energies of all of the dimer structures incorporated in these noncyclic structures with E_2 and the sum of the corresponding trimer energies of Table 1 with E_1. The ratio $E_1/E_2 = 0.9905$ shows the noncooperativity of these noncyclic structures. A noncooperative effects also exists for a trimer conformation if the basicity of the two N atoms of at least one of its monomers is increased because of hydrogen bonding. This situation occurs three times for conformation **2b2b**. For most of the listed trimer structures, this noncooperative effect occurs once. For the conformations **3a3a-3** and **3a3b1**, this effect occurs in such a way that one of its $\mathrm{NH_2}$ groups is only connected with a second monomer, while its other $\mathrm{NH_2}$ group is only connected with the third monomer. Such a situation is unfavorable for the binding energy.

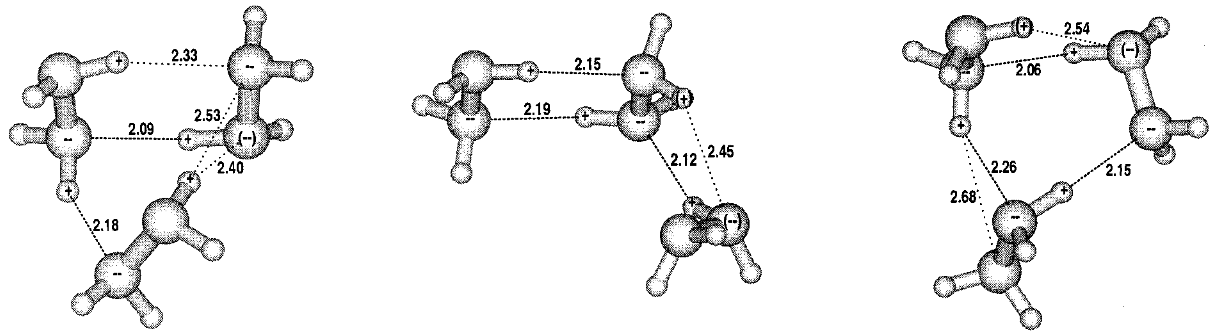
5. Short Hydrogen Bonds

The strongly bonded conformations **1a3a-2, A1, A2, B1, B2, B6**, and **B9** all have one hydrogen bond length that is less than 2.1 Å. This is much shorter than the shortest hydrogen bond length of the dimers (at the same level 2.20 Å for structure **3b1**). All of these trimers have two monomers M1 and M2 that are both involved in three hydrogen bonds. In the case of the monomer M1, two H atoms and one N atom are incorporated in these hydrogen bonds. This means that the three induced charges, $+ + -$, exist for M1. The other monomer M2 participates in the hydrogen bonds with one H atom and two N atoms, so the induced charges here are $- - +$. Because the charge transfer is small for the trimers (the only exception is the conformation **C2**, which has a charge of 0.054 au on that monomer being in a saddle-point state), a high partial charge exists for the N atom of monomer M1 and a high positive charge on the H atom of M2. Therefore, a short hydrogen bond exists between these two atoms. Further the short hydrogen bonds of all of these trimers are involved in a cyclic ring of dipoles that enhance each other.

6. Stability of the Trimers: Tunneling Processes and Some Rearrangement Reactions

To investigate the stability of the trimers, both tunneling processes and rearrangement reactions must be analyzed.

(1) Tunneling Processes. A necessary condition for successful tunneling is that the quantum levels are close together in the reactant well and in the product well, because otherwise the intensity of thermal fluctuations is too low to be effective. The monomer of hydrazine has a low barrier to rotation (see section 2), and of course, the same wells exist for its two structures **A** and **B**. Tunneling therefore takes place. The same is true for all dimer and trimer "conformations" that possess a $\mathrm{NH_2}$ group that is not involved in hydrogen bonds. This is true for the dimer conformations **3b1** and **3b2** and the trimer conformations **A3, A4**, and **B7**. For the conformation **3b2**, this was tested with fixed positions of the N atoms: the barrier height is 14.7 kJ mol^{-1}, and one obtains a small energy gain for this tunneling process of 0.2 kJ mol^{-1}. In the following cases, it is also obvious which new confomations the tunneling process generates: **3b1** → **3a**, **3b2** → **3a** (see Dyczmons,[6] Figure 4), **A3** → **B1**, and **A4** → **B3**. For all other dimer and trimer structures, a rotation tunneling of a $\mathrm{NH_2}$ group breaks at least one hydrogen bond. This increases the barrier to rotation. If the product well has a higher energy than the zero-point level in the reactant, then tunneling is impossible. This means that, starting from a stable conformation, the new structure generated by a tunneling process must be "close" to the geometry of a more stable conformation. We have searched for such a process; the only one for dimer conformations is the rearrangement reaction **1a** → **1b**. Here, we have used the MP2/basis 1 method to calculate the barrier height and the energy difference between the tunneled structure and the educt with three different approximations: (1) only the parameters of the one tunneling $\mathrm{NH_2}$ group are optimized; (2) all parameters of the hydrogen atoms of the one monomer involved in the tunneling process were optimized; (3) only the positions of the four N atoms were fixed. For the barrier height, one obtains the following results with the approximations 1−3: 18.9, 13.5, and 12.4 kJ mol^{-1}, respectively. For the energy difference between the tunneled structure and the educt, one obtains 19.1, 6.4, and 5.0 kJ mol^{-1},



B3 → B1; ΔE=0.6 **1b1b → B1; ΔE=6.6** **A2 → A1; ΔE=0.5**

Figure 6. Some saddle points for rearrangement reactions. The barrier heights are low due to the two weak hydrogen bonds for the saddle-point structures of the reactions **B3** → **B1** and **A2** → **A1**.

TABLE 2: The Frequency Shifts of the Antisymmetric Wagging Vibrations in cm^{-1} for the Dimers (the IR Intensities in km mol^{-1} Are Added in Parentheses)

conf	sym	MP2/basis 1	B3LYP/basis 1	MP2/basis 4[b]	intensity[c]	expt[a]
1a	C_2	47.5 (143.6)	46.5 (162.1)	49.1 (155.4)	121.2	48.6
		44.4 (57.6)	48.3 (63.4)	52.1 (83.5)	65.1	48.6 (51.5)
1b	C_i	30.6 (0.0)	43.6 (0.0)	46.4 (0.0)	0	
		51.3 (189.3)	63.1 (201.8)	66.1 (218.6)	477.3	64
2b	C_2	9.6 (28.2)	15.7 (46.4)	12.3 (33.2)	3.9	
		36.3 (169.8)	43.5 (163.3)	39.6 (204.4)	24.0	42.7
3a	C_1	36.8 (124.7)	37.9 (126.8)	40.2 (148.5)	136.5	42.7
		44.1 (88.7)	48.2 (97.1)	52.7 (105.7)	97.2	48.6 (51.5)

[a] Beu et al.[7] [b] Basis 4 is the 6-31++G(2df,2p) basis. [c] MP2/basis 4 results for the intensities due to a Boltzmann distribution for $T = 264$ K with CCSD(T)/avtz[6] energy values.

respectively. Because the zero-point vibration energy of ν_7 (torsion) of hydrazine is 4.49 kJ mol^{-1} (see ref 21), the tunneling process **1a** → **1b** probably is not possible. The same is true for nearly all of the tunneling processes for which at least one hydrogen bond is broken.

(2) Rearrangement Reactions. The following three rearrangement reactions between some of the most stable trimer structures were examined (see Figure 6): **B3** → **B1**, **1b1b** → **B1**, and **A2** → **A1**. For these reactions, only one hydrogen bond is broken. Only relatively low barrier heights are expected for this reason. The barrier heights for the first two reactions are, on the MP2/basis 1 level, 0.60 and 6.59 kJ mol^{-1}, respectively. The reaction **A2** → **A1** was calculated only on the MP2/6-31++(d,p) level. Here, the barrier height is 0.55 kJ mol^{-1}. If one adds up the zero-point energies to barrier heights for the reactions **B3** → **B1** and **A2** → **A1**, then one obtains −0.05 and −0.28 kJ mol^{-1}, respectively. Thus, the conformations **B3** and **A2** are not stable.

In both cases, the educt and product differ only by one hydrogen bond. These hydrogen bonds of the educt and product have a common H atom but two different neighboring N atoms belonging to the same monomer. The saddle-point structure possesses two weak hydrogen bonds, which are the cause of the low barrier height (see Figure 6). A similar situation exits for the dimer rearrangement reaction **3b2** → **3b1**: here, a N atom slides from one H atom to a neighboring H atom (see Dyczmons,[6] Figure 8). It is plausible that the educts are generally not stable for such reactions. As a result, the global minimum structure **B1** and the conformations **A1** and **3b1** are probably floppy structures.

7. The Frequency Shifts of the Antisymmetric Wagging and the NH Stretching Modes

Harmonic frequency shifts on the MP2/6-31+G* level for the antisymmetric wagging and the NH stretching frequencies have been calculated by Cabalerio-Lago and Rɪos[8] only for their most stable trimer conformation. Most of the very stable conformations are needed to understand the antisymmetric wagging spectrum.

The experimental frequency of the antisymmetric NH_2 wagging mode of hydrazine is $\nu_{12} = 937$ cm^{-1} (see Beu et al.[7]). The measured photodissociation spectrum for the trimer of hydrazine (see ref 7) cannot directly be compared with our calculations because the abundances of the stable conformers are not known. What can be seen from the measured spectrum is the following: nonvanishing intensities are between 970 (33) and 1060 (123) cm^{-1}, one pronounced shoulder is at 1000 (63), and a maximum is around 1025 (88) cm^{-1}. Here, the numbers in parentheses indicate the shifts from the monomer value. The ratio of the intensity at the pronounced shoulder to that of the maximum is between 0.75 and 0.8. The photodissociation curve has a small descent on the red side of the maximum and a steep descent on its blue side. The width of the measured curve, in which the intensity has half the value of the maximum, is 56 cm^{-1}.

Our study on the dimers[6] yielded the frequency shifts listed in Table 2. Because the conformations **3b1** and **3b2** are not stable because of the tunneling process, they are omitted. Further, the abundances for 264 K (see ref 7) due to the Boltzmann distribution are listed. What one can see in comparison to the measured photodissociation spectrum is the following: (1) These four conformations are sufficient for its understanding. (2) There is a good correspondence between the calculated harmonic frequency shifts and the experimental shifts due to compensatory effects. (3) No Boltzmann distribution exists for 264 K and lower temperatures. One gets a qualitatively better understanding, if one takes a larger abundance (approximately a factor of 4) for conformation **3a**. This is expected because of the fact that the abundance of conformation **3a** is increased by the tunneling processes **3b1** → **3a** and **3b2** → **3a**.

TABLE 3: Calculated Shifts of the Harmonic Antisymmetric Wagging Vibrational Wavenumbers[a]) Due to B3LYP/Basis 1 Results in cm^{-1}

conf	sym	$\Delta\nu_{19}$	$\Delta\nu_{20}$	$\Delta\nu_{21}$
1b1b	C_2	52.2 (132.8)	57.6 (0.1)	110.3 (161.5)
1b1a	C_1	56.2 (85.3)	61.5 (66.1)	99.1 (144.5)
1a3a-1	C_1	53.7 (152.5)	58.7 (105.6)	71.7 (49.3)
1a3a-2	C_1	49.0 (126.1)	61.9 (91.7)	67.4 (83.0)
3a3b1	C_1	35.7 (142.7)	40.5 (58.3)	61.8 (188.1)
A1	C_1	67.8 (89.7)	79.4 (72.4)	82.9 (114.7)
A2	C_1	52.7 (186.9)	74.0 (13.9)	85.4 (80.2)
A6	C_1	57.6 (28.6)	63.2 (129.1)	78.9 (96.7)
B1	C_1	57.3 (71.7)	71.1 (43.6)	97.4 (156.4)
B2	C_1	58.3 (48.4)	77.5 (64.7)	90.7 (157.1)
B3	C_1	64.0 (46.4)	78.8 (98.4)	84.6 (134.6)
B4	C_1	45.3 (157.1)	63.8 (64.5)	88.7 (123.5)
B5	C_1	41.4 (68.1)	62.8 (121.6)	78.6 (108.2)
B6	C_1	61.9 (100.5)	65.8 (99.5)	81.8 (67.2)
B8	C_1	45.2 (32.3)	67.6 (46.2)	96.9 (173.9)
B9	C_2	45.4 (8.5)	60.1 (98.1)	65.8 (174.3)

[a] Absolute IR intensities (in km mol^{-1}) are given in parentheses.

TABLE 4: Calculated Shifts of the Harmonic Antisymmetric Wagging Vibrational Wavenumbers[a]) Due to MP2/Basis 1 Results in cm^{-1}

conf	sym	$\Delta\nu_{19}$	$\Delta\nu_{20}$	$\Delta\nu_{21}$	ν_1
1b1b	C_2	53.3 (112.9)	59.0 (0.0)	113.1 (53.0)	23.4
1b1a	C_1	55.9 (84.8)	62.0 (44.1)	101.1 (137.5)	18.8
3a3a-1	C_2	51.3 (85.4)	51.9 (69.5)	72.5 (131.1)	25.5
3a3a-2	C_1	44.1 (158.3)	48.4 (53.9)	83.8 (96.3)	30.2
1a3a-1	C_1	54.5 (198.1)	66.3 (36.9)	73.7 (59.8)	45.1
1a3a-2	C_1	54.8 (137.4)	64.2 (27.7)	67.7 (105.0)	36.8
3a3b1	C_1	40.7 (145.1)	58.2 (146.7)	69.7 (41.6)	47.1
A1	C_1	64.9 (101.8)	84.7 (70.1)	89.6 (84.3)	39.2
A2	C_1	52.1 (182.0)	70.6 (25.4)	82.0 (48.1)	30.2
A6	C_1	43.6 (8.4)	54.9 (108.8)	62.4 (146.3)	32.4
B1	C_1	55.8 (47.5)	69.9 (52.4)	96.5 (147.8)	36.2
B2	C_1	53.6 (29.2)	80.4 (66.6)	82.9 (143.1)	59.6
B3	C_1	53.0 (32.5)	68.2 (54.9)	85.4 (178.1)	18.8
B4	C_1	36.8 (159.5)	56.1 (29.0)	82.7 (134.5)	30.4
B5	C_1	40.2 (65.1)	63.4 (111.7)	80.1 (100.8)	40.5
B6	C_1	53.4 (52.9)	66.9 (95.9)	67.1 (92.6)	38.4
B8	C_1	44.1 (27.3)	62.9 (33.5)	93.3 (159.6)	48.4
B9	C_2	41.4 (16.8)	58.3 (83.7)	65.7 (161.3)	30.7
B11	C_1	44.8 (61.6)	49.3 (84.1)	72.2 (139.0)	57.7

[a] Absolute IR intensities (in km mol^{-1}) are given in parentheses.

A least-squares fit between the calculated shift of the antisymmetric wagging mode and the experimental values for the dimers yielded the following optimal frequency scaling factors: 1.134 for MP2/basis 1 and 1.023 for B3LYP/basis 1.

The results for the antisymmetric stretching modes with these optimal stretching parameters are listed for B3LYP/basis 1 in Table 3 and for MP2/basis 1 in Table 4. The conformations with low binding energies are omitted; in the case of B3LYP and MP2, we take as limits −37.5 and −42.5 kJ mol^{-1}, respectively. Also, the structures **A3**, **A4**, and **B7**, which are not stable due to tunneling processes, are omitted. With both methods, the calculated shift values are between 36 and 113 cm^{-1}, in full agreement with the experimental data.

To get a theoretical predicted spectrum (see Figure 7), one needs the abundances of the different structures. In a first attempt, a Boltzmann distribution was taken using the enthalpies of Table 1. The half-width value τ of the experiment is not well-known. It lies between 10 and 25 cm^{-1}. One gets good fits of the experimental spectrum with $15 \leq \tau \leq 25$ cm^{-1}. In the following, we take $\tau = 18$ cm^{-1}. When the gas passes the nozzle, the temperature drops from 300 K (temperature of the reservoir) to 60 K (temperature of the beam). A Boltzmann distribution cannot be expected for the cold beam because of some high barriers between the conformations. Therefore, we take the following additional approximation: a Boltzmann distribution is frozen in for a certain temperature during the decrease of temperature. So we use the temperature as a fit parameter for the experimental spectrum. For the $T = 220$ K (see Figure 7), we get 92 cm^{-1} for the shift value of the maximum and 62 cm^{-1} for that of the shoulder. The width of the spectrum, at which the intensity has half the value of the maximum, is 55 cm^{-1} and the ratio q_r of the intensity at the pronounced shoulder to that of the maximum is 0.8 ($q_r = 0.75$ at 200 K). So, with the parameter $\tau = 18$ cm^{-1} and with a T value between 200 and 220 K, we get a good approximation of the measured spectra of Buck et al. (compare with the above values).

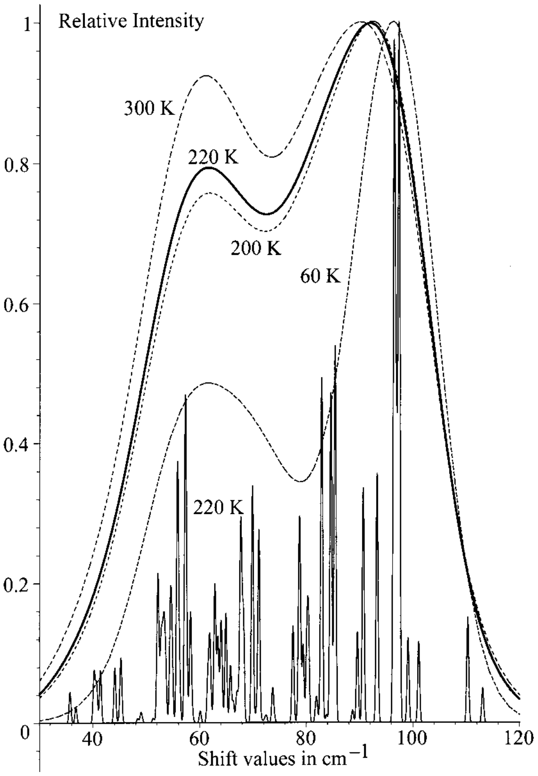


Figure 7. The calculated spectra for four temperatures of the antisymmetric wagging spectrum of $(N_2H_4)_3$. A Boltzmann distribution was taken for the abundances, and a half-width value 18 cm^{-1} was used. For 220 K, a good accordance with the experimental curve of Buck et al.[4,7] exists. Further, the spectral lines with a half-width value of 0.3 cm^{-1} and with $T = 220$ K are shown.

This is a suprising result because for the dimers no Boltzmann distribution exits. An explanation for this is the fact that the dominant global minimum **B1** (see curve for 60 K) has shift values for its two maxima that are only a few cm^{-1} inside the shoulder and outside the maximum. The frequencies of the other conformations are mainly between these two shift values. Their intensities fill mainly the minimum between the "shoulder" and the maximum together with a raising of the shoulder. A comparison with the experimental curve shows that probably some conformations are missing that fill this minimum. Whether this minimum exists in the measured spectrum is not quite clear: between 70 and 77 cm^{-1}, no measuring points exist. Another aspect for the good accordance with the experimental spectrum is probably a statistical effect: because the number of lines is here larger than for the dimers, deviations from the Boltzmann distribution will partially compensate. For a more

TABLE 5: The Frequency Shifts of the NH Stretching Vibrations ν_1 and ν_9 of Hydrazine in cm^{-1} Calculated with the MP2/Basis 1 Method[a]

conf	shifts of ν_1			shifts of ν_9		
1b1b	−64.3 (110.8)	−56.6 (0.2)	−55.9 (114.9)	−65.3 (1.4)	−61.4 (312.7)	−49.1 (75.9)
1b1a	−60.3 (103.3)	−58.0 (32.2)	−56.0 (73.8)	−66.9 (34.6)	−63.7 (9.6)	−51.1 (4.8)
3a3a-1	−53.6 (5.1)	−53.3 (58.0)	−35.8 (3.4)	−52.66 (1.9)	−51.9 (150.1)	−24.5 (6.8)
3a3a-2	−48.0 (26.0)	−47.3 (19.3)	−41.8 (61.8)	−43.8 (41.8)	−35.9 (15.0)	−23.3 (14.9)
1a3a-1	−58.7 (10.7)	−46.4 (69.5)	−35.7 (10.4)	−63.2 (52.9)	−60.1 (89.8)	−44.8 (91.8)
1a3a-2	−59.4 (38.6)	−47.2 (60.2)	−39.9 (66.1)	−79.6 (123.3)	−37.1 (48.1)	−29.3 (33.6)
3a3b1	−56.0 (8.7)	−38.2 (56.1)	−36.5 (24.7)	−49.1 (33.9)	−35.4 (10.9)	−29.8 (27.1)
A1	−77.2 (53.0)	−72.9 (53.7)	−38.2 (23.1)	−123.1 (188.3)	−83.7 (164.6)	−62.1 (118.9)
A2	−78.4 (45.7)	−74.6 (8.0)	−34.8 (20.1)	−110.4 (38.7)	−97.3 (323.9)	−52.6 (101.2)
B1	−75.6 (36.3)	−63.9 (73.3)	−49.9 (55.8)	−108.5 (119.7)	−75.0 (105.7)	−61.4 (168.7)
B2	−72.5 (51.7)	−66.8 (43.4)	−47.6 (69.5)	−106.2 (143.8)	−76.4 (145.9)	−32.7 (26.4)
B3	−79.8 (50.8)	−64.8 (52.5)	−34.7 (31.3)	−96.0 (138.4)	−71.2 (121.3)	−33.8 (25.5)
B4	−71.6 (63.0)	−37.3 (37.6)	−31.8 (22.4)	−83.0 (54.8)	−68.9 (143.2)	−36.4 (12.9)
B5	−68.5 (56.5)	−65.0 (57.2)	−29.0 (40.0)	−78.2 (124.3)	−48.9 (65.4)	−32.3 (14.6)
B6	−66.2 (36.2)	−59.9 (56.3)	−51.4 (75.2)	−89.8 (164.7)	−65.0 (93.4)	−36.1 (55.9)
B8	−77.8 (41.2)	−63.0 (40.8)	−53.1 (109.4)	−94.2 (112.9)	−54.2 (83.1)	−32.5 (27.3)
B9	−52.9 (2.0)	−50.8 (106.8)	−29.3 (53.0)	−54.1 (27.7)	−53.4 (54.2)	−42.8 (100.3)
B11	−50.9 (33.5)	−38.9 (12.4)	−36.7 (55.4)	−53.0 (44.8)	−50.1 (28.1)	−29.2 (55.8)

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

precise spectrum, one needs of course more of the particularly stable conformations together with their true abundances.

In Figure 7 also, the narrow lines with a half-width value of 0.3 cm^{-1} and a Boltzmann distribution of 220 K are shown. Further, the spectrum with $T = 300$ K is drawn in; because the q_r value does not agree with the experimental one, the Boltzmann distribution of the temperature of the reservoir seems not to be a good approximation.

Beu and Buck[4] also calculated the shifts with their model potential. They took into account only six of their most stable conformations (three of the **A** type and three of the **B** type), all with the same abundance. Their shift values are too small by approximately a factor of 0.83.

The shifts of the hydrogen stretching vibrations are listed in Table 5. No experimental information is available. The four NH stretching modes of hydrazine are grouped by pairs, corresponding to the symmetric (ν_2, ν_9) and asymmetric vibrations (ν_1 and ν_8). The calculated maximum red shifts were given with regard to the asymmetric stretching mode ν_1 and the symmetric stretching mode ν_9 of hydrazine. They are a measure of the strength of the hydrogen bonds and correlate with the length of the hydrogen bonds. The red shift is associated with a large increase in the infrared intensity; the monomer intensities for ν_1,ν_8 and ν_2,ν_9 are only 6.5,3.8 and 1.2,6.9 km mol^{-1}, respectively! The conformations that have one very short hydrogen bond (see conformations **A1**, **A2**, **A3**, **B1**, **B2**, **B3**, **B6**, and **B8**) have the highest shift values of ν_1 and ν_9 (see Table 4).

Conclusions

The trimer structures of hydrazine are mainly composed of dimer structures. Of the 28 analyzed stable trimer structures, 13 contain two dimer structures and 12 contain one dimer structure. On the average, the outer H atoms of hydrazine are significantly more often involved in the hydrogen bonds than the inner ones, and the average number of hydrogen bonds here is 4.4.

Because of the cooperative effects, the ratio of the average binding energies is $E_{av}(\text{trimer})/E_{av}(\text{dimer}) = 2.16$. In this case, only the cyclic trimers contribute to this cooperative effect.

Because both NH$_2$ groups of a monomer cannot be optimally orientated in the trimer conformations, high defomation energies exist and the geometry optimization was often tedious. Two trimer conformations were found in which one of the monomers has a trans saddle-point structure.

Because of the tunneling effect, three minima of the PES are not stable. The global minimum **B1** and the most stable conformation of the **A** type are probably floppy molecules.

The calculated harmonic frequency shifts for the antisymmetric wagging mode of the trimer of hydrazine range between 36 and 113 cm^{-1}. With a half-width value of 18 cm^{-1} and with $T = 220$ K, the calculated spectrum is in a good qualitative agreement with the measured photodissociation spectrum of Buck et al.[4] for this mode.

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