Ab Initio Investigation of the Structure, Vibrational Frequencies, and Intensities of HNnH, HNnF, and FNnF (n = 3, 4)

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Ab Initio Investigation of the Structure, Vibrational Frequencies, and Intensities of HN$_n$H, HN$_n$F, and FN$_n$F (n = 3, 4)

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Ab initio studies of the structure, vibrational frequencies, and intensities have been carried out on the open-chain species HN$_n$H, HN$_n$F, and FN$_n$F (n = 3, 4). Particular attention has been focused on the species HN$_3$H, which is isoelectronic with NO$_2$ and exhibits many of the same features in its electronic structure. HN$_3$H is shown to have a planar trans structure with R_{N-N} = 1.252 Å, indicating considerable double-bond character. HN$_3$H also exhibits a low-lying $^2A_2$ state separated from the ground state by about 36 kcal mol^{-1}. Replacement of one or more of the hydrogens in HN$_3$H by fluorines alters the electron distribution, spin density, and geometry, most importantly the NNN angle. The biradical species N$_4$ in its trans planar structure is shown to be of significantly higher energy than two N$_2$ molecules.

Introduction

The spectroscopic properties of NO$_2$ are quite complex owing to coupling between a number of low-lying electronic states. The open-chain radical HN$_3$H is isoelectronic with NO$_2$, and we were interested in determining whether the former molecule shared some of the electronic complexity of the latter. In reviewing the literature for this study it became clear that there were very few experimental or theoretical studies on open-chain catenated nitrogen molecules containing more than two nitrogens. Since we are interested in determining whether extended catenation involving oxygens or nitrogens is feasible and since we had recently completed a study of catenation in simple oxygen-containing molecules,[1] we decided to extend this study by investigating the structure and vibrational properties of the species HN$_n$H, HN$_n$F, and FN$_n$F, where n = 3, 4. The triatomic radical N$_3$ has been studied extensively both in terms of its vibrational spectra[2] and its electronic spectra[3] and has been shown to be both linear and symmetric, with an N—N bond length of 1.181$_5$ Å, though a theoretical calculation[4] predicted that it would be asymmetric. Theoretical calculations have also been carried out on the structure and electronic properties of N$_3^-$ and N$_3^+$.[4,5] The molecule hydrazoic acid, HN$_3$, was studied theoretically[6] and was predicted to be planar but nonlinear. Lee and Rice[7] investigated N$_4$ as a tetrahedral species, considering its potential as a high energy density material. Alexander, Werner, and Dagdigian[8] have studied the dissociation of HN$_3$ into N$_2$ and NH. There have been numerous theoretical studies of the species H$_2$N$_2$,[9] F$_2$N$_2$,[10] and to a lesser extent HN$_2$F.[11] The only study we are aware of on any of the molecules investigated herein is on HN$_3$H by Baird and Taylor,[12] which was carried out at the Hartree—Fock level using an STO-3G and a 4-31G basis set. The minimal basis set predicted a Π ground state with an N—N bond length of 1.39 Å, an ∠NNN = 107°, and an ∠HNN = 102°, whereas the split-valence basis set predicted the ground state to be Σ and to have a N—N bond length of 1.32 Å, an ∠NNN = 126°, and an ∠HNN = 107°.

The purpose of this study was to investigate the bonding and structure of catenated nitrogen species with a view to providing an incentive to experimentalists to determine whether they in fact exist. The structural and spectroscopic data provided by this study should be of value to experimentalists in identifying these species. In particular, the intent was to explore the properties of HN$_3$H, a species isoelectronic with NO$_2$, to compare and contrast its properties with the latter molecule.

Theory

The majority of the calculations were carried using either the Gaussian 90[13] or Gaussian 92[14] package of programs. The calculations were carried out employing a 6-311G** basis set using both the "MP2 = FULL" and "MP2 = FC" options, indicating the inclusion or noninclusion, respectively, of the core electrons in the correlation treatment. The correlation corrections were determined using a perturbative approach of Moeller and Plesset.[15] Additional calculations on HN$_3$H were carried out at the CISD and the CIS level, in the latter case to identify the lowest lying excited states. MCSCF calculations using the GAMESS package of programs[16] were also performed on HN$_3$H. Vibrational frequencies and intensities were determined at the MP2 level using the MP2/6-311G** optimized geometries. The SPECTRO program[17] was used to evaluate vibrational frequencies for isotopically substituted isomers as well as to determine centrifugal distortion constants.

Results and Discussion

Table 1 lists the results of geometry optimization calculations performed on HN$_3$H, including a geometry optimization on its first excited state. Table 2 summarizes the equilibrium geometries obtained for all of the molecules studied using a consistent level of calculation and basis set. Vibrational frequencies and intensities including frequencies of selected isotopically substituted isomers are given in Tables 3—5. Rotational and centrifugal distortion constants obtained using the SPECTRO[17] program are listed in Table 6.

TABLE 1: Optimized Geometries of HN₃H[a]

parameters	"MP2 = FULL"	"MP2 = FULL"*	"MP2 = FC"*	MCSCF(6→3)[#]	CISD	CIS[†]
R_{N-N}	1.2934	1.2522	1.2535	1.2548	1.2316	1.2639
R_{N-H}	1.0238	1.0195	1.0202	1.0032	1.0125	1.0067
∠NNN	109.3664	131.194	131.1079	132.369	134.9961	109.3931
∠HNN	103.6796	109.1994	109.0999	110.0232	109.5082	108.2274
∠HNNN	180.0152	180.001	180.0004	180.0 (fixed)	183.6521	180.0 (fixed)
energy	−164.959 695	−165.001 771	−164.945 279	−164.538 642	−164.887 751	−164.918 934

[a] Bond lengths are in angstroms, angles are in degrees, energy is in Hartrees. All calculations used the 6-311G** basis set. "MP2 = FULL" means all electrons are included in the correlation energy calculation. "MP2 = FC" means inner shell electrons are excluded from the correlation energy calculation. * Calculations use the "CALCALL" option such that MP2 force constants are calculated at every point. # CAS geometry optimization. Terms in parentheses indicate occupied and virtual orbitals used to determine configurations. † Calculation of lowest excited state geometry.

TABLE 2: Optimized Geometries of HN$_n$H, HN$_n$F, and FN$_n$F (n = 3, 4)[a]

parameter	HN₃H	HN₄H	HN₃F	HN₄F	FN₃F	FN₄F
R_{N-H}	1.0202	1.0415	1.0223	1.0273		
$R_{N-N(H)}$	1.2535	1.2354	1.2747	1.2491		
$R_{N-N(F)}$			1.2952	1.2315	1.2738	1.2422
R_{N-N}		1.5126		1.4258		1.4247
R_{N-F}			1.3545	1.3874	1.3521	1.3701
∠NNH	109.1003	108.7454	104.0977	103.8106		
∠NNF			105.7895	107.3878	106.0269	106.55
∠(H)NNN(H)	131.1082					
∠(H)NNN(F)			107.9609			
∠(H)NNN(N)		111.1403		110.4137		
∠(F)NNN(N)				108.6762		104.568
∠(F)NNN(F)					108.0179	
∠HNNN	180.0	0.0	180.000	177.2941		
∠FNNN			180.000	177.4736	180.0	180.0
∠NNNN		180.0		79.6453		180.0
energy	−164.945 279	−219.642 374	−264.000 972	−318.680 317	−363.036 553	−417.715 331

[a] Bond lengths are in angstroms, angles are in degrees, energy is in Hartrees. All results are determined at the "MP2 = FC" level using a 6−311G** basis set.

TABLE 3: Vibrational Frequencies and Intensities of HN$_n$H, and DN$_n$D (n = 3, 4)[a]

assignment	HN₃H	DN₃D	assignment	HN₄H	DN₄D
a₁ N−H str	3526.714 (16.4)	2584.71	a$_g$ N−H str	3229.70 (0.0)	2355.76
N−N str	1404.533 (0.4)	1339.23	N=N str	1603.014 (0.0)	1585.87
HNN bend	1249.008 (14.9)	997.26	HNN bend	1394.744 (0.0)	1110.81
NNN bend	618.956 (17.5)	555.68	N−N str	821.948 (0.0)	691.10
			NNN bend	513.925 (0.0)	504.35
a₂ HNNN twist	3589.646 (0.0)	2732.44	a$_u$ HNNN twist	920.482 (204.9)	732.63
			NNNN twist	103.196 (4.4)	98.90
b₁ HNNN twist	744.663 (123.6)	585.08	b$_g$ HNNN twist	1092.778 (0.0)	886.55
b₂ N−H str	3523.796 (87.2)	2581.35	b$_u$ N−H str	3208.681 (49.3)	2345.29
N−N str	2092.534 (169.9)	2005.15	N=N str	1628.560 (19.4)	1617.68
HNN bend	1270.532 (513.1)	1018.69	HNN bend	1434.092 (185.5)	1143.45
			NNN bend	400.021 (48.6)	368.27

[a] Frequencies are in cm⁻¹; intensities are in km·mol⁻¹. All frequencies are determined at the MP2 level using MP2/6−311G** optimized geometries.

The first geometry optimization carried out on HN₃H was carried out at the MP2 level including all electrons in the correlation energy calculation and allowed for optimization of all parameters. The HNNN dihedral angle indicated an essentially planar structure, though the angle was fractionally different from 180°, thus lowering the symmetry to C_2. The N−N bonds were clearly partial double bonds, and the atomic spin densities were fairly evenly distributed among the three nitrogens, with the terminal nitrogens having the same spin and the central nitrogen an opposing spin. It was also notable that the ∠NNN = 109.37° was significantly less than that found for the ∠ONO = 134° in NO₂.[18] However when this calculation was repeated using the "CALCALL" option, which requires the determination of the force constants at every point during the gradient optimization procedure, substantial differences were observed in the geometry, total energy, and atomic spin densities. In this latter calculation the HNNN dihedral angle again came out to be essentially 180°, indicating a preference for a planar structure. However the ∠NNN = 131.19° was now

similar to the ONO angle in NO₂. In addition the N−N bond length was significantly shorter than in the earlier calculation, indicating a greater degree of double-bond character, the energy also indicated a more stable structure, and the atomic spin densities were significantly changed, with most of the spin density being concentrated on the central nitrogen with smaller amounts of the same sign on the two terminal nitrogens. It is of importance to emphasize that there are no imaginary frequencies associated with either structure so they both represent true minima. When the geometry optimization was again repeated this time without the "CALCALL" option but fixing the ∠HNNN = 180°, the geometry obtained corresponded to that found using the "CALCALL" option. This suggested that in the C_2 nonplanar geometry there was a mixing of configurations which was forbidden in the planar geometry, with symmetry C_{2v}. Since the ground state of the molecule was ²A₁, this indicated that there might be a relatively low-lying excited state of symmetry A₂ which in the lower C_2 symmetry could mix with the A₁ state. It should be pointed out that in NO₂ the

TABLE 4: Vibrational Frequencies and Intensities of HN$_n$F and DN$_n$F (n = 3, 4)[a]

assignment		HN$_3$F	DN$_3$F	assignment	HN$_4$F	DN$_4$F
a′	N−H str	3501.185 (8.1)	2560.38	N−H str	3427.631 (3.0)	2506.91
	N−N(H) str	1530.346 (31.2)	1476.96	N=N(H) str	1559.551 (13.7)	1553.46
	HNN bend	1406.314 (10.8)	1154.41	N=N(F) str	1513.581 (48.9)	1510.04
	N−F str	1117.200 (201.5)	1069.58	HNN bend	1444.010 (44.0)	1136.88
	N−N(F) str	708.956 (12.2)	704.18	N−N str	1057.079 (96.2)	1012.59
	NNF bend	570.173 (1.0)	552.73	HNNN twist	964.988 (99.6)	772.10
	NNN bend	442.910 (0.2)	430.35	N−F str	913.555 (11.2)	902.10
				NNN(H) bend	722.442 (45.9)	686.89
a″	HNNN twist	734.439 (60.1)	556.60	NNF bend	523.442 (19.3)	517.44
	FNNN twist	268.296 (1.9)	268.14	NNN(F) bend	378.993 (2.9)	364.29
				FNNN twist	252.162 (0.5)	248.18
				NNNN twist	121.933 (1.2)	120.44

[a] Frequencies are in cm^{-1}, and intensities are in km·mol^{-1}. All frequencies are determined at the MP2 level using MP2/6-311G** optimized geometries.

TABLE 5: Vibrational Frequencies and Intensities of FN$_n$F (n = 3, 4)[a]

assignment		FN$_3$F	assignment	FN$_4$F
a$_1$	N−N str	1449.087 (7.1)	a N=N str	1511.322 (0.0)
	N−F str	1193.812 (25.9)	N−F str	1076.655 (0.0)
	NNF bend	582.733 (0.9)	N−N str	1048.632 (0.0)
	NNN bend	294.152 (3.9)	NNN bend	538.146 (0.0)
			NNF bend	446.429 (0.0)
a$_2$	FNNN twist	279.272 (0.0)	FNNN twist	231.980 (3.2)
			NNNN twist	53.428 (0.01)
b$_1$	FNNN twist	295.818 (2.2)		
			b N=N str	1528.309 (85.2)
b$_2$	N−F str	1039.818 (344.7)	N−F str	1044.167 (246.4)
	NNF bend	856.970 (0.1)	NNF bend	748.649 (82.5)
	N−N str	414.459 (8.2)	NNN bend	473.247 (0.0)
			FNNN twist	209.128 (4.5)

[a] Frequencies are in cm^{-1}, and intensities are in km·mol^{-1}. All frequencies are determined at the MP2 level using MP2/6-311G* optimized geometries.

ground state $^2A_1$ has the computed parameters R_{N-O} = 1.23 Å and $\angle ONO$ = 133°, while there is a low-lying excited state, $^2A_2$, with computed parameters R_{N-O} = 1.32 Å and $\angle ONO$ = 102°[19] which supports this postulate. A CIS single point calculation was carried out on the planar structure to determine the lowest lying excited states, and the lowest excited state was found to be a $^2A_2$ state separated from the ground state by about 35.7 kcal·mol^{-1}. The CIS calculation was repeated again holding the molecule planar but optimizing the first excited state geometry (Table 1). It is notable that this state has an $\angle NNN$ = 109.4°, in conformity with the equivalent state in NO$_2$ and with the geometry first obtained for HN$_3$H. Another way of looking at this is to note that in the Walsh diagram for an AB$_2$ molecule[20] the 1a$_2$ and 6a$_1$ orbitals cross at a low BAB angle. If the symmetry is reduced to C_2, these two orbitals will have the same symmetry, resulting in an avoided crossing. This could potentially affect the relative occupancies of the two orbitals and therefore the overall symmetry of the state. A CISD calculation on the ground state of HN$_3$H also reproduced the larger NNN angle but with a somewhat shorter N−N bond length and a dihedral angle somewhat further away from 180°.

An MCSCF geometry optimization was performed for the planar C_{2v} structure using excitations between the six highest occupied orbitals and the three lowest unoccupied virtual orbitals to determine the configurations to be included. The MCSCF geometry corresponded to the one obtained using the "CAL-CALL" option ("MP2 = FULL"* column in Table 1) but the dominant configuration, with one unpaired electron, contributed only about 74% to the ground state, while a configuration with three unpaired electrons, presumably associated with each of the nitrogens, contributed most of the remaining 16%. This correlates well with the atomic spin densities observed in both

of the "MP2 = FULL" calculations, in which the lower energy structure has one unpaired electron located primarily on the central nitrogen and the higher energy structure has unpaired electrons on each nitrogen, and with the different geometries observed. When the molecular symmetry was lowered to C_2 in the MCSCF calculation, the optimized structure obtained is equivalent to that given in the "MP2 = FULL" column in Table 1. The dominant configuration contributes about 77%, but there are now two equivalent configurations of "a" symmetry (corresponding to one of a$_1$ and one of a$_2$ symmetry in the C_{2v} point group) with three unpaired electrons each making significant contributions, one of 13.6% and one of 5.6%. This tends to confirm our belief that the structure shown in the "MP2 = FULL" column of Table 1 results from mixing of the excited A$_2$ state with the ground state due to the lowering of symmetry to C_2 and to the relatively small energy separation between the ground and first excited state. The other conformations of HN$_3$H (trans−cis and cis−cis) were also optimized but were found to be significantly less stable than the trans−trans conformation.

In both HN$_3$F and FN$_3$F the preferred conformations are trans−trans, as in HN$_3$H, though the N−N bond lengths are somewhat longer than in the latter molecule and the NNN angle is substantially smaller, at about 108°, than in HN$_3$H. This smaller NNN angle observed for HN$_3$F and FN$_3$F resembles that found in the $^2A_2$ excited state of HN$_3$H, and the spin density distribution in the former two molecules also resembles that of the $^2A_2$ state of HN$_3$H rather than that of its ground state. In fact, the ground state of FN$_3$F is $^2A_2$. There is no evidence of the alternative geometries observed in HN$_3$H though incomplete MCSCF calculations do indicate that there is no truly dominant configuration, particularly in FN$_3$F, where the largest contribution is about 60%. In HN$_3$F a CIS calculation indicates the lowest excited state is about 63.54 kcal·mol^{-1} above the ground state, almost twice that found for HN$_3$H. A CIS calculation on FN$_3$F found that the first excited state was still further separated from its ground state at 89.62 kcal·mol^{-1} above the ground state so there is less likelihood of mixing between the excited and ground states than in HN$_3$H.

The N$_4$ species are all closed shell molecules with the two terminal N−N bonds being double bonds and the central N−N bond being a single bond. The latter bond in HN$_4$H is unusually long at 1.5126 Å, whereas the equivalent bonds in the other two molecules are typical single bonds. There are a considerable number of possible conformations for HN$_4$H, and the first geometry optimization performed in which all parameters were allowed to vary (assuming a symmetric structure) produced an $\angle HNNN$ = 177.98° and an $\angle NNNN$ = 79.18°, but this turned out to be only the minimum for conformations in which the HNNN dihedral angle was essentially that for a trans conforma-

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TABLE 6: Rotational and Centrifugal Distortion Constants of HN_nH, HN_nF, and FN_nF ($n = 3, 4$)[a]

parameter	HN_3H	HN_4H	HN_3F	HN_4F	FN_3F	FN_4F
$A^{(S)}$	5.386 582	1.764 730	2.361 623	0.990 901	1.404 511	0.848 426
$B^{(S)}$	0.389 103	0.185 028	0.173 736	0.097 683	0.085 686	0.052 881
$C^{(S)}$	0.362 888	0.167 470	0.161 832	0.093 485	0.080 760	0.051 285
$D_J \times 10^6$	0.1834	0.0620	0.0362	0.0441	0.0077	0.0120
$D_{JK} \times 10^5$	−0.4694	0.0954	0.0283	−0.1532	−0.0104	−0.1185
$D_K \times 10^4$	5.3735	0.1737	0.5932	0.3360	0.3421	0.4613
$d_1 \times 10^6$	−0.0204	−0.0051	−0.0035	−0.0111	−0.0008	−0.0025
$d_2 \times 10^8$	−0.10	−0.05	−0.04	−0.09	−0.01	−0.01

[a] All constants are in units of cm^{-1}. Rotational constants include distortion due to quartic centrifugal distortion constants. Rotational constants are in the S-reduced Hamiltonian.

tion. When other possible conformations were studied, the minimum energy conformation was the cis—trans—cis one given in Table 2, though the potential energy surface is quite flat. FN_4F appears to prefer a trans—trans—trans conformation, while HN_4F is the only species studied to show a preference for a clearly nonplanar structure about the central N—N bond, though once again the energy surface is quite flat.

For completeness we have also examined the biradical open-chain N_4 in its trans ^3B_u state. The terminal N—N bonds are double bonds, N=N = 1.1609 Å, while the central bond is single, N—N = 1.4656 Å, and ∠NNN = 117.93°. The a_g modes are the N=N (s) stretch at 2590.29 cm^{-1}, the N—N stretch at 742.77 cm^{-1}, and the NNN (s) bend at 524.96 cm^{-1}, all of which are infrared inactive. The infrared active modes are the a_u NNNN twist at 152.53 cm^{-1} (1.1) and the b_u modes, N=N (a) stretch at 4425.38 cm^{-1} (1567.8) and the NNN (a) bend at 271.18 cm^{-1} (24.1), the intensities being given in parentheses. The total energy is −218.377 449 hartrees, which is incidentally significantly less stable than the energy for two N_2 molecules calculated at the same level of theory (−218.594 017 hartrees), as is the case for the tetrahedral form of N_4.[7]

No imaginary frequencies were found for any of the structures determined, so all of them can be considered to represent true minima. The vibrational frequencies listed in Tables 3—5 are assigned using a combination of the normal coordinates, isotopic shifts (not all isotopic species used are listed: in addition to ^2H and ^{15}N pseudoisotopic fractional masses between 1 and 2 were used for hydrogen as well as pseudoisotopic masses for fluorine), and correlation of similar modes in related molecules. The rotational constants which are corrected for centrifugal distortion and the centrifugal distortion constants given in Table 6 should be of value to experimentalists in identifying these species.

In conclusion, HN_3H strongly resembles NO_2 in its structure, spin distribution, and in the presence of a low-lying excited $^2A_2$ state. The replacement of one or both of the hydrogens in HN_3H by fluorine alters the electron and spin distribution leading, specifically, in the case of FN_3F to a $^2A_2$ ground state and an NNN angle resembling that of the $^2A_2$ excited state of HN_3H. The species HN_4H, HN_4F, and FN_4F are characterized by multiple conformations on relatively flat potential energy surfaces. The biradical species N_4 in its trans planar structure has a significantly higher energy than two N_2 molecules.

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