Physical Chemistry

Ab initio calculations of the structure and harmonic force fields for the amine forms of dinitramine and methyldinitramine. Vibrational spectra and their interpretation using a scaling procedure

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Ab initio geometries and vibrational spectra have been calculated for the amine structures of dinitramine and methyldinitramine, $HN(NO_2)_2$ and $CH_3N(NO_2)_2$. It is shown at the RHF and MP2 levels with the use of the 6-31G* and 6-31G** basis sets that these molecules have different symmetries in their equilibrium states, C_s and C_1 respectively. The quantum chemical RHF/6-31G* force fields were scaled with the set of transferable factors previously obtained by the authors to assign the available experimental vibrational bands and predict the positions of bands for the unmeasured spectral regions. Some common patterns of the geometrical parameters, vibrational spectra, and force fields of the simplest nitramines are discussed.

Key words: dinitramines, quantum chemistry, molecular structures, force fields, vibrational spectra.

Nitramines are one of the most interesting classes of high-energy and biologically active compounds. For this reason, the special features of their molecular structure and spectra have been the focus of interest of researchers. However, obtaining experimental data on the simplest nitramines as model systems and their detailed interpretation very often involve insuperable difficulties.[1,2]

Dinitramine (**1**) is extremely unstable and reactive. No experimental investigations of its structure have been carried out. For the nonionized form **1**, the ultraviolet spectra (in the range of 200—250 nm) and the infrared spectra (in the range of 800—3300 cm^{-1}) of its solutions in organic solvents, as well as the low-temperature (~110 K) infrared spectra of the solid samples deposited *in vacuo* together with CH_2Cl_2 (in the range of 800—1700 cm^{-1}), were studied.[3] The analysis of the positions of the absorption bands in these spectra and their comparison with some literature data showed that, depending on the method of synthesis, **1** can be obtained in two

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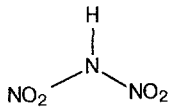
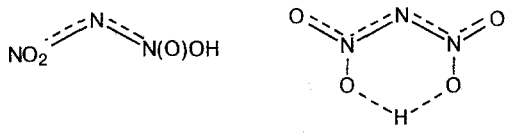
isomeric covalent forms, which differ in the location of the hydrogen atom:



1a

NH-form (amine)



1b or **1c**

OH-form (aci)

The infrared spectrum of the aci-form of **1** has no intense bands in the ranges of 1550—1650 and 1250—1350 cm^{-1}, which are characteristic of stretching vibrations of NO_2 groups. Hence it was concluded that "normal" nitro groups were completely absent in the identified aci-form, and the **1c** structure was suggested, in which the hydrogen atom forms equivalent bonds with the two oxygen atoms of different nitro groups.[3]

Recently a more complete infrared spectrum of **1** isolated in the Ar-matrix has been recorded in the range of 400—3400 cm^{-1}.[4] Only one fairly strong absorption band was found in the 3000 to 3600 cm^{-1} region corresponding to NH or OH stretching vibrations. This indicated that exactly one structural isomer was present under the experimental conditions. The observed frequency of the stretching band at 3347 cm^{-1} closely agrees with the $\nu(NH_2)$ frequencies at 3359 and 3478 cm^{-1} of the analogous spectrum of H_2NNO_2,[5] which is the most compelling evidence that the obtained[4] spectrum belongs to amine structure **1a**. A tentative assignment of some bands, mainly for NH-isomer stretching vibrations, was suggested,[4] using the vibrational assignment for H_2NNO_2 in Ref. 5 and the RHF/6-31G** frequency calculation.[6] However, no detailed interpretation of the discussed spectrum based on the quantum chemical force field[6] was performed. It should be noted that infrared spectra of the amine form,[3,4] which were registered under different conditions, are consistent and complement one another quite well (see below).

Ab initio calculations at the RHF and MP2 levels showed[6] that the equilibrium structure of **1a** belongs to the C_s symmetry group with the amine nitrogen atom having a pyramidal bond configuration and the NH bond being in the symmetry plane. As to the aci-forms, only the **1b** structure was calculated, in which the hydrogen atom forms a bond with only one oxygen atom. Four energy minima were obtained for the C_s conformations, which differ in the rotational angles of the $-NO_2$, $-N(O)OH$, and $-OH$ groups. According to the MP2/6-311+G**//MP2/6-31G** calculations, the amine form **1a** is more stable than the aci-form **1b** by 6 kcal/mol.[6]

The structure of the *N*-methyl substituted dinitramine $CH_3N(NO_2)_2$ (**2**) was investigated by the gas-phase electron diffraction method.[7] The analysis of trial models for a three-dimensional net of possible discreet values of rotational angles of the two nitro groups and the angle of CN bond deviation from the NNN plane showed that there are fairly many configurations of **2**, for which equally satisfying agreement with experiment can be achieved. The potential surface corresponding to these internal coordinates must have vast gently sloping valleys. Hence appears the necessity of considering intramolecular large-amplitude motions. Such an approach demands a reliable force field for calculating a large number of vibrational parameters for a molecular model. However, up to present, no force field of **2** and no strict interpretation of its vibrational spectra have been reported. Only recently, the infrared and Raman spectra of the parent substance (without isotopic substitution) have been published, the infrared spectra being obtained in a limited frequency range of 400—3100 cm^{-1}.[3,8] This is why the structural analysis of the electron diffraction data[7] could be performed only at the level of small-amplitude motions and even without any attempts to consider shrinkage effects. The C_s model with a pyramidal configuration of the amine nitrogen atom (the sum of its valence angles is $\Sigma_\alpha = 342.6°$, and the angle between the CN bond and the NNN plane is $\gamma = 42.2$ (20)°) and with a planar $N(NO_2)_2$ moiety showed a little better agreement with experiment.

In contrast to this, *ab initio* Hartree—Fock calculations[9] predicted a practically planar bond configuration for the amine nitrogen atom in $CH_3N(NO_2)_2$ when the 6-31G basis set was used ($\Sigma_\alpha = 359.4°$, $\gamma = 8.1°$) or a very weak pyramidal one in the case of the 6—31G* basis set ($\Sigma_\alpha = 355.4°$, $\gamma = 21.9°$). The NN bond length, even when polarization functions were included, proved to be considerably smaller than the experimental one (1.395 and 1.480(5) Å, respectively), which indicates the necessity of considering electron correlation. Conformational characteristics related to internal rotation of the NO_2 groups were not dealt with in the calculations.[9]

Thus, there are still a lot of obscurities in various aspects of the structure of the molecules **1** and **2**, and a complete interpretation of their vibrational spectra, *i.e.*, assignment of frequencies and other measured spectral parameters to particular structural units, have not been undertaken.

We have already noted the high efficiency of using *ab initio* force fields and the procedure of their scaling

with a small number of factors in the analysis of vibrational spectra of a series of nitro derivatives.[10,11] For three aliphatic nitramines and nitrobenzene a common set of scale factors was successfully obtained, which allowed us not only to reproduce the experimental frequencies well but also to define rather strictly the modes and the potential energy distributions of vibrations in terms of an unique basis, and therefore to assign the frequencies in the spectra of these compounds. It is all the more essential because an unambigous interpretation of the spectra by the traditional empirical methods of vibrational spectroscopy turned out to be impossible.

In this work the suggested approach is successfully extended to the analysis of vibrational spectra of the simplest dinitramines **1** and **2**. The harmonic force fields of their amine forms, together with the infrared and Raman intensities and the depolarization ratios, have been calculated for the equilibrium geometries optimized by the gradient method at the RHF/6-31G* level, which was used in analogous calculations before.[10,11] The force constants in the Cartesian coordinate system obtained from the analytical expressions for second derivatives of the SCF energy have been transformed into complete and nonredundant sets of standard internal coordinates of local symmetry. That should facilitate comparison of force constants in the series of related molecules.

Because the vibrational spectra of $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ were investigated incompletely and the spectral data for their isotopic modifications are entirely absent, an unambiguous solution of the inverse spectral problem is unrealistic even with the use of a scaling procedure. This is why we are compelled to confine ourselves to solving only the direct spectral problem. To this end, the standard set of scale factors that we recommended earlier[10] has been succesfully applied and their good transferability has been confirmed.

The equilibrium conformations of both molecules were optimized not only by the RHF method but also at the MP2 level involving electron correlation. All the *ab initio* calculations were carried out using the GAUSSIAN-92 series of programs,[12] and the spectral ones were performed with the help of the ANCO program.[13]

Experimental

The available experimental spectra of $CH_3N(NO_2)_2$[3,8] were supplemented with the long-wave infrared absorption spectra of the solid substance in pellets of chemically pure adamantane in the frequency range of 50—400 cm^{-1} and also with the infrared spectra of the liquid substance and solutions in dioxane and methylene chloride in the range of 400—3100 cm^{-1} (see below).* The spectra were registered on a Bruker IFS-113 vacuum IR Fourier spectrometer with a resolution of no more than 1 cm^{-1} and on a UR-20 spectrometer respectively.

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Table 1. Calculated geometrical parameters for $HN(NO_2)_2$ molecule in equilibrium conformation (C_s)

Parameter[a]	RHF/6-31G*[b]	RHF/6-31G**[c]	MP2/6-31G**[b]	MP2=FULL/6-31G**[c,d]
Bond		Bond length (Å)		
NH	1.0006	1.0001	1.0209	1.0199
NN	1.3937	1.3920	1.4602	1.4582
NO(5), NO(8)	1.1889	1.1891	1.2310	1.2301
NO(6),NO(7)	1.1733	1.1733	1.2224	1.2214
Valence angle		Angle value (degrees)		
HNN	109.87	—	105.39	—
NNN	121.30	121.60	115.27	115.26
ONO	128.66	—	129.69	—
NNO(5), NNO(8)	111.91	111.85	112.34	112.35
NNO(6), NNO(7)	119.35	119.45	117.81	117.80
Angle between bond and plane		Angle value (degrees)		
NN/ONO plane	3.2	—	4.4	—
NH/NNN plane	46.1	—	60.3	—
Dihedral angle		Angle value (degrees)		
O(5)NNH, O(8)NNH	±17.5	17.4	±20.7	20.5
O(6)NNH, O(7)NNH	∓165.6	—	∓163.4	—
O(5)NNN, O(8)NNN	±147.5	±148.4	±136.4	±136.4
O(6)NNN, O(7)NNN	∓35.5	∓34.6	∓47.7	∓47.7
Total energy (hartrees)	−463.052813	−463.056623	−464.312072	−464.333226

[a] Numbering of atoms is given in Fig. 1. [b] This work. [c] See Ref. **6**. [d] All electrons are included in a correlation energy calculation.

Results and Discussion

Equilibrium geometries of the amine structures of dinitramine and methyldinitramine

The *ab initio* geometrical parameters obtained for the equilibrium forms of $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ are compared with literature data in Tables 1 and 2. When analyzing structural characteristics we pay primary attention to three correlated factors: 1) molecular conformation defined by rotation of nitro groups, 2) degree of amine nitrogen atom pyramidality, which is characterized by the sum of its valence angles or by the angle between the NH(CN) bond direction and the NNN plane, and 3) NN bond lengths. The close interdependence of these structural characteristics of the simplest nitramines was discussed in particular in our previous publications[1,14,15] and can be explained using qualitative concepts of p-π conjugation.

The difference of the symmetry of the equilibrium amine forms **1** (C_s; the nitro groups are rotated by ~40—50° relative to the NNN plane) and **2** (C_1; different rotation angles of the nitro groups: by ~10—20 ° about the N(2)N(1) bond and by ~70—80 ° about the N(3)N(1) bond) appeared to be rather unexpected (see Fig. 1). The total energy of the equilibrium form of **2** is by 2 kcal/mol lower than that of the structure optimized with C_s symmetry. The latter conformation is a transition state of the nitro group rotations, since, unlike the C_s equilibrium form of **1**, the C_s structure of **2** is characterized by an imaginary frequency of one of the normal modes corresponding to these vibrations (therefore, motion along this coordinate lowers the total energy of the molecule).

In its turn, additional optimization of $HN(NO_2)_2$ geometry, starting with C_1 symmetry and the parameter values close to those obtained for the equilibrium form of $CH_3N(NO_2)_2$, led again to a stable conformation with C_s symmetry. In the equilibrium states of both molecules, virtually equal minimum distances between the oxygen atoms of the adjacent NO_2 groups (2.62—2.67 Å) are realized. They remain at the level of the sum of the van der Waals radii, irrespectively of the calculation method used (RHF or MP2). These distances considerably depend on the nitro group rotation angles as well as on the pyramidality of the amine nitrogen atom, which is apparently defined by the effective electronegativity of the substituents at the nitrogen atom.[14]

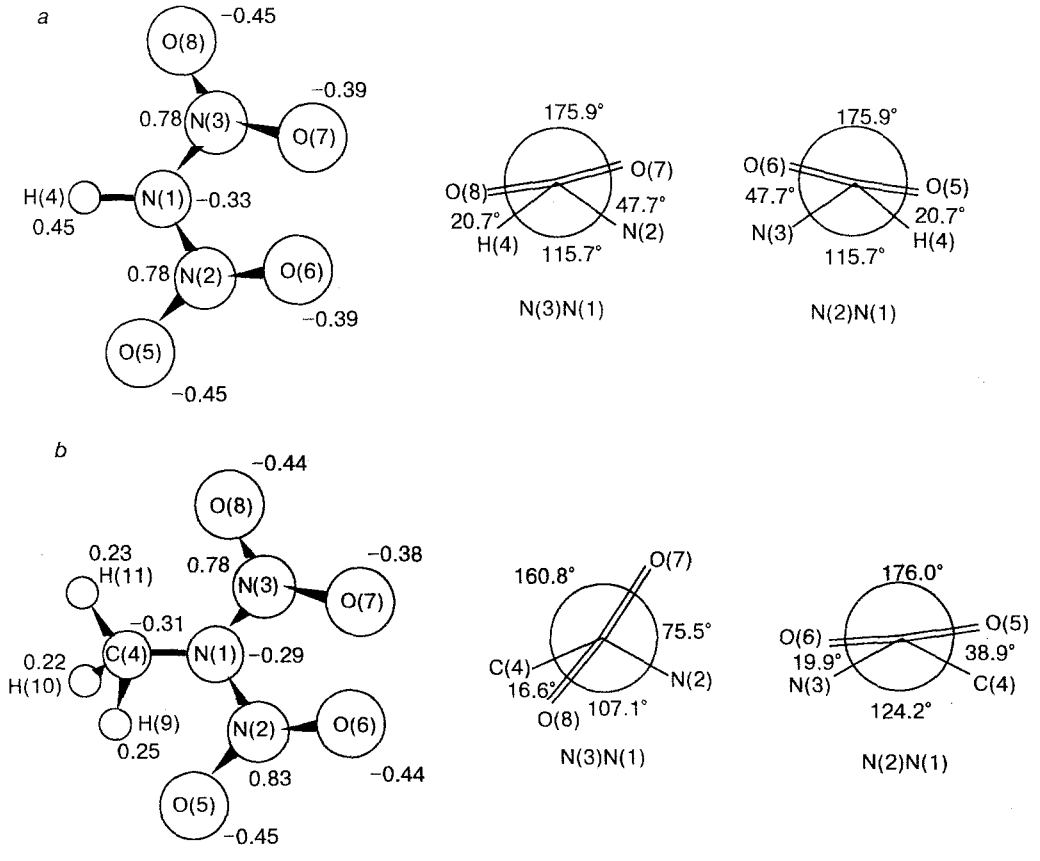

Fig. 1. Equilibrium conformations of the amine forms of dinitramine (*a*) and methyldinitramine (*b*): Mulliken atomic charges calculated at the RHF/6-31G* level, Newman projections of nitro groups with the values of dihedral angles, according to MP2/6-31G** calculation (see Table 2), which characterize internal rotation about the N(3)N(1) and N(2)N(1) bonds.

Table 2. Geometrical parameters of $CH_3N(NO_2)_2$ molecule in equilibrium conformation (C_1) and in transition state of nitro group internal rotations (C_s)

Parameter[a]	Calculation[b]			Experiment[c]
	RHF/6-31G*		MP2/6-31G**	
	C_1	C_s	C_1	C_s
Bond	Bond length (Å)			
CN	1.4718	1.4724	1.4675	1.494(6)
N(1)N(2)	1.3962	1.4012	1.4694	1.480(5)
N(1)N(3)	1.4163	1.4012	1.4765	
N(2)O(5)	1.1855	1.1898	1.2286	1.231(3)
N(2)O(6)	1.1803	1.1757	1.2259	
N(3)O(7)	1.1753	1.1757	1.2262	
N(3)O(8)	1.1868	1.1898	1.2314	
CH(10)	1.0802	1.0796	1.0882	1.121[d]
CH(11)	1.0768	1.0741	1.0851	
CH(9)	1.0746	1.0741	1.0831	
Valence angle	Angle value (degrees)			
CN(1)N(2)	115.11	116.29	111.59	112.8
CN(1)N(3)	115.32	116.29	112.28	
NNN	112.54	117.50	108.39	117.0(11)
ON(2)O	127.58	126.94	128.71	132.0(10)
ON(3)O	128.11	126.94	128.99	
N(1)N(2)O(5)	114.02	113.88	113.55	114.0
N(1)N(2)O(6)	118.40	119.11	117.65	
N(1)N(3)O(7)	115.76	119.11	114.37	
N(1)N(3)O(8)	116.00	113.88	116.58	
NCH(10)	111.80	111.70	112.73	111.4
NCH(11)	106.88	106.95	106.60	
NCH(9)	106.85	106.95	106.58	
H(9)CH(11)	109.79	110.00	109.77	107.5(15)
H(9)CH(10)	111.20	110.56	110.93	
H(10)CH(11)	110.18	110.56	110.09	
Angle between bond and plane	Angle value (degrees)			
N(1)N(2)/ON(2)O plane	0.4	2.7	3.1	0.0[d]
N(1)N(3)/ON(3)O plane	3.9	2.7	2.7	
CN/NNN plane	39.9	31.4	50.3	42.2(20)
Dihedral angle	Angle value (degrees)			
O(5)NNC	40.4	2.1	38.9	—
O(6)NNC	−140.0	−180.7	−144.1	—
O(7)NNC	−156.5	180.7	−160.8	—
O(8)NNC	19.8	−2.1	16.6	—
O(5)NNN(3)	174.9	—	163.1	180.0[d]
O(6)NNN(3)	−5.5	—	−19.9	0.0[d]
O(7)NNN(2)	68.9	—	75.5	0.0[d]
O(8)NNN(2)	−114.8	—	−107.1	180.0[d]
H(9)CNN(3)	166.8	—	173.4	C_{3v} local symmetry of the methyl group
H(10)CNN(3)	−71.4	—	−64.7	
H(11)CNN(3)	49.3	—	56.2	
H(9)CNN(2)	−59.5	—	−64.7	
H(10)CNN(2)	62.4	—	57.2	
H(11)CNN(2)	−177.0	—	178.1	
Total energy (hartrees)	−502.083403	−502.080328	−503.491826	—

[a] See footnote[a] to Table 1. [b] This work. [c] Gas phase electron diffraction,[7] r_a-structure. [d] Fixed parameter.

The degree of the amine nitrogen pyramidality changes insignificantly (Table 3), but in the case of $CH_3N(NO_2)_2$, a sizable diminution of the NNN valence angle occurs (by 7—9°, Tables 1 and 2). As a result of the two nitro groups coming together, each of them rotates by ~30° counterclockwise with symmetry lowering of the $CH_3N(NO_2)_2$ equilibrium structure (see Fig. 1). According to our calculations, the preservation

of C_s symmetry requires a flattening of the amine nitrogen configuration in this molecule, owing mostly to a 5° increase of the NNN angle (Table 2), but nevertheless the minimum distance O...O between the adjacent NO_2 groups decreases by about 0.15 Å compared the C_1 equilibrium structure.

Note that in Ref. **9** the RHF/6-31G and RHF/6-31G* calculations are apparently carried out for the C_s amine form of **2**, though the authors do not mention this. The 6-31G* geometrical parameters they obtained are very close to those that we found with the preservation of C_s symmetry of this molecule, and the total energy (−502.075 hartrees) is even a little higher than in our calculation.

The data in Tables 2 and 3 show that the inclusion of electron correlation at the MP2 level considerably removes the discrepancy with experiment concerning the NN and NO bond lengths. Using the 6-31G* and 6-31G** basis sets with polarization functions makes it possible to obtain the upper and lower bounds of a narrow interval of estimates of amine nitrogen pyramidality by the MP2 and RHF methods respectively. Therefore, it can be claimed that the results of such calculations quite adequately reflect not only the changes of the geometrical parameters, which take place in related molecules, but also their magnitudes.

It follows from Table 3 that the difference in effective electronegativities of substituents at nitrogen atom is a factor, that determines to a great extent the length of the very labile NN bond and the amine nitrogen configuration in nitramines. An increase in the electronegativity of substituents leads to a reduction of the substituted amino group electron-donor properties and the p—π conjugation between the lone electron pair of the amine nitrogen atom and the π-system of the NO_2 fragment. This manifests itself in an elongation of the NN bonds and a decrease of the sum of valence angles of amine nitrogen atom (*i.e.*, in a larger pyramidality of amino group). In the amine forms of **1** and **2** both the considered parameters have values characteristic of hydrazine and some of its methylsubstituted derivatives (1.43—1.45 Å and 320—330° respectively).[20—23] For the hypothetical trinitramine, the calculation[19] predicts a further intensification of this effect (see Table 3).

At the same time, the concept of p—π conjugation alone is insufficient for explaining some geometrical changes. Thus, in mononitramines the passage from secondary to tertiary amine derivatives by way of introducing a methyl substituent, which is more bulky compared with the hydrogen atom, flattens the amine nitrogen configuration noticeably, but influences the NN bond length rather insignificantly. However, the introduction of a methyl substituent in dinitramine causes unequal elongations of the two NN bonds, apparently by virtue of the steric and conformational features considered above. A deviation of $CH_3N(NO_2)_2$ equilibrium structure from C_s to C_1 symmetry and, as a consequence of this, non equivalence of the two N—NO_2 fragments lead in particular to a difference of about 0.01 Å in their NN bond lengths.

Figure 1 shows the Newman projections of the nitro groups along NN bonds for the equilibrium amine forms of **1** and **2**. Both nitro groups in **1** and one of them (ON(2)O) in **2** are located favorably for p—π interaction with the amine nitrogen atom, which is typical of the simplest mononitramines.[1,14,15] It is of interest that, if the nitro groups are in a favorable position for p—π interaction, the NN bonds of **1** and **2** are similar in length. But such a bond between the amine nitrogen atom and the ON(2)O nitro group in $CH_3N(NO_2)_2$ is shorter than the bond with the ON(3)O nitro group located unfavorably for p—π interaction.

Table 3. NN bond lengths (Å) and sums of amine nitrogen valence angles (Σ_α, degrees) in the simplest nitramines according to the experimental data and the results of *ab initio* calculations for equilibrium structures

Molecule	Experiment					Calculation				
	Method	Parameter	r(NN)	Σ_α	References	RHF/6-31G* r(NN)	RHF/6-31G* Σ_α	MP2/6-31G* r(NN)	MP2/6-31G* Σ_α	References
Primary and secondary amines										
CH_3NHNO_2	GED	r_a	1.381(6)	Not found out	17	1.346	346.9	1.389	340.2	14
H_2NNO_2	MW	r_o	1.427(2)	334.0(20)	17,18	1.356	338.0	1.399	330.9	14
		r_o	1.381	340.3						
$HNClNO_2$	—	—	—	—	—	1.384	335.8	1.449	326.3	14
$HN(NO_2)_2$	—	—	—	—	—	1.394	341.0	1.460[a]	326.1[a]	This work
Tertiary amines										
$(CH_3)_2NNO_2$	GED	r_a	1.382(3)	360.0(6)	16	1.344	351.8	1.387	346.0	14
CH_3NClNO_2	GED	r_a	1.469(5)	336.3(15)	17	1.381	344.3	1.447	335.3	14
$CH_3N(NO_2)_2$	GED	r_a	1.480(5)	342.6(11)	7	1.396	343.0	1.469[a]	332.3[a]	This
						1.416		1.477[a]		work
$N(NO_2)_3$	—	—	—	—	—	1.444	332.7	1.545	315.6	19

[a] MP2/6-31G** calculation.

A transferable set of scale factors and the interpretation of the experimental spectra of the amine forms of dinitramine and methyldinitramine

RHF calculations using double zeta basis sets in the valence shell augmented by polarization functions yield harmonic force constants for simple well-studied molecules within an accuracy of typically 10—30 %, their values always being overestimated. Calculation errors are caused mainly by incompleteness of the basis set used and failure to consider electron correlation. Scaling the force field with a small number of factors to fit experimental vibrational frequencies allows these errors to be compensated effectively, although at the same time a certain error is made because of an insufficiency of the harmonic approximation. For analogous internal coordinates in related molecules, overestimation of the force constants obtained by the same *ab initio* method is of a quantitative systematic nature. Hence, scale factors, as distinct from force constants themselves, must be readily transferable.

In spite of the above noted incompleteness of the experimental spectra for the amine forms of the simplest dinitramines **1** and **2**, solving the direct spectral problem with the use of the recommended[10] set of transferable scale factors for the RHF/6-31G* force fields allowed us to assign the available experimental vibrational bands reliably and predict band position in the unmeasured spectral regions. As long as our experience in using the RHF/6-31G* force fields of mononitramines showed[10] that the majority of scale factors does not go beyond the limits of 0.75—0.85, we considered it justified to set the missing value of the factor for the NNN bending internal coordinate equal to 0.80.

In a systematic analysis of the spectra of related compounds it is convenient to use nonredundant sets of standard internal coordinates of local symmetry.[24] Such coordinates for $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ were chosen with regard for our previous studies of some nitro derivatives.[10,11]

Due to the scaling, good agreement between the calculated and experimental data has been achieved (see Tables 4 and 5). This concerns not only the frequency values but also the infrared and Raman intensities and depolarizations. For assignment of the spectral bands, calculations of modes and potential energy distributions for normal vibrations have been used. Because many normal vibrations show a high degree of mixing, the assignments made sometimes reflect only the main contributions and are therefore rather conventional. In contrast to the more symmetric $HN(NO_2)_2$ (C_s), in $CH_3N(NO_2)_2$ (C_1) the participation of two nonequivalent

Table 4. Experimental and calculated spectral parameters for $HN(NO_2)_2$ molecule

Symmetry type	No.	Experiment,[a] ν/cm^{-1}			Calculation (this work)[b]				
		Matrix isolation		Solutions (CH_2Cl_2, ether) IR[3]	Frequency, ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
		Ar IR[4]	CH_2Cl_2 IR[3]			IR / km mol^{-1}	Raman / Å^4 a.m.u.$^{-1}$		
A′	1	3347(166)	—	3295 s	3401.9	126.5	21.4	0.19	100 NH(str)
	2	1670(1000)	1660 s	1645 s	1659.6	978.8	4.1	0.45	84 NO_2(as.str synph) 9 NO_2(s.rock)
	3	1334(34)	1355 vw	—	1357.6	21.2	20.8	0.10	78 NO_2(s.str synph) 15 ONO(s.bend) 7 NN(s.str)
	4	1047 v.w	1045 w	—	1018.7	30.4	10.2	0.16	30 NNN(NH)(wag) 21 NO_2(s.str synph) 19 NN(s.str) 18 NO_2(s.rock) 4 ONO(s.bend)
	5	864 (433) 819 (125)	835 w	835 m	833.7	72.1	3.0	0.13	59 ONO (s.bend) 15 NO_2(s.str.synph) 8 NO_2(s.rock) 8 NNN(NH)(wag) 5 NN(s.str)
	6	778 (57)	—	—	785.9	123.8	1.6	0.18	78 NO_2(s.wag) 10 NNN(NH)(wag) 9 NNN(bend)
	7	623 (47) 615 (75)	—	—	652.0	47.8	0.7	0.63	27 NO_2(s.rock) 26 NNN(NH)(wag) 19 NO_2(s.tors) 18 NO_2(s.wag)

Table 4 (*continued*)

Symmetry type	No.	Experiment,[a] ν/cm^{-1}			Calculation (this work)[b]				
		Matrix isolation		Solutions (CH_2Cl_2, ether)	Frequency, ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
		Ar IR[4]	CH_2Cl_2 IR[3]	IR[3]		IR km mol^{-1}	Raman $Å^4$ a.m.u.$^{-1}$		
	8	400(53)	—	—	443.7	0.8	5.5	0.28	66 NN(s.str) 20 ONO(s.bend) 16 NO_2(s.rock)
	9	—	—	—	254.6	3.2	0.6	0.37	62 NNN(bend) 22 NO_2(s.rock) 9 NO_2(s.tors)
	10	—	—	—	120.3	11.1	0.9	0.75	65 NO_2(s.tors) 20 NNN(NH)(wag) 17 NNN(bend)
A″	11	1646 (92)	1630 sh	1625 s	1643.2	141.6	0.1	0.75	58 NO_2(as.str antiph) 36 NNN(NH)(twist)
	12	—	1388 vw	1390 w	1391.5	227.2	0.2	0.75	56 NNN(NH)(twist) 42 NO_2(as.str antiph)
	13	1251 (642)	1250 m	1255 m	1283.8	382.9	2.0	0.75	84 NO_2(s.str antiph) 9 ONO(as.bend) 5 NNN(NH)(twist)
	14	1012 (45)	945 m	910 m	993.0	198.7	0.1	0.75	76 NN(as.str) 9 NO_2(s.str antiph) 7 ONO(as.bend)
	15	730 (6)	—	—	745.0	73.0	1.4	0.75	69 ONO(as.bend) 17 NO_2(as.wag) 5 NN(as.str) 5 NO_2(as.rock)
	16	714 (8)	—	—	731.3	2.0	0.7	0.75	81 NO_2(as.wag) 11 ONO(as.bend)
	17	400 (53)	—	—	426.4	1.7	3.4	0.75	83 NO_2(as.rock) 11 NN(as.str)
	18	—	—	—	27.0	0.0	0.4	0.75	98 NO_2(as.tors)

[a] Intensities of IR[4] bands (in parentheses) were estimated relative to the strongest absorption band with a conditional intensity of 1000. The notations are generally used. [b] Frequencies and potential energy distributions for normal vibrations have been obtained by solving the direct spectral problem with the use of scaling of the *ab initio* force field with the recommended set of scale factors.[10] Vibration notations: str — stretching; bend — bending; wag — wagging; rock — rocking; tors — torsional; def — deformation for methyl group; s — symmetrical; as — antisymmetrical; synph and antiph — synphase and antiphase.

nitro groups in certain normal vibrations is not always of equal value, and in some cases we can speak only about separate contributions of each of the nitro groups (see Table 5).

The passage from mono- to dinitramines is accompanied by splitting of the spectral bands, which correspond to nitro group vibrations, into two components (see Fig. 2). Splitting values $\Delta\nu$ generally increase in the spectra of **1a** compared with the spectra of **2a** and can reach about 200—300 cm^{-1}, as in case of the nitro group rocking or bending vibrations. The frequency of one of the components remains in the spectral region characteristic of the given nitramine vibration, whereas the second component usually has a lower frequency.

The frequencies of the stretching vibrations $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ in dinitramine spectra split into synphase and antiphase components, the synphase one being in a more high-frequency range. The infrared bands of the synphase $\nu_s(NO_2)$ vibration in both molecules are of a medium intensity, whereas in the Raman spectra this vibration corresponds to very intense and polarized bands. In accordance with the calculations, the infrared bands of the other three stretching vibrations of nitro groups (the antiphase symmetric, the synphase and antiphase antisymmetric modes) must be very intense, contrary to rather weak and essentially depolarized bands of these vibrations in the Raman spectra. The antiphase $\nu_{as}(NO_2)$ vibrations must be virtually inactive in the Raman spec-

Table 5. Experimental and calculated spectral parameters for $CH_3N(NO_2)_2$ molecule[a]

No.	Experiment, ν/cm^{-1}				Calculation (this work)				
	Gaseous phase IR[3,8]	Liquid, solutions, or solid phase		Depolarization ratio	Frequency, ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
		IR (this work)	Raman[8]			IR, km mol^{-1}	Raman, Å^4 a.m.u.$^{-1}$		
1	—	—	3058 w	0.63	3077.4	0.1	49.3	0.72	88 CH_3(as.str′) 10 CH_3(as.str)
2	3020 w	3055 w	3042 w	0.47	3045.9	6.0	48.2	0.60	82 CH_3(as.str) 12 CH_3(as.str′) 6 CH_3(s.str)
3	2960 w	2960 w	2968 vs	0.05	2957.4	10.3	87.4	0.03	91 CH_3(s.str) 8 CH_3(as.str)
4	1652 vs, B	1645 vs	1646 w	—	1637.5	743.3	2.5	0.46	86 NO_2(as.str synph) 9 NO_2(s.rock)
5	1630 s, br	1605 vs	1608 w	—	1578.0	467.7	0.3	0.47	90 NO_2(as.str antiph) 6 NO_2(as.rock)
6	1462 sh	1475[b] w	1452 m	0.77	1476.2	25.4	10.8	0.75	60 CH_3(as.def′) 30 CH_3(as.def) 7 CH_3(rock′)
7	1455 w	1448 m			1469.9	48.2	9.2	0.54	58 CH_3(as.def) 27 CH_3(as.def′) 6 CH_3(rock) 5 CH_3(s.def)
8	1422 w	1416 m	1418 m	0.24	1431.3	31.3	5.1	0.32	78 CH_3(s.def) 13 NO_2(s.str synph)
9	1320 m	1324 m	1327 vs	0.09	1353.6	38.0	16.3	0.18	67 NO_2(s.str synph) 17 CH_3(s.def) 10 ONO(s.bend)
10	1258 vs	1250 s	1255 w	0.85	1300.5	413.9	7.4	0.65	83 NO_2(s.str antiph) 10 ONO(as.bend) 5 NN(as.str)
11	—	1233[b] m	—	—	1201.1	8.8	0.7	0.70	58 CH_3(rock′) 11 NN(as.str) 9 NNN(CN)(twist) 8 CH_3(as.def′) 7 NO_2(s.str antiph)
12	1160 w, C	1162 w	1142 w	—	1170.0	5.2	2.7	0.55	35 CN(str) 28 CH_3(rock) 8 NO_2(as.str synph) 7 NN(s.str) 7 NO_2(s.rock) 5 NNN(CN)(wag)
13	1080 vw, A	1072 w, br	1080 vw	—	1107.7	19.3	2.8	0.51	61 CH_3(rock) 17 CN(str) 6 CH_3(as.def) 5 NN (s.str)
14	—	922[c] w	—	—	929.5	161.8	1.1	0.64	48 NN(as.str) 19 ONO(as.bend) 18 CH_3(rock′) 9 NO_2(s.str antiph)
15	—	860 s	859 vs	0.08	860.5	27.1	9.4	0.07	61 ONO(s.bend) 19 NO_2(s.str synph) 14 NN(s.str)
16	825 vs, br	830 s,br	825 vw, sh.	—	789.9	34.1	1.4	0.16	75 NO_2(s.wag) 11 NNN(bend) 6 CN(str)

Table 5 (*continued*)

No.	Experiment, ν/cm^{-1}				Calculation (this work)				
	Gaseous phase IR[3,8]	Liquid, solutions, or solid phase		Depolarization ratio	Frequency, ν/cm^{-1}	Intensity		Depolarization ratio	Potential energy distribution (%)
		IR (this work)	Raman[8]			IR, km mol^{-1}	Raman, $Å^4$ a.m.u.$^{-1}$		
17	—	780 m	779 w	—	748.2	15.6	0.7	0.70	48 NO_2(as.wag) 24 ONO(as.bend) 7 CN(str) 6 NNN(CN)(twist)
18	—	710[b]m	704 w	—	733.7	38.6	2.8	0.73	40 ONO(as.bend) 38 NO_2(N(1)N(2))(wag) 7 NO_2(as.rock) 6 NN(as.str)
19	580 m	565 s	597 w	0.23	586.0	29.2	4.8	0.34	40 NO_2(s.rock) 27 CN(str) 8 NO_2(N(1)N(3))(wag) 6 N1N2(str) 6 NNN(CN)(wag) 5 ONO(s.bend)
20	535 w	525 w	—	—	519.0	2.0	2.8	0.46	54 NO_2(as.rock) 30 N(1)N(2)(str) 8 ON2O(bend)
21	—	430 w	433 s	0.28	441.7	0.9	5.9	0.38	50 NN(s.str) 33 NO_2(N(1)N(2))(rock) 15 ONO(s.bend)
22	—	371[d]	346 vw	0.75	359.8	1.7	0.1	0.74	69 NNN(CN)(twist) 10 CH_3(tors) 9 NO_2(as.rock) 6 NN(as.str)
23	—	264[d]	250 m	0.48	266.6	7.3	0.6	0.60	42 NNN(bend) 23 NNN(CN)(wag) 14 NO_2(s.rock) 10 NO_2(N(1)N(3))(wag) 5 NO_2(N(1)N(3))(tors)
24	—	244[d]	—	—	231.8	2.5	1.0	0.67	63 NNN(CN)(wag) 27 NNN(bend) 6 NO_2(N(1)N(3))(tors)
25	—	211[d]	—	—	199.3	0.1	0.2	0.75	88 CH_3(tors) 9 NNN(CN)(twist)
26	—	78[d]	77[c] s	—	72.7	0.5	2.8	0.75	92 NO_2(as.tors) 4 NNN(bend)
27	—	—	—	—	29.1	4.3	1.4	0.75	95 NO_2(s.tors) 4 NNN(bend)

[a] See footnotes[a,b] to Table 4; A, B, C are the types of contours of vibrational-rotational bands in IR spectra of gaseous phase. Numbering of atoms corresponds to Fig. 1. [b] IR spectra of the solutions in dioxane and methylene chloride. [c] Spectra of the crystalline phase.[8] [d] Far IR spectra of the crystalline phase.

tra. All this corresponds to the experimental data very well (Tables 4 and 5).

An analogous ratio of NO_2 stretching band intensities and depolarizations was also found in the spectra of the simplest gem-dinitroalkanes $CH_2(NO_2)_2$ and $CH_3CH(NO_2)_2$.[2] It should be mentioned, however, that no splitting of antisymmetric NO_2 stretching bands was observed in these spectra. The modes of all the fundamentals assigned to nitro group stretching vibrations in $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ are quite characteristic. Vibrations mix mostly within the $N(NO_2)_2$ fragment. But the antiphase stretching vibrations of NO_2 groups in **1a** are also considerably mixed with the twisting vibration of the amino group, while the synphase $\nu_s(NO_2)$ vibration in **2a** is mixed with the symmetric deformation of the methyl group.

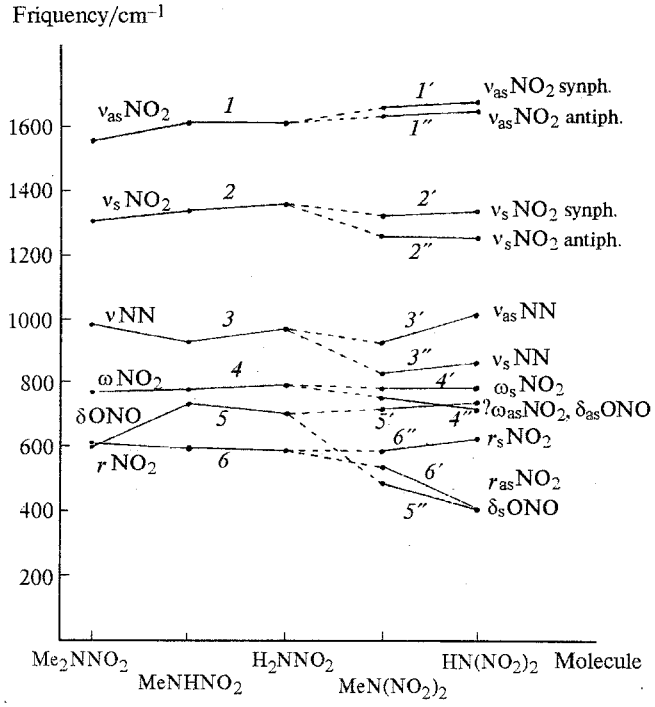

Fig. 2. Vibrational frequencies of NNO_2 and $N(NO_2)_2$ fragments in the simplest mono- and dinitramines.

The contributions of NN stretching vibrations in $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ are essentially delocalized and appear to some extent in most of the fundamentals. Unlike the $\nu_{as}(NN)$ vibrations, which are quite characteristic in both molecules and the interpretation of which is unambigous (the bands ν_{14}, Table 4, and ν_{14}, Table 5), the assignment of the $\nu_s(NN)$ vibrations to the lower frequencies ν_5 (Table 4) and ν_{15} (Table 5) is to a great extent conventional. We took into account that the corresponding fundamentals represent the totally symmetrical vibrations of $N(NO_2)_2$ moiety and the bands ν_5 (Table 4) and ν_{15} (Table 5) themselves are arranged near the characteristic spectral region of the analogous totally symmetrical vibrations of $N—NO_2$ fragments in mononitramines.[10] The ν_{15} band in the spectra of **2a** corresponds to the only totally symmetrical vibration of the $N(NO_2)_2$ moiety with an appreciable contribution of the $\nu_s(NN)$ vibration.

In the spectra of $HN(NO_2)_2$ the totally symmetrical modes correspond not only to the ν_5 band but also to the ν_4 one. The wagging vibration of the amine fragment noticeably contributes to both these normal vibrations, as well as to a series of other $HN(NO_2)_2$ fundamentals of A′ symmetry type. The suggested assignment of the ν_5 band to the $\nu_s(NN)$ vibration allows an analogy in the interpretation of the vibrational spectra of **1a** and **2a** to be retained. The ν_4 frequency in the spectra of $HN(NO_2)_2$ is higher than the ν_{14} frequency assigned to the $\nu_{as}(NN)$ vibration. If we preferred the ν_4 band, we would come to a mutually opposite arrangement of the bands assigned to the $\nu_{as}(NN)$ and $\nu_s(NN)$ stretching vibrations in the spectra of the two simplest dinitramines. Therefore, we assign the ν_4 band to the wagging vibration of the amine fragment, which is considerably mixed with the totally symmetrical vibration of the $N(NO_2)_2$ moiety (Table 4).

The frequencies of the wagging and twisting vibrations of the amine fragment of $HN(NO_2)_2$ (the ν_4 and ν_{12} bands, Table 4) are essentially higher than the frequency of the NNN bending vibration (the ν_9 band, Table 4), since the NH bond is considerably involved into both of these fundamentals, as distinct from the ν_9 band. The low-frequency deformation vibrations of the amine fragment of $CH_3N(NO_2)_2$ (the ν_{22}, ν_{23} and ν_{24} bands, Table 5) are mixed with each other to different extents.

As in case of mononitramines,[10] the NN stretching vibrations make a significant contribution to some bands in the range of 400—600 cm^{-1}, which is characteristic of deformation vibrations. In the spectrum of $HN(NO_2)_2$, one band at 400 cm^{-1} (ν_8) contains a contribution of the $\nu_s(NN)$ vibration (Table 4). For $CH_3N(NO_2)_2$ there are already two such bands: at 535 cm^{-1} (ν_{20}) with a separate contribution of the N(1)N(2) bond stretching vibration, and at 430 cm^{-1} (ν_{21}) with a $\nu_s(NN)$ contribution (Table 5).

However, the ν_8 band in the spectrum of **1a** and the ν_{21} one in the spectrum of **2a** are not related to the totally symmetrical vibration of the $N(NO_2)_2$ moiety, since they do not contain a contribution from nitro group stretching vibrations: the $\nu_s(NN)$ vibration is mixed here only with the nitro group deformations. In particular, there is a noticeable contribution from the $\delta_s(ONO)$ bending vibration, to which we assign the discussed bands. Although the calculated proportions of mixing in these vibrations, both in this case and in the case of the totally symmetrical fundamentals, are opposite to the assignment we have suggested, the very existence of this interconnection serves as some additional argument in favor of the considered interpretation of the spectral bands.

Rather mixed modes, which reflect nonequivalence of the nitro groups of **2a**, correspond to the ν_{20} and ν_{21} bands in its spectra. The frequency of 535 cm^{-1} (ν_{20}) is to a large extent defined by the $r_{as}(NO_2)$ rocking vibration. An analogous fundamental in the spectrum of $HN(NO_2)_2$ is more characteristic, and its frequency, according to the calculation, is by 100 cm^{-1} shifted to the low-frequency region (ν_{17}, Table 4). To this vibration we assign the same experimental band at 400 cm^{-1} as to the $\delta_s(ONO)$ vibration (ν_8, Table 4).

In the spectra of the simplest dinitramines, the $\delta_{as}(ONO)$ bending and $\omega_{as}(NO_2)$ wagging vibrations are considerably mixed with each other. Both the calculated and experimental frequencies, assigned to these vibrations (ν_{15} and ν_{16}, Table 4; ν_{17} and ν_{18}, Table 5), are very close in value, and the available data do not allow to identify them with confidence (see Fig. 2).

Rather complicated vibrational modes correspond to the bands assigned to the $\omega_s(NO_2)$ wagging and especially to the $r_s(NO_2)$ rocking vibrations (ν_6 and ν_7, Table 4; ν_{16} and ν_{19}, Table 5). A mixture chiefly with amine fragment deformations takes place, and in the case of $CH_3N(NO_2)_2$ with the ν(CN) stretching vibration as well. Actually, the latter is very delocalized, and in the ν_{12} fundamental assigned to this vibration its essential mixture with the methyl group rocking vibration appears (Table 5).

In this work, for the first time the frequencies of the torsional vibrations of **1a** (ν_{10} and ν_{18}, Table 4) and **2a** (ν_{25}, ν_{26} and ν_{27}, Table 5) are reliably predicted. Some of these predictions are verified experimentally (see Table 5). All the torsional vibrations of the studied molecules are highly characteristic, only the $\chi_s(NO_2)$ torsional vibration in $HN(NO_2)_2$ (the ν_{10} band, Table 4) being mixed with the amine fragment deformations.

The scaled quantum chemical force fields of nitramines

The validity of quantum chemical force fields and the reliability of the procedure of scaling them are confirmed by vast experience.[25] The agreement achieved in this work between the theoretical and experimental spectra of the amine forms of **1** and **2** demonstrates the effectiveness of using a transferable set of scale factors in normal coordinate analysis. This idea allowed us not only to fulfill an assignment of fundamental bands, but also to predict the frequencies missing in the experiment. Therefore, the analysis of both the structure of the potential energy matrices and the patterns of the changing of some force constants in a series of nitramine derivatives seems to be well-grounded and demonstrative.

A comparison of the harmonic force fields of $HN(NO_2)_2$ and $CH_3N(NO_2)_2$ with the data for the simplest mononitramines $(CH_3)_2NNO_2$, CH_3NHNO_2 and H_2NNO_2[10] confirms the resemblance of the general structures of the potential energy matrices of various nitramines. They are all characterized by the presence of very large interactions between internal coordinates within the $N—NO_2$ fragment, in particular, NO(str)/NO(str) (1.4—1.6 mdyn $Å^{-1}$), NO(str)/NN(str) (0.7—1.0 mdyn $Å^{-1}$), NO(str)/ONO(bend) (0.2—0.4 mdyn), NO(str)/NO_2(rock) (±0.3—0.5 mdyn), NN(str)/ONO(bend) (from −0.7 up to −0.5 mdyn).* As a rule, there are no large interactions between nitro and amino group coordinates (>0.2 in the corresponding units).

In mononitramines the stretching vibration of the central NN bond interacts with the stretching vibrations of the adjacent CN bonds (0.2 mdyn $Å^{-1}$) and with the deformation vibrations of the amino group (0.2—0.8 mdyn). Accordingly, the increasing number of nitro groups in the molecule leads to the appearance of large interactions between the stretching vibrations of the adjacent NN bonds (0.3—0.4 mdyn $Å^{-1}$), and also with the NNN bending vibration (0.6—0.7 mdyn). Such significant interactions do not take place between internal coordinates of different nitro groups. In mono- as well as in dinitramines, the stretching vibrations of CN bonds are characterized by large interactions with the deformation vibrations of the amine fragment (up to ±0.4 mdyn) and methyl substituents (CH_3(s.def) from −0.5 up to −0.4 mdyn).

Changes of force constants, just as those of geometry, must to a sufficient extent reflect the differences in the electronic structures of molecules. In Table 6, the diagonal force constants characterizing $N—NO_2$ fragments in various nitramines are displayed. All the constants are found by means of scaling the *ab initio* force fields (RHF/6-31G*) transformed into sets of standard internal coordinates of local symmetry,[24] which makes them comparable. A comparison of the force constants for stretching vibrations of both NO and NN bonds as well as for NO_2 group torsional vibrations clearly demonstrates a general tendency for successive decrease of p—π conjugation as the effective electronegativity of the amine nitrogen substituents increases. The same tendency has been indicated by comparing the geometrical parameters of the simplest nitramines (see above, Table 3).

On the other hand, attention should be paid to the fact that in $CH_3N(NO_2)_2$, the force constants for the torsional vibrations of both nitro groups are increased as compared with those for the more symmetric $HN(NO_2)_2$ molecule, although in the first of them, the NN bonds are longer (Table 3), and the stretching force constants of these bonds are a little less (Table 6). Moreover, for $CH_3N(NO_2)_2$ itself an analogous contradiction, concerning its two nonequivalent nitro groups, takes place. All this may be related to steric strain, which has already been discussed when the equilibrium geometries for **1a** and **2a** have been considered. Judging from the large value of its torsional force constant (0.147 mdyn Å, Table 6), the ON(3)O nitro group in $CH_3N(NO_2)_2$ must undergo much more essential steric strain than the ON(2)O one. This can cause both elongation of the N(1)N(3) bond up to 1.477 Å (Table 3) and noticeable increase in the off-diagonal force constants for the interactions of the ON(3)O nitro group torsional vibration with the N(1)N(2) stretching vibration (0.21 mdyn) and NNN bending vibration (0.31 mdyn Å), as well as an increase in the magnitude of the constant of the interaction between the ON(3)O torsional vibration and the rocking vibration of the adjacent nitro group (−0.16 mdyn Å).

The changing of the mutual orientation of the adjacent nitro groups in $CH_3N(NO_2)_2$ compared with $HN(NO_2)_2$ (Fig. 1) leads to a decrease by one half in the magnitude of the interaction constant of their rocking vibrations (−0.11 against −0.19 mdyn Å). It occurs

* See the vibration notations in Table 4.

Table 6. Scaled *ab initio* force constants of N-NO_2 fragment of nitramines[a]

Molecule	Symmetry		Force constants						References
			NO(str)	NN(str)	NO_2(wag)	ONO(bend)	NO_2(rock)	NO_2(tors)	
			Primary and secondary amines						
CH_3NHNO_2	C_1		8.94 9.16	5.23	0.57	2.19	1.45	0.208	10
H_2NNO_2	C_s		9.28	4.91	0.55	2.11	1.36	0.175	10
$HN(NO_2)_2$	C_s		9.40 10.40	4.22	0.50	2.08	1.38	0.096	This work
			Tertiary amines						
$(CH_3)_2NNO_2$	C_s		9.07	5.25	0.58	2.15	1.62	0.195	10
$CH_3N(NO_2)_2$	C_1	ON(2)O group	9.57 9.92	4.22	0.52	2.16	1.53	0.103	This work
		ON(3)O group	10.36 9.60	3.92	0.50	2.08	1.36	0.147	

[a] Force constants of stretching vibrations (str) are expressed in mdyn $Å^{-1}$ deformations (bend, wag, rock, and tors) are expressed in mdyn Å. Torsional coordinate was defined as the sum of motions in tetraatomic fragments. Numbering of atoms corresponds to Fig. 1.

despite the above mentioned decrease by 7—9° of the NNN valence angle in $CH_3N(NO_2)_2$ compared with $HN(NO_2)_2$ (Tables 1 and 2), which causes an approach of the nitro groups. It is also interesting that the latter entails a considerable increase of the constant module of the interaction between the NNN bending vibration and the rocking vibration of only one ON(2)O nitro group (−0.31 mdyn Å). The other nitro group (ON(3)O) has such an orientation that the changing of the NNN angle influences its rocking vibration very slightly.

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References

1. N. I. Sadova, L. S. Khaikin, and L. V. Vilkov, *Usp. Khim.*, 1992, **61**, 2129 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
2. V. A. Shlyapochnikov, *Kolebatel'nye spektry alifaticheskikh nitrosoedinenii* [*Vibrational Spectra of Aliphatic Nitro Compounds*], Nauka, Moscow, 1989, 134 pp. (in Russian).
3. V. A. Shlyapochnikov, N. O. Cherskaya, O. A. Luk'yanov, V. P. Gorelik, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1610 [*Russ. Chem. Bull.*, 1994, **43**, 1522 (Engl. Transl.)].
4. A. Snelson, A. J. Tulis, D. C. Heberlein, and D. L. Patel, *Proceedings of the 19-th International Pyrotechnics Seminar*, Christchurch, New Zealand, February 20—25, 1994, South Pacific Information Services Ltd., 531.
5. M. Nonella, R. P. Muller, and J. R. Huber, *J. Mol. Spectrosc.*, 1985, **112**, 142.
6. H. H. Michels and J. A. Montgomery, *J. Phys. Chem.*, 1993, **97**, 6602.
7. N. A. Tarasenko, L. V. Vilkov, G. E. Slepnev, and Yu. A. Pankrushev, *Zh. Strukt. Khim.*, 1977, **18**, 953 [*J. Struct. Chem.*, 1977, **18** (Engl. Transl.)].
8. V. G. Avakyan, V. A. Shlyapochnikov, B. S. Fedorov, L. N. Margolin, and V. V. Volkova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1503 [*Russ. Chem. Bull.*, 1995, **44**, 1444 (Engl.Transl.)].
9. D. M. Zirl and T. Vladimiroff, *J. Mol. Struct. (THEOCHEM)*, 1993, **279**, 291.
10. L. S. Khaikin, O. E. Grikina, V. A. Shlyapochnikov, and J. E. Boggs, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2106 [*Russ. Chem. Bull.*, 1994, **43**, 1987 (Engl. Transl.)].
11. V. A. Shlyapochnikov, L. S. Khaikin, O. E. Grikina, C. W. Bock, and L. V. Vilkov, *J. Mol. Struct.*, 1994, **326**, 1.
12. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. J. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *GAUSSIAN-92*, Revision C, Gaussian Inc., Pittsburgh, 1992.
13. S. V. Krasnoshchekov, *Author's Abstract, Ph. D. (Chem.) Thesis*, Moscow State University, Moscow, 1986, 18 pp. (in Russian).
14. L. S. Khaikin, O. E. Grikina, L. V. Vilkov, M. Alcolea Palafox, and J. E. Boggs, *Zh. Strukt. Khim.*, 1993, **34**, 4 [*J. Struct. Chem.*, 1993, **34**, 2 (Engl. Transl.)].
15. L. S. Khaikin, O. E. Grikina, L. V. Vilkov, and J. E. Boggs, *Zh. Strukt. Khim.*, 1993, **34**, 12 [*J. Struct. Chem.*, 1993, **34**, 9 (Engl. Transl.)].
16. R. Stolevik and P. Rademacher, *Acta Chem. Scand.*, 1969, **23**, 672.
17. N. I. Sadova, G. E. Slepnev, N. A. Tarasenko, A. A. Zenkin, L. V. Vilkov, I. F. Shishkov, and Yu. A. Pankrushev, *Zh. Strukt. Khim.*, 1977, **18**, 865 [*J. Struct. Chem.*, 1977, **18** (Engl. Transl.)].
18. J. K. Tyler, *J. Mol. Spectrosc.*, 1963, **11**, 39.

19. J. A. Montgomery and H. H. Michels, *J. Phys. Chem.*, 1993, **97**, 6774.
20. K. Kochata, T. Fukuyama, and K. Kuchitsu, *J. Phys. Chem.*, 1982, **86**, 602.
21. N. Murase, K. Yamanouchi, T. Egawa, and K. Kuchitsu, *J. Mol. Struct.*, 1991, **242**, 409.
22. O. A. Litvinov, L. I. Ermolaeva, V. V. Zverev, and V. A. Naumov, *Zh. Strukt. Khim.*, 1989, **30**, 64 [*J. Struct. Chem.*, 1989, **30** (Engl. Transl.)].
23. K. Yamanouchi, M. Sugie, H. Takao, C. Matsumura, M. Nakata, and K. Kichitsu, *J. Phys. Chem.*, 1987, **91**, 823.
24. P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, 1979, **101**, 2550.
25. G. Fogarasi and P. Pulay, in *Vibrational Spectra and Structure*, Ed. by J. R. During, Elsevier, Amsterdam, 1985, **14**, 125—219.

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