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Structural relaxations and energy effects of intramolecular motions in *N,N*-dimethylnitramine: a theoretical study

L. S. Khaikin,[a]* *O. E. Grikina,*[a] *V. I. Perevozchikov,*[b] *A. V. Abramenkov,*[a]
V. A. Shlyapochnikov,[c] *F. R. Cordell,*[b] *and J. E. Boggs*[b]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846
[b]*Department of Chemistry, The University of Texas at Austin,*
Austin, Texas 78712, USA. Fax: (512) 471 8696
[c]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

The equilibrium geometry of the *N,N*-dimethylnitramine molecule and changes in the energy and structural parameters due to the internal rotation of the nitro group and the inversion of the N atom in the amino fragment were calculated by the restricted Hartree—Fock (RHF) method and at the second-order Møller-Plesset (MP2) level of perturbation theory with inclusion of electron correlation using the 6-31G* and 6-31G** basis sets. The one-dimensional potential functions of these motions calculated at the RHF/6-31G* level were approximated by a truncated Fourier and power series, respectively. The frequencies of torsional and inversion transitions were determined by solving direct vibrational problems for a non-rigid model, *i.e.*, taking into account the molecular geometry relaxation.

The equilibrium conformation of the molecular skeleton of *N,N*-dimethylnitramine is nonplanar. Transition states of the internal rotation of the nitro group and inversion of the amine N atom are characterized by pronounced concerted changes in its bond angles and the length of the N—N bond. In the MP2/6-31G* approximation, the height of the barrier to internal rotation calculated taking into account the difference in the zero-point vibrational energies is equal to 9.7 kcal mol^{-1}. Inversion in the amino fragment is accompanied by a relatively small energy change at the barrier height of ~1.0 kcal mol^{-1} calculated in the same approximation.

Key words: *N,N*-dimethylnitramine, quantum-chemical calculation, molecular structure, internal rotation, inversion of the amine nitrogen atom.

The specific properties of a large number of complex energetic compounds containing the C_2N-NO_2 nitramino fragment are determined by structural flexibility and conformational mobility of this fragment.[1,2] However, experimental and theoretical investigations of the simplest nitramines (which can be considered as model systems) carried out up to the present did not lead to a clear understanding of specific features of their structure and intramolecular dynamics.

The structure of the *N,N*-dimethylnitramine molecule, Me_2NNO_2, was studied experimentally in the gas phase[3] and in the crystal,[4—8] as well as by *ab initio* quantum-chemical calculations.[9—11] The authors of the electron diffraction study[3] believe that the molecule has a planar skeleton of C_{2v} symmetry. At the same time, they could not totally reject nonplanar models of C_2 and C_s symmetry, although they reason that the nonplanar structure is an artifact caused by vibrational effects.

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According to calorimetry and Raman spectroscopy data, a structural phase transition occurs in the crystalline *N,N*-dimethylnitramine at 107 K (at 111 K for the deuterated sample).[4–6] This transition is reversible and non-destructive for the crystal and has a very small thermal effect corresponding to an entropy change of ~0.04 cal K^{-1} mol^{-1}.

The results of X-ray and neutron diffraction studies[7,8] make it possible to draw conclusions concerning the character of changes in the molecular structure upon phase transition. In the high-temperature crystalline phase, the molecule of *N,N*-dimethylnitramine has a planar skeleton of symmetry close to C_{2v}; however, its geometric parameters appreciably differ from those found in the gas phase. Transition to the low-temperature crystalline phase results in the change in the symmetry of the molecular structure from $\sim C_{2v}$ to $\sim C_s$ (see Ref. 8). In this case the angle between the N—N bond and the CNC plane becomes equal to 10.4(9)°, while the angle of rotation of the nitro group about the N—N bond differs insignificantly from zero (1.6(9)°). The values of other geometric parameters in both crystalline phases are nearly the same. Therefore the change in the bond configuration of the amine nitrogen atom occurs with minor expenditure of energy and, hence, the observed deformations are due to intermolecular interactions in the crystal. However, no quantitative experimental data on the energy change in the course of inversion of the amine N atom are available.

Calculations by the restricted Hartree—Fock (RHF) method showed[9,10] that the amino fragment of the *N,N*-dimethylnitramine molecule has a planar equilibrium structure. At the same time, the 3-21G basis set used in Refs. 9 and 10 is known to be insufficient for an adequate description of the bond configuration of the amine nitrogen atom since it includes no polarization d-functions on the atoms of the molecular skeleton.[12–14] The structure of the *N,N*-dimethylnitramine molecule has also been calculated[11] using a basis set augmented with d-functions at the RHF and multiconfigurational complete active space self-consistent field (CASSCF) levels. However, only partial optimization of the geometry was performed in this case (values obtained in the X-ray study[7] were used as parameters of the methyl groups), while the configuration of the easily deformable amino fragment was not characterized.[11]

Only a rough experimental value of the barrier to internal rotation about the N—N bond in the *N,N*-dimethylnitramine molecule (≥9 kcal mol^{-1}) [15] is known at present. The estimates of this barrier obtained by RHF calculations using different basis sets vary over a wide range from 4 to 13 kcal mol^{-1}. [10,16] Recently,[17,18] it has been shown that the inclusion of electron correlation is of great importance when calculating rotational energy barriers for molecules with considerable delocalization of the electron density, to which *N,N*-dimethylnitramine belongs.

Recently, in the framework of a joint investigation of the structure, intramolecular motions, and vibrational spectra of the simplest nitramines, we have performed a number of quantum-chemical calculations at both the RHF level and second-order Møller—Plesset (MP2) level of perturbation theory with inclusion of electron correlation. Some data obtained for the *N,N*-dimethylnitramine molecule have been reported previously.[19–23] In this work, new results for *N,N*-dimethylnitramine and their relation to the most important of those already reported are considered in detail.

Methods of Calculations

The geometries of the equilibrium structure and transition states of *N,N*-dimethylnitramine were optimized by the gradient method in the RHF and MP2 approximations using the 6-31G* and 6-31G** basis sets. To characterize stationary points, the results of calculations of the frequencies of normal vibrations were also used.

In the studies of internal rotation about the N—N bond and wagging-inversion vibrations in the amino and nitro fragments, the potential energy values were calculated at several fixed points along the coordinate of the corresponding motion with optimization of other geometric parameters. Such an approach makes it possible to take into account structural relaxation in the course of one-dimensional motion considered and, hence, to a certain extent, interaction of the motion in question with other internal vibrations.[24–26] As has been shown previously,[25] the consideration of geometry relaxation (the so-called non-rigid model) is often necessary for a correct determination of the shape of the potential function and the height of the barrier.

In order to estimate the frequencies of torsional and inversion transitions, direct problems[26] were solved using theoretical potential functions in the framework of the one-dimensional non-rigid model and energy spectra were obtained. In the case of internal rotation about the N—N bond, the dependence of the potential function on the angle of rotation (φ) was approximated by a truncated Fourier series

$$V(\varphi) = 0.5\sum_{k=1}^{N} V_k\,(1 - \cos k\varphi),$$

where V_k is the maximum amplitude of the *k*th term of the expansion. The potential curve of the wagging-inversion motion of the amino fragment was approximated by a truncated power series

$$V(x) = V_2x^2 + V_4x^4 + V_6x^6$$

or by the following combined function

$$V(x) = V_2x^2 + V_4x^4 + V_6x^6 + B\exp(-\gamma x^2),$$

where V_n are the coefficients of the power series, and x is the chosen coordinate of one-dimensional motion. The functions characterizing the kinetic energy in corresponding internal coordinates and required for solving the direct problems were calculated following the known procedure[27] using data of quantum-chemical calculations of geometric parameters for different points of the potential curves. These functions were approximated by a truncated Fourier or power series for internal rotation and wagging-inversion motion, respectively.

All quantum-chemical calculations were performed using the GAUSSIAN-88,[28], GAUSSIAN-92,[29] and TEXAS [30] program complexes on a Cray XMP-24 computer at the Center for High Performance Computing at the University of Texas at Austin (Austin, Texas, USA). To solve the one-dimensional torsional and inversion problems, the TORSIO program[26] was used.

Results and Discussion

Geometric parameters of N,N-dimethylnitramine in the equilibrium and transition states. The amino fragment and nitro group directly bonded in nitramines have strongly different chemical properties. When analyzing structural manifestations of their interaction in *N*,*N*-dimethylnitramine, primary attention should be given to three correlated factors (Table 1): 1) the degree of pyramidality of the N atom in the amino fragment, which is characterized by the sum of its bond angles as well as by the angle between the N—N bond and the CNC plane (β_{amino}) or the dihedral angle between the NNC planes (τ_{amino}); 2) the N—N bond length; and 3) the molecular conformation determined by the rotation of the nitro group. The close interdependence of these structural characteristics can be explained using qualita-

Table 1. Geometric parameters and dipole moments of the equilibrium state (ES) and transition states of inversion (TS_{inv}) and internal rotation (TS_{rot}) for the *N*,*N*-dimethylnitramine molecule according to the *ab initio* calculations and experimental data

Parameter[a]	Calculation							Experiment[b]		
	ES (C_s)			TS_{inv} (C_{2v})		TS_{rot} (C_s)		C_{2v}	C_2	C_s
	RHF/ 6-31G*	MP2/ 6-31G*	MP2/ 6-31G**	RHF/ 6-31G*	MP2/ 6-31G*	RHF/ 6-31G*	MP2/ 6-31G*			
Bond length, r/Å										
N—N	1.344	1.387	1.388	1.326	1.359	1.424	1.463	1.383(8)	1.384(8)	1.402(10)
N—C(3, 7)	1.454	1.457	1.456	1.453	1.450	1.460	1.467	1.463(8)	1.463(9)	1.454(6)
N—O(11, 12)	1.197	1.240	1.240	1.200	1.244	1.182 1.192	1.231 1.236	1.225(3)	1.225(3)	1.226(2)
C—H(4, 8)	1.080	1.090	1.085	1.079	1.089	1.081	1.091	1.115(16)	1.111(15)	1.114(15)
C—H(5, 9)	1.085	1.097	1.092	1.081	1.092	1.085	1.097			
C—H(6, 10)	1.077	1.087	1.082	1.081	1.092	1.082	1.092			
Bond angle, φ/deg										
C—N—C	120.2	118.4	118.1	125.1	126.4	113.3	111.3	127.6(17)	127.1(13)	128.6(11)
N—N—C(3,7)	115.8	113.8	113.8	117.4	116.8	108.8	107.0	116.2(8)	116.5(7)	115.7(6)
O—N—O	125.2	126.1	126.2	125.3	126.5	126.1	126.8	130.4(42)	129.1(31)	125.5(20)
N—N—O(11, 12)	117.4	116.9	116.9	117.4	116.8	115.9 117.9	115.3 117.9	114.8(20)	115.4(16)	115.5(11)
N—C—H(4, 8)	107.0	106.9	106.9	107.3	107.2	107.0	106.9	101.9(58)	99.1(45)	101.0(47)
N—C—H(5, 9)	112.0	112.1	112.1	111.0	110.8	112.8	112.8			
N—C—H(6, 10)	110.0	109.5	109.4	111.0	110.8	109.2	108.8			
Dihedral angle, τ/deg										
C(3)NNO(12) C(7)NNO(11)	±16.3	±21.4	±21.7	0.0	0.0	±118.1	±120.3	0.0	14.0	±12.0
C(3)NNO(11) C(7)NNO(12)	±165.1	±161.1	±160.8	180.0	180.0	±61.9	±59.7	180.0	−166.0	±172.0
H(4, 8)CNC	±37.2	±45.2	±46.3	0.0	±0.3	±65.1	±67.0			
H(4, 8)CNN	±175.5	±177.1	±176.5	180.0	±179.7	±173.8	±176.5			
H(5, 9)CNC	±82.7	±75.0	±73.9	±119.4	±120.0	±55.6	±53.7			
H(5, 9)CNN	±64.6	±62.7	±63.4	±60.6	±60.0	±65.5	±62.8			
H(6, 10)CNC	±155.7	±163.7	±164.9	±119.5	±119.4	±177.9	±175.9			
H(6, 10)CNN	±57.0	±58.6	±57.9	±60.5	±60.6	±56.7	±59.4			
τ_{amino}[c]	31.2	40.4	40.9	0.0	0.0	56.1	60.7	0.0	0.0	4.0
τ_{nitro}[c]	1.4	2.5	2.5	0.0	0.0	0.0	0.0	0.0	0.0	20.0
Angle between the bond and the plane, β/deg										
N—N/CNC (β_{amino})	27.8	36.4	36.8	0.0	0.0	51.8	56.5	0.0	0.0	3.6
N—N/ONO (β_{nitro})	1.2	2.2	2.2	0.0	0.0	0.0	0.0	0.0	0.0	18.0
Dipole moment, μ/D	4.85	4.82	4.81	5.14	5.22	3.94	4.09	4.52—4.61 [34–37]		
Total energy, $-(E+337.0)$/au	0.701058	1.687941	1.736686	0.700422	1.686099	0.683051	1.672143			

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[a] The numbering of the atoms is shown in Fig. 1. [b] The gas-phase electron diffraction experiment[3] was performed at 343 K and analyzed in the framework of the r_a-structure, which is characterized by thermally averaged internuclear distances defined as the center of gravity of the $P(r)/r$ function; triple standard deviations of the least squares method are given in parentheses. [c] The τ_{amino} and τ_{nitro} angles are dihedral angles between the NNC or NNO planes, respectively.

tive concepts of the p—π-conjugation between the lone electron pair of the N atom in the amino fragment and the π-system of the nitro group.

As we have shown previously,[20,23,31–33] RHF and MP2 calculations (using the 6-31G* and 6-31G** basis sets) make it possible to obtain lower and upper estimates of the degree of pyramidality of the bond configuration of the amine N atom, respectively. At the same time, the experimental values of the bond angles in the amino fragments for a number of nitramines as well as for *N,N*-dimethylnitrosamine and formamide are somewhat better reproduced by the RHF method. However, the inclusion of electron correlation appears to be very essential when calculating the lengths of multiple bonds or bonds in conjugated systems such as N=O and N—N bonds in *N,N*-dimethylnitramine. In the RHF approximation, these bond lengths are appreciably underestimated as compared with the experimental values in the gas phase, while the differences go far beyond the limits of experimental errors. The use of the MP2 method makes it possible to substantially reduce these deviations.

As in the case of other simplest nitramines we have studied,[20,31] our calculations give a nonplanar bond configuration of the amine N atom in *N,N*-dimethylnitramine, though its equilibrium structure of symmetry C_s, in which the symmetry plane of the molecule is perpendicular to the NO_2 group plane (Fig. 1), is the most favorable for the p—π-interaction. At the same time, in this case the deviation from the planar configuration is less than in the rest of the nitramines ($MeNHNO_2$, H_2NNO_2, $MeNClNO_2$, $HNClNO_2$, $MeN(NO_2)_2$, and $HN(NO_2)_2$),[20,31] which are characterized by the successive increase in the overall electronegativity of the substituents and pyramidality of the amine N atom. The increased electronegativity of the substituents must result in a decrease in the electron-donor ability of the amino fragment and, hence, in a decrease in the p—π-conjugation. This is in good agreement with the observed tendency for the N—N bond to be successively lengthened in the same series of compounds, where the lengthening amounts to 0.1 Å.

Compared to the equilibrium structure, considerable changes in geometric parameters, primarily in the N—N bond length and the bond angles of the N atom, occur in the transition states corresponding to inversion of the amine N atom (C_{2v}) and internal rotation of the nitro group (C_s) (see Table 1). Irrespective of the level of calculations, the increased delocalization of the lone electron pair of the N atom in the planar transition state of inversion results in a shortening of the N—N bond by 0.02—0.03 Å, while in the transition state of internal rotation (with the nitro group in the symmetry plane of the molecule) unfavorable for p—π-conjugation this bond is lengthened by 0.08 Å. It is interesting to note that in the equilibrium structure of the $MeN(NO_2)_2$ molecule with two nonequivalent NO_2 groups,[31] the N—N bond with the nitro group rotated less favorably for conjugation is longer. In addition, it is characteristic that a shortening of the N—N bond is accompanied by a lengthening of the N=O bonds and an increase in the bond angles of the amine N atom, whereas opposite changes in these parameters occur in the case of lengthening of the N—N bond. Analogous correlations have also been found for other simplest nitramines.[20,21]

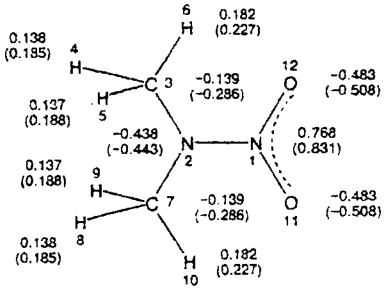
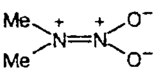


Fig. 1. The molecule of *N,N*-dimethylnitramine: numbering of atoms; Mulliken atomic charges calculated for geometric parameters optimized in the MP2/6-31G** approximation (the results of the RHF/6-31G* calculations are given in parentheses).

Mulliken atomic charges and electric dipole moments. Data on Mulliken atomic charges and dipole moments of the molecule as well as on their changes in the case of intramolecular motions are useful when discussing the chemical properties of compounds. Since the notion of the charge on a particular atom in the molecule has no unambiguous theoretical definition, the adequacy of a particular method for calculating the estimate of the charge distribution can only be inferred by comparing the calculated and experimental dipole moments.

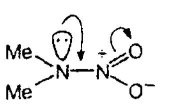
The calculated charge distributions and electric dipole moments of the *N,N*-dimethylnitramine molecule are presented in Fig. 1 and Table 1, respectively. Though a very large positive charge corresponds to the N atom of the nitro group, it is more than compensated for by the negative charges of two O atoms bonded to this N atom, so the total charge of the nitro group is negative. The calculated negative charge of the amine N atom is insufficient to neutralize the positive charges of two methyl groups of the amino fragment. In the case of MP2 calculations, the inclusion of polarization p-functions on the H atoms into the basis set results in a considerable decrease in the charges on the atoms of the methyl group; however, its total charge in both the equilibrium and transition forms is not sensitive to the changes in the basis set and calculated geometric parameters. The estimates of the dipole moment for the equilibrium structure lie within the very narrow interval 4.81—4.85 D. The value of the dipole moment obtained by the CASSCF method (4.81 D)[11] is in good agreement with our results (in spite of some differences in the atomic charges). The experimental values of the dipole moment of *N,N*-dimethylnitramine obtained from measurements for solutions in dioxane and CCl_4 at room temperature are equal to 4.52(2) D [34] and 4.61 D,[35–37] respectively.

In the case of inversion of the amine N atom, the charge changes are minimum as compared to the equilibrium structure. In the planar transition state, the atomic charges increase in absolute values by only 0.01 to 0.03. This results in a slight increase in the dipole moment (to ~5.2 D). Assuming that the total positive charge of the dimethylamino group is localized on the N atom, the predicted change in this charge can be explained by the increasing contribution of the resonance form:



Shortening of the N—N bond in the transition state of inversion obtained from the calculations (see Table 1) indicates the increase in the multiplicity of this bond.

For the transition state of internal rotation about the N—N bond, the calculations predict an appreciable decrease in the atomic charges (by 0.05 to 0.15 in the absolute value) and a decrease in the dipole moment to 3.9—4.1 D compared to the equilibrium structure. This can be considered as the increase in the contribution of the other resonance form:



which is also consistent with the changes in geometric parameters (see Table 1).

It is known[38] that except for strongly polar structures, the dipole moments calculated in the RHF/6-31G* approximation usually appear to be overestimated by 0.4 to 0.6 D. Hence, our estimates of the dipole moments for the equilibrium and transition forms far exceed possible calculation errors and the direction of the dipole moments in the symmetry plane of the molecule from the nitro group toward the amino fragment as well as the values themselves can be considered as fairly reliable.

Barriers to internal rotation and inversion. Estimates of the potential barriers can be obtained directly from quantum-chemical calculations as the difference between the total electronic energies of the equilibrium form and the corresponding transition state. For many isodesmic processes, such estimates, even obtained at the Hartree—Fock level, are in good agreement with the experimental values because of the small changes in the contributions of electron correlation.[37] Since a substantial redistribution of the electron density occurs in *N*,*N*-dimethylnitramine and related conjugated compounds in the course of internal rotation of the nitro group or inversion of the amine N atom, a reliable determination of energy barriers is impossible without inclusion of electron correlation. This is confirmed by the data in Table 2, where the results of calculations at different levels and experimental data for *N*,*N*-dimethylnitramine are compared. The dependence of the calculated rotational barriers of the nitro group on the approximation used was considered in detail previously[17,18] for molecules of nitroethylene and nitrobenzene taken as examples.

The inclusion of electron correlation even by the energy refinement at the MP2 level using the geometry optimized in the RHF approximation (MP2/6-31G*//RHF/6-31G*) decreases the barrier to internal rotation of the nitro group by 1 kcal mol^{-1}.[16] The full geometry optimization we performed by the MP2 method resulted in an additional decrease in the barrier height by 0.4 kcal mol^{-1}, making the theoretical estimate closer to the experimental value. At the same time, attempts[16] aimed at including electron correlation by the local density functional (LDF) method seem to be less convincing. The obtained estimates of the barrier height (13 to 15 kcal mol^{-1})[16] are substantially overestimated as compared to both the experiment and the above RHF and MP2 calculations, whereas a reverse relation takes place when performing analogous calculations of nitroethylene and nitrobenzene.[17]

The previously reported data[17,18] suggest that the MP2/6-31G* approximation estimates the barrier with an accuracy of ~1 kcal mol^{-1}. The result we obtained (9.9 kcal mol^{-1}) is in good agreement with the experimental value (≥9 kcal mol^{-1}).[15] The difference in the zero-point vibrational energies (ΔZPE = −0.2 kcal mol^{-1}) calculated at the RHF/6-31G* level is much less than the possible error in calculating the barrier. The relative effectiveness of the RHF/4-21NO* approximation, which estimates the rotational energy barrier and the barrier to inversion considered below in good agreement with MP2 calculations, can be due to the fortuitous cancellation of errors from basis set truncation and neglect of electron correlation.

No experimental data on the barrier to inversion of the amine N atom of *N*,*N*-dimethylnitramine are available, and the results of our calculations in Table 2 are the only data of this sort at present. A comparison of the estimates obtained at the RHF and MP2 levels using the

Table 2. Theoretical and experimental estimates of the barriers to internal rotation (ΔE_{rot}) and inversion in the amino group (ΔE_{inv}) for *N*,*N*-dimethylnitramine

Method[a]	ΔE_{rot}	ΔE_{inv}	Reference
	kcal mol^{-1}		
RHF/STO-3G	4.4	—	16
RHF/3-21G	13.0	—	16
RHF/4-21NO*	10.4	1.6	c
RHF/6-31G*	11.3	0.4	16,c
LDF(DMOL)/DNP//STO-3G	12.6	—	16
LDF(DMOL)/DNP//3-21G	15.3	—	16
LDF(DMOL)/DNP//6-31G*	15.2	—	16
MP2=FULL/6-31G*//6-31G*	10.3	—	16
MP2=FULL/6-31G*	9.9	1.2	c
Difference in the zero-point vibrational energies	−0.19	−0.21	c
Experiment[b]	≥9	—	15

[a] LDF(DMOL)/DNP denotes the DMOL version of the local density functional (LDF) method using the DNP basis set equivalent to the two-exponential basis set with polarization functions; FULL denotes that the correlation energy calculations were performed taking into account all the electrons. [b] Experimental estimate of the barrier to internal rotation[15] was obtained from the temperature dependence of the quadrupole relaxation time in the NQR spectrum. [c] This work.

same 6-31G* basis set shows that the inclusion of electron correlation results in an increase in the barrier height. The MP2 method gives the value of 1.2 kcal mol^{-1}, which is much less than the height of the barrier to internal rotation.

A comparison of geometric parameters and barriers to intramolecular motions in the simplest nitramines we calculated[20,21] confirms the general relationship: the barrier to rotation increases while the barrier to inversion decreases as the N—N bond length becomes shorter and the degree of pyramidality of the bond configuration of the N atom in the amino fragment decreases in the equilibrium state of the molecule. This relationship can be explained by increased delocalization of the lone electron pair of the amine N atom. The conjugation in nitramines increases as the electronegativity of the substituents at the amine N atom decreases. At the same time, it is likely that the effect of conjugation in nitramines is less pronounced than in some other amino derivatives with unsaturated substituents. For instance, the barriers to internal rotation in amides and nitrosamines are 1.5 to 2 times higher than those in nitramines (see Refs. 23, 32, 33, and 39—43).

Potential function of internal rotation of the nitro group, frequencies of torsional transitions, and relaxation of geometry in the course of rotation. The theoretical potential curve of internal rotation $V(\varphi)$ was obtained in the RHF/6-31G* approximation by geometry optimization at two stationary points (see Table 1) and ten intermediate at different fixed values of the rotation coordinate φ. For the non-rigid model used in our calculations, the choice of the φ coordinate is ambiguous. We define it as the half-sum of two dihedral angles between the ONN and NNC planes, namely, the O(12)N(1)N(2)C(3) and O(11)N(1)N(2)C(7) angles (see Fig. 1). At stationary points, the φ angle thus defined is rigorously equivalent to the dihedral angle between the normals to the ONO and CNC planes, while at other points the equivalence holds at least if the symmetry planes are retained for both the top and frame.

The calculated potential function $V(\varphi)$ is satisfactorily approximated by a truncated Fourier series with the first three even coefficients V_2, V_4, and V_6 (Table 3, where variants I, II, and III differ in the number of coefficients of the Fourier series, and Fig. 2). The main contribution comes from the expansion term with coefficient V_2, which determines the height of the barrier to rotation. However, the use of only this term is insufficient for an adequate description of the curvature of the potential curve near stationary points. Since coefficients V_6 and V_8 are an order of magnitude smaller than V_4, it is just the latter coefficient that determines changes in the curvature in this case. Since the coefficient V_4 obtained in our calculations is positive, the curvature of the potential function must increase in the region of its minimum and decrease in the region of its maximum.[44]

Table 3. Coefficients of the Fourier-series expansion (V_n) of the potential function $V(\varphi)$ of internal rotation of the nitro group calculated for the *N,N*-dimethylnitramine molecule in the RHF/6-31G* approximation

Coefficient	V_n/cm^{-1}		
	I	II	III
V_2	3975.8	3974.4	3970.7
V_4	315.3	336.7	313.9
V_6	—	−26.5	−30.2
V_8	—	—	26.5
Standard deviation	42.6	42.2	43.1

Note. I, II, and III are variants differing in the number of coefficients of the Fourier series.

In contrast to this, the potential functions of internal rotation of the nitroethylene and nitrobenzene molecules calculated using various *ab initio* methods are considerably flattened in the region of equilibrium conformations, which corresponds to negative values of coefficients V_4 in the Fourier expansions.[17,18] In the case of nitrobenzene such a flattening of the potential function is confirmed by the electron diffraction data[45] indicating a large-amplitude torsional motion of the nitro group with an average deviation from the planar configuration of 13.3±1.4° at ~353 K.

Using the RHF-optimized geometric parameters, we calculated the function $F(\varphi)$[46,47] characterizing the kinetic energy taking into account the effects of structural relaxation and obtained the coefficients of its approximation by a truncated Fourier series up to the eighth expansion term (Table 4). The values of the coefficients decrease so sharply that taking into account the expansion terms after F_0 only slightly affects the final result. This is not surprising, since the *N,N*-dimethylnitramine molecule has a symmetry plane, and the center of mass of the NO_2 top is on the axis of rotation. The obtained function $F(\varphi)$ and the potential function $V(\varphi)$ including the expansion terms V_2, V_4, and V_6 (see Table 3, II), were used to estimate energy levels and frequencies of

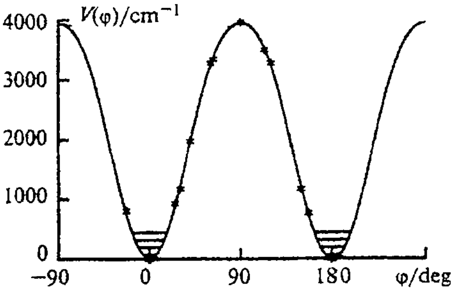


Fig. 2. Approximation of the potential function of internal rotation about the N—N bond in Me_2NNO_2 by a truncated Fourier series with the coefficients V_2, V_4, and V_6. The lowest torsional levels are shown. The values of the total electronic energy calculated in the RHF/6-31G* approximation are shown by asterisks. The angle of rotation φ is defined as the half-sum of the C(3)—N—N—O(12) and C(7)—N—N—O(11) dihedral angles (see the text).

torsional transitions (Table 5, see Fig. 2) by solving the direct one-dimensional problem in the framework of the non-rigid model of internal rotation.[25,26] The lowest energy levels are nearly doubly degenerate, and the splitting equal to ~0.1 cm^{-1} appears only after the twenty-sixth level. Thus, each of the potential wells can be considered independently.

It has been shown by *ab initio* calculations[17] that unlike the coefficients V_2, the coefficients V_4 of the potential functions of internal rotation for nitroethylene and nitrobenzene depend only slightly on the size of the basis set used or the inclusion of electron correlation. The estimates obtained using the RHF/6-31G* approximation differ from those obtained from the MP2/6-31G* and higher level calculations by no more than 5% and ~10%, respectively, *i.e.*, the RHF/6-31G* approximation reproduces the V_4 values for these molecules fairly well. If this is also assumed to be valid for *N,N*-dimethylnitramine, then its potential function can be approximated using the V_2 value of 3467.1 cm^{-1} obtained from the MP2/6-31G* estimate of the rotational energy barrier (see Table 2) and the V_4 and V_6 coefficients from the best variant of the Fourier-series expansion obtained using the results of RHF/6-31G* calculations (see Table 3, II). In combination with the function $F(\varphi)$ for the semi-rigid rotational model corresponding to the equilibrium structural parameters obtained by the MP2/6-31G* method (see Table 1), the function $V(\varphi)$ thus constructed was also used for solving the direct problem (the results are listed in Table 5). In this case, the energy levels and frequencies of transitions are slightly decreased as compared to those calculated in the RHF/6-31G* approximation.

The solution of the direct one-dimensional problem obtained using data of quantum-chemical calculations predicts that the fundamental frequency of torsional vibration must lie in the 110—125 cm^{-1} region. This is in good agreement with the assignment of the torsional vibration of the nitro group to the experimental band at 120 cm^{-1} resulting[48] from solution of the inverse spectral problem by scaling of the MP2 force field.

Table 4. Coefficients of the Fourier-series expansion (F_n) of the function $F(\varphi)$ calculated for internal rotation of the nitro group in the *N,N*-dimethylnitramine molecule using geometric parameters optimized in the RHF/6-31G* and MP2/6-31G* approximations

Coefficient	F_n/cm^{-1}	
	RHF/6-31G* (non-rigid model)	MP2/6-31G* (semi-rigid model)
F_0	0.7585 (2)	0.7169
F_2	−0.0017 (2)	−0.0009
F_4	−0.0016 (3)	
F_6	−0.0008 (2)	
F_8	−0.0003 (2)	

Note. Standard deviations are given in parentheses.

Table 5. The lowest energy levels (E) and frequencies of torsional transitions (ν) for internal rotation of the nitro group in the *N,N*-dimethylnitramine molecule[a]

Level[b]	E/cm^{-1}		Transition	ν/cm^{-1}	
	RHF/ 6-31G*	MP2/ 6-31G*		RHF/ 6-31G*	MP2/ 6-31G*
0	61.7	57.0			
1	184.4	170.4	0—1	122.8	113.4
2	306.1	282.7	1—2	121.7	112.3
3	426.8	393.9	2—3	120.6	111.2
4	546.3	504.1	3—4	119.5	110.1
5	664.6	613.0	4—5	118.4	109.0
6	781.9	720.8	5—6	117.2	107.8
7	897.9	827.4	6—7	116.0	106.6
8	1012.7	932.9	7—8	114.8	105.4
9	1126.3	1037.0	8—9	113.6	104.2
10	1238.6	1139.9	9—10	112.3	102.9

[a] The solution of the direct problem using the data of the RHF/6-31G* calculations was obtained in the framework of the non-rigid model using the potential function presented as the Fourier-series expansion terms with the V_2, V_4, and V_6 coefficients (see Table 3, II); the solution based on the data of the MP2/6-31G* calculations was obtained in the framework of the semi-rigid model using an approximate potential function differing from the preceding function only in the value of the V_2 coefficient (3467.1 cm^{-1}) (see the text). [b] Each of the levels is nearly doubly degenerate.

Changes in geometric parameters of the *N,N*-dimethylnitramine molecule in the course of internal rotation of the nitro group taken into account in solving the one-dimensional problem nearly coincide for both the RHF and the MP2 approximations (see Table 1). A more detailed analysis of the results of the RHF/6-31G* calculations indicates the synchronism and mutual consistency of deviations of the total electronic energies and optimized geometric parameters from their equilibrium values (Figs. 3 and 4).

The shape of the curve of the dependence of the N—N bond length on the angle of rotation (φ) is nearly identical to that of the potential curve. In the transition state of internal rotation ($\varphi = 90°$), the length of this bond has the maximum value, whereas the values of the C—N—C and C—N—N bond angles are minimum, which corresponds to the maximum pyramidality of the amine N atom (see Fig. 3). The dependence of the N—C bond length on the φ angle is not described by a sinusoidal function (see Fig. 4): the maxima are observed at $\varphi = 90°$ and 270°, whereas the minima are shifted by ~20° from 0° and 180° toward larger angles. Configurations in which the N—C bond is eclipsed by one of the N=O bonds correspond to the minima.

Rotation of the nitro group from the equilibrium position breaks the C_s symmetry and leads to the nonequivalence of the intramolecular environment of the two N=O bonds. If at $0° < \varphi < 180°$ the N=O bond considered is in the *syn*-position relative to the methyl substituents of the amine N atom, then at $180° < \varphi < 360°$ this bond will be closer to the lone electron pair of this

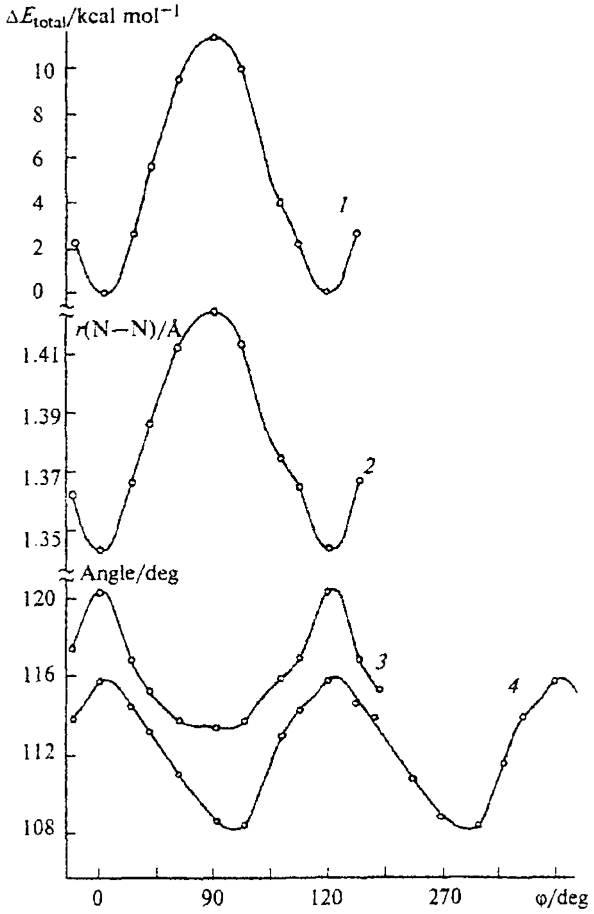


Fig. 3. Dependences of the total electronic energy (*1*), N—N bond length (*2*), and C—N—C (*3*) and C—N—N (*4*) bond angles on the angle of rotation of the nitro group calculated in the RHF/6-31G* approximation.

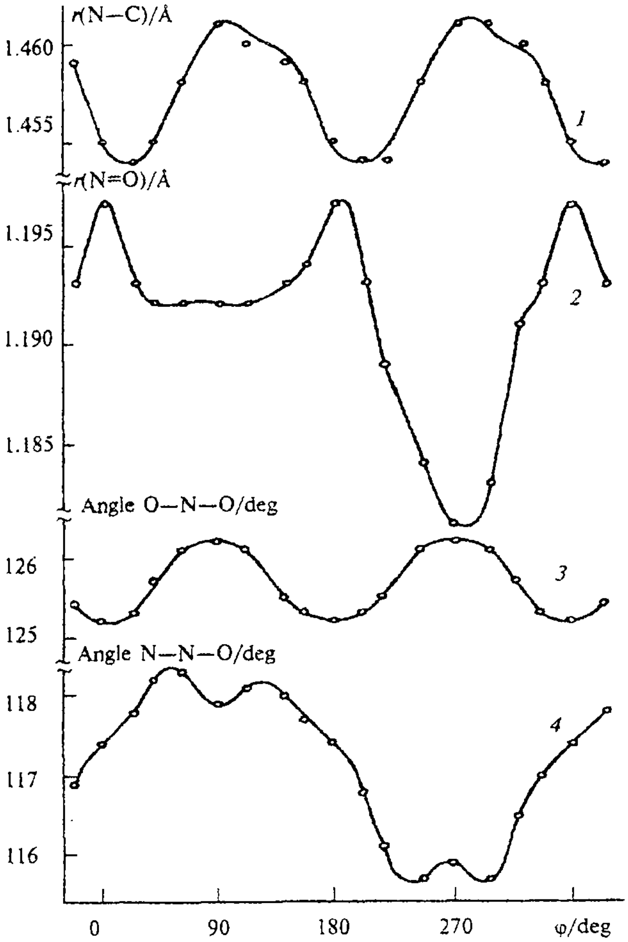


Fig. 4. Dependences of the N—C (*1*) and N=O (*2*) bond lengths and O—N—O (*3*) and N—N—O (*4*) bond angles on the angle of rotation of the nitro group calculated in the RHF/6-31G* approximation.

atom. In both intervals, the dependence of the N=O bond length on the φ angle has minima, of which the minimum at φ = 90° is much more shallow than that at φ = 270°. It can be assumed that the difference in the N=O bond lengths corresponding to the two minima is due to steric interactions. In the transition state, increase in pyramidality of the bond configuration of the amine N atom increases the repulsion between its methyl substituents and the closest of the N=O bonds, which prevents the shortening of the given bond. On the contrary, it is likely that the interaction of the other N=O bond with the lone electron pair of the N atom is weaker, which causes a considerable shortening of this bond.

Shortening of the lengths of both N=O bonds results in an increase in the repulsion between their bonding electron pairs, which explains the simultaneous increase in the O—N—O angle. As in the case of the N—N bond length, the shape of the curve of changes in the O—N—O angle in the course of internal rotation is analogous to that of the potential curve. The above explanation of the nonequivalence of the N=O bonds by steric reasons is also valid for changes in the N—N—O angles. At the same time, the dependence of this angle on the φ angle (see Fig. 4) has a peculiar double maximum near 90° and an analogous minimum near 270°. The origin of the calculated doublet separations of ±30° from the extrema expected from symmetry considerations is hardly explainable, since we failed to relate them to any essential structural interactions.

The considered relaxation changes in the geometry can be evidence that the degree of delocalization of the lone electron pair of the amine N atom decreases sharply in the transition state of internal rotation, although it is appreciable in the equilibrium structure of *N,N*-dimethylnitramine.

Potential function of inversion of the amine N atom, frequencies of transitions, and geometry relaxation in the course of inversion. The potential curve of inversion of the N atom in the amino fragment was obtained in the RHF/6-31G* approximation by optimization of geometric parameters at two stationary points (see Table 1) and four additional points at different fixed values of the angle β_{amino} between the N—N bond and its projection on the CNC plane. To solve the direct inversion problem, we introduced the internal coordinate x (in Å), which was defined as the product of the angle β_{amino} (in radians) and the N—N bond length, analogously to that accepted in the previously reported Refs. 49 and 50. When using the least squares method, the approximation of the quantum-chemical potential function of inversion by a power series in x (Fig. 5) gives a better description than that by a combination of the power series with the exponential term (see above).

The V_2, V_4, and V_6 coefficients of the power series are listed in Table 6. On the basis of geometric parameters optimized at the RHF level we calculated the function $g_{44}(x)$,[27] which includes the effects of structural relaxation; the coefficients of its power-series expansion are also listed in Table 6. The obtained function $g_{44}(x)$ and the potential function $V(x)$ were used to estimate the inversion energy levels and frequencies of inversion transitions (Table 7, see Fig. 5) by solving the direct one-dimensional problem in the framework of the nonrigid model.[25,26]

Unlike the internal rotation of the nitro group, the inversion of the amine N atom of *N*,*N*-dimethylnitramine occurs with little energy change and can proceed with ease under normal conditions. The barrier to inversion calculated in the RHF/6-31G* approximation (0.4 kcal mol^{-1}) is somewhat lower than its estimate obtained using the MP2/6-31G* method (1.2 kcal mol^{-1}). The latter is likely closer to the real value (see Table 2). Nevertheless, the distribution of the energy levels obtained using the results of RHF/6-31G* calculations makes it possible to explain the planar configuration of the amino fragment in the effective structure of the molecule found from the electron diffraction experiment.[3] Since only the lowest slightly split energy level lies under the barrier to inversion, a mixture of several vibrational states with approximately equal thermally averaged probability densities corresponding to planar and nonplanar geometries must be observed under conditions of the electron diffraction experiment[3] performed at 343 K. To a certain extent, this also can explain the difference between the experimental value of the C—N—C angle[3] and its quantum-chemical estimates for the equilibrium state, which amounts to 7—9°. The C—N—C angles calculated for the planar transition state of inversion are 5 to 8° larger than their equilibrium values (see Table 1).

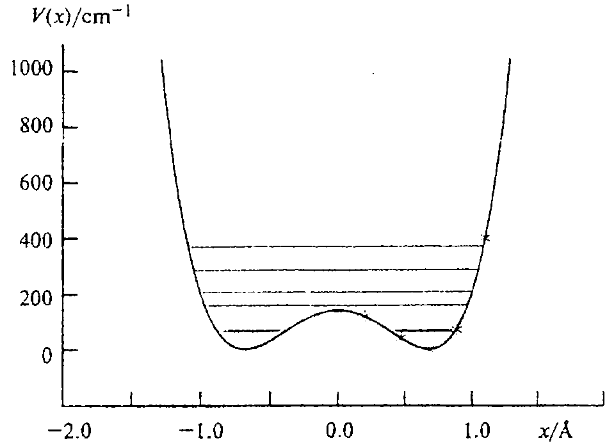


Fig. 5. Approximation of the potential function of inversion of the amine N atom of Me_2NNO_2 by an even polynomial of the sixth power. The lowest inversion levels are shown. The values of the total electronic energy calculated in the RHF/6-31G* approximation are shown by asterisks. The inversion coordinate x is the product of the N—N bond length and the angle β_{amino}(NN/CNC) between the N—N bond and the CNC plane (see the text).

The change in pyramidality of the amine N atom has a substantial effect on other structural parameters of the molecule. As in the case of internal rotation of the nitro group, the deviations of the total energy and geometric parameters from their equilibrium values occur synchro-

Table 6. Coefficients of the power-series expansion of the $g_{44}(x)$ and $V(x)$ functions characterizing the inversion of the amine N atom of *N*,*N*-dimethylnitramine

Coefficient of $g_{44}(x)$ expansion	A_n	Coefficient of $V(x)$ expansion	V_n /cm^{-1}
A_0	0.2927 (2)	V_2	−583 (6)
A_2	−0.1104 (20)	V_4	585 (15)
A_4	0.0371 (45)	V_6	58 (9)
A_6	−0.0063 (25)		

Note. Obtained using the data of the RHF/6-31G* calculations; standard deviations are given in parentheses.

Table 7. The lowest energy levels (E) and frequencies of transitions (ν) for the inversion of the amine N atom of *N*,*N*-dimethylnitramine obtained using the data of the RHF/6-31G* calculations

Level	E/cm^{-1}	Transition	ν/cm^{-1}
0^+	63.8		
0^-	68.1	0^+—0^-	4.7
1^+	157.0	0^-—1^+	88.6
1^-	205.0	1^+—1^-	48.0
2^+	282.8	1^-—2^+	77.8
2^-	367.6	2^+—2^-	84.8
3^+	461.9	2^-—3^+	94.3
3^-	563.6	3^+—3^-	101.7
4^+	671.8	3^-—4^+	108.3
4^-	785.0	4^+—4^-	114.2
5^+	905.5	4^-—5^+	119.6
5^-	1030.0	5^+—5^-	124.5

nously and are mutually consistent (Fig. 6). The N—N and N—C bond lengths are minimum in the planar transition state ($\beta_{amino} = 0°$) and increase when shifting toward symmetrically located potential wells. Simultaneously, opposite changes occur with the N=O bond length and C—N—C angle. All this can be attributed to change in delocalization of the lone electron pair of the amine N atom; however, the effect of conjugation is likely insufficient for retaining the planar geometry in the equilibrium structure. The O—N—O and N—N—O bond angles remain nearly unchanged in the studied interval of changes in the inversion coordinate.

Wagging vibration of nitro group. The RHF and MP2 calculations of the equilibrium structure of *N,N*-dimethylnitramine performed in this work predict a slightly pyramidal bond configuration of the N atom of the nitro group with the angle between the N—N bond and the ONO plane (β^{eq}_{nitro}) of −1.2° and −2.2°, respectively (see Table 1). The substituents at the amine and nitro N atoms are in *anti*-position relative to each other. As we have shown previously,[20,31] the increase in the electronegativity of the substituents at the amine N atom stimulates the decrease in the π-delocalization of the lone pair; this not only results in the greater pyramidality of the equilibrium configuration of bonds of the amine N atom, but also in the increase in the $\beta_{nitro}{}^{eq}$ angle to 5—6°. In the transition state of internal rotation as well as in the case of planar bond configuration of the amine N atom in the transition state of inversion, the fragment containing the nitro group is planar. The concerted character of such changes can be explained from the viewpoint of the symmetry of interactions between the nitro group and the intramolecular environment.

The curve of the change in the potential energy of *N,N*-dimethylnitramine in the case of deviation of the fragment containing the nitro group from the planar configuration obtained from the geometry optimization in the RHF/6-31G* approximation at five fixed values of the angle between the N—N bond and the ONO plane (β_{nitro}) is shown in Fig. 7. The curve has the only minimum and, hence, the vibration is not the inversion vibration. Since wagging vibration of the nitro group is affected by steric interactions of different nature (with methyl groups and the N—C bonds in the case of displacement in one direction and with the lone electron pair of the amine N atom in the case of displacement in the opposite direction), it could be expected that the potential function has a rather asymmetrical shape. However, the calculated potential curve in the studied interval of the change in the β_{nitro} angle corresponds to a nearly harmonic motion. The following approximation of the potential function was obtained using the least squares method:

$$V(\beta_{nitro}) = 0.00376 + 0.00418(\beta_{nitro} - \beta^{eq}_{nitro}) + $$
$$+ 0.01737(\beta_{nitro} - \beta^{eq}_{nitro})^2,$$

where $V(\beta_{nitro})$/kcal mol^{-1} is the potential energy, and ($\beta_{nitro} - \beta^{eq}_{nitro}$)/deg is the difference between the current value of the angle β_{nitro} and its equilibrium value, and the standard deviation was 0.029 kcal mol^{-1}. The values of the potential energy at the angle β_{nitro} of −21.2 and 18.8° (at the points located symmetrically relative to the minimum) differ only by 0.2 kcal mol^{-1}.

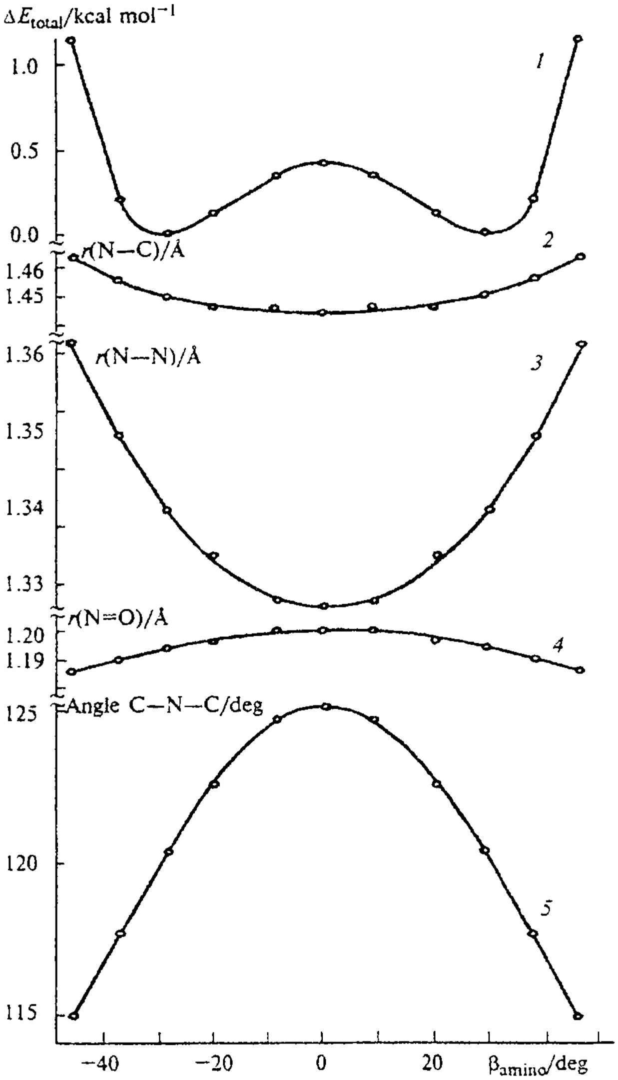


Fig. 6. Dependences of the total electronic energy (*1*), N—C (*2*), N—N (*3*), and N=O (*4*) bond lengths, and C—N—C bond angle (*5*) on the angle of inversion β_{amino}(NN/CNC) between the N—N bond and the CNC plane calculated in the RHF/6-31G* approximation.

Changes in geometric parameters in the case of wagging vibration of the nitro group confirm that the energy effects accompanying its displacements from the equilibrium position in two different directions are of essentially different nature. The N—N bond lengthens as the nitro group approaches the lone electron pair of the amine N atom, *i.e.*, at more negative values of β_{nitro}.

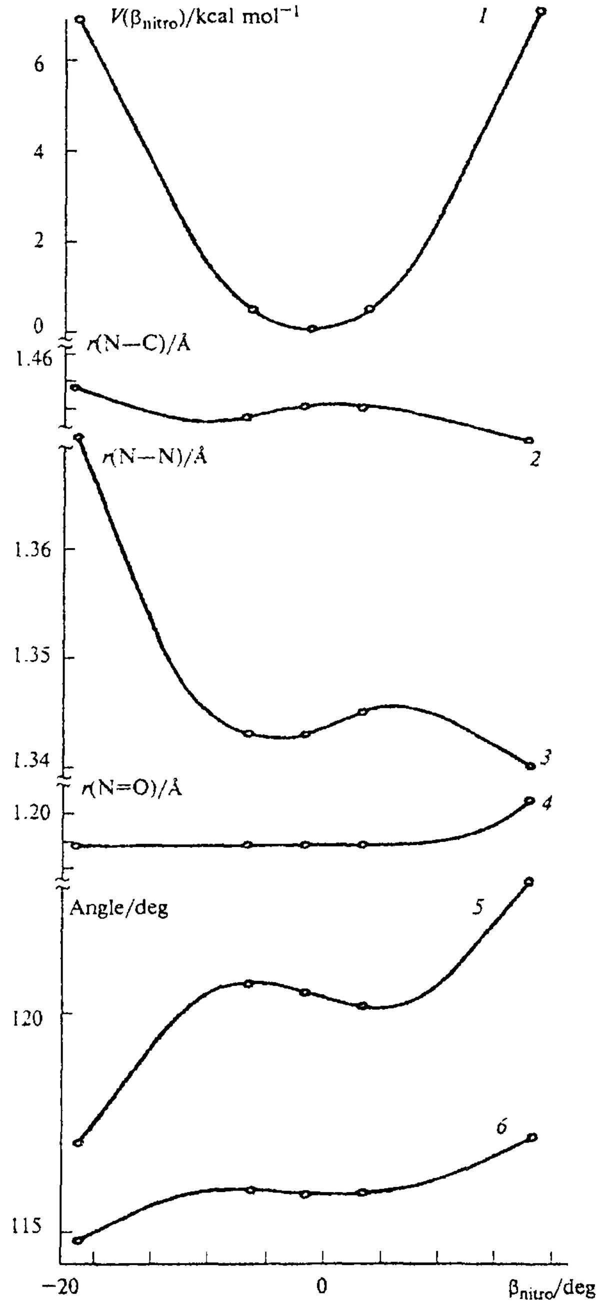


Fig. 7. Approximation of the potential function of the wagging vibration of the nitro group in Me_2NNO_2 by the quadratic trinomial (*1*) (the values of the total electronic energy calculated in the RHF/6-31G* approximation are shown by open circles). Dependences of the N—N (*2*), N—C (*3*), and N=O (*4*) bond lengths and C—N—C (*5*) and N—N—C (*6*) bond angles on the β_{nitro}(NN/ONO) angle between the N—N bond and the ONO plane calculated in the RHF/6-31G* approximation.

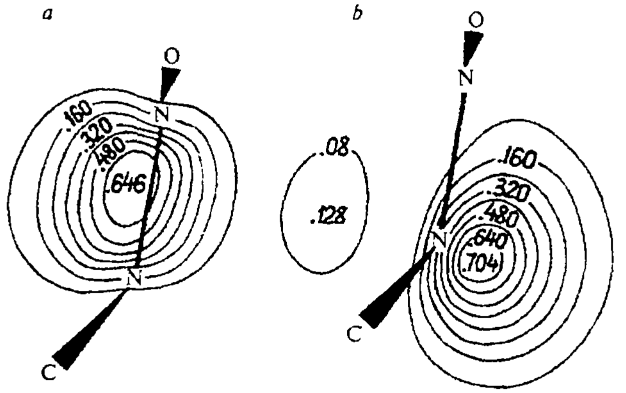


Fig. 8. The electron density contour maps (in the symmetry plane of the Me_2NNO_2 molecule) of the orbitals of the N—N bond (*a*) and lone electron pair of the amine N atom (*b*) obtained for the wave functions of the RHF/6-31G* approximation and localized according to Boys.

However, the length of this bond remains nearly unchanged as the nitro group moves in the opposite direction approaching the methyl substituents. The C—N—C and C—N—N angles decrease in the first case and increase in the second case. Other parameters including the N=O and N—C bond lengths and the O—N—O angle are not sensitive to this vibration. The considered geometry relaxation suggests that the potential function $V(\beta_{nitro})$ is mainly determined by weakening of the p—π-conjugation at $\beta_{nitro} < 0$ and the increase in the Coulomb repulsion when β_{nitro} changes in the opposite direction.

To illustrate the above conclusions, it can be useful to consider the localized orbitals constructed according to the Boys' criterion[51] on the basis of our calculations in the RHF/6-31G* approximation for the equilibrium form of *N*,*N*-dimethylnitramine. In Fig. 8, the sections of the localized orbitals corresponding to the N—N bond (diagram *a*) and lone electron pair of the amine N atom (diagram *b*) in the symmetry plane of the molecule are shown. In the case *a*, the center of the electron density is slightly shifted from the line of the N—N bond in the same direction as the methyl substituents in the pyramidal amino fragment. In the other diagram, the major portion of the electron density of the lone electron pair is on the opposite side from the N—N bond and is shifted toward the nitro group. The lone electron pair of the amine N atom makes a substantial contribution to the N—N bond giving some π-character to it. This contribution changes in the case of intramolecular motions and also depends on the electronegativity of the substituents at the amine N atom.[20] Changes in geometric parameters occurring in both cases are in agreement with those expected on the basis of the concept of the p—π-conjugation, which most likely indicates that they have a common basis.

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