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The nature of chemical bonding in nitramide*

I. V. Ananyev,[a] Yu. V. Nelyubina,[a] A. A. Korlyukov,[a] P. Yu. Barzilovich,[b]
M. Yu. Antipin,[a] S. M. Aldoshin,[b] and K. A. Lyssenko[a]*

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5085. E-mail: kostya@xray.ineos.ac.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow region, Russian Federation.
Fax: +7 (496) 515 5420. E-mail: pjietro@yandex.ru

The spatial and electronic structure studies of nitramide NH_2NO_2 suggest that the change in its molecular geometry upon transition from the gas phase to the condensed state is caused by an increase in the contribution of conjugation between functional groups. According to the analysis of the Bader atomic charges, the effects of such conjugation are to a considerable extent governed by intramolecular charge transfer from the amino to the nitro group. From estimation of the contribution of conjugation to the charge transfer it follows that conjugation remains in the isolated molecule. The influence of hydrogen bonding on the increase in the contribution of conjugation and the corresponding charge redistribution in the molecule was considered. Despite the presence of conjugation between functional groups, the planar configuration of the molecule in the crystal is not realized and the crystallographic twofold axis corresponds to superposition of two molecular configurations with C_s symmetry.

Key words: nitramide, conjugation, quantum chemical calculations, density functional theory (DFT), topological analysis, electron density distribution function, thermal motion analysis, "Atoms in molecules" theory.

The chemical and physical properties of nitramide NH_2NO_2 (**1**), the simplest representative of nitroamine compounds, have been described in detail in the literature. In particular, a review dedicated exclusively to this compound was published.[1] Interest in the nitramide molecule is to a large extent due to its frequent use as the simplest model (reference) for studying the features of chemical bonding in nitroamines.

As is well known, the geometry of nitroamines can change upon transition from the crystal to the gas phase, which makes them different in principle from the majority of organic compounds. In particular, the N—N bond length in molecule **1** is 1.381 Å according to gas-phase electron diffraction (GED) data[2] (*cf.* 1.322(2) Å in the crystal at 100 K according to the X-ray diffraction data[3]). This decrease in the bond length is accompanied by flattening of the molecule; namely, the sum of the angles at the N atom of the amino group (Σ_N) is 340.3° in the gas-phase and 360° in the crystalline state. According to quantum chemical calculations, planar molecule **1** (C_{2v}) in the gas phase is characterized by a saddle point with one imaginary frequency corresponding to a transition to the pyramidal configuration.[3]

Based on the aforesaid and taking into account the fact that in the crystal (space group $C2/c$, $Z' = 0.5$), the molecule occupies a special position (on the twofold axis), one cannot exclude that flattening of the molecule in the solid can be induced by dynamic disordering, which, in particular, is caused by the crystal symmetry (symmetry imposed disorder).[4] Multitemperature X-ray diffraction studies of the nitramide crystal[3] demonstrated significant vibrational anisotropy of the N atom of the amino group in the direction perpendicular to the plane of the molecule, which does not allow one to exclude unambiguously the dynamic positional disorder of this atom despite a small value of the temperature factor.

Quantum chemical calculations show[3] that the N—N bond length and the degree of pyramidality in the molecule are susceptible to the polarity of the medium. This is manifested when model clusters containing hydrogen-bonded nitramide molecules are considered with inclusion of specific solvation. This molecule is structurally similar to the donor-acceptor boron complexes and/or silicon compounds with the expanded coordination sphere (see Ref. 5). A special name, *viz.*, "partly bonded" mole-

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cules,[6] was proposed for the latter; some extent of double bonding between the N atoms is assumed for nitramide (see Ref. 1 and references cited therein), which, conversely, should suggest the presence of a sufficiently strong N—N bond.

Based on the aforesaid, it was interesting to perform a detailed study of the features of chemical bonding in the nitramide molecule in the crystal and in the gas phase in order to estimate how the observed geometry changes are reflected in the charge redistribution and whether these parameters can be used to assess conjugation. The problem of conjugation in nitramide is not only of theoretical interest, but also of practical significance to understand the causes of a high basicity of the O atoms of the nitro group and, consequently, possible decomposition mechanism of this molecule.[1]

To study chemical bonding in nitramide, we applied the "Atoms in Molecules"[7] (AIM) theory based on the topological analysis of the electron density distribution functions $\rho(\boldsymbol{r})$ in the crystal, in isolated molecule, and in a model H-bonded cluster using the results of a precise X-ray diffraction study and quantum chemical calculations. This approach was chosen because the topological analysis can be applied equally to both experimental and theoretical electron density distribution functions being,[8] in essence, the only method dealing with the integral atomic characteristics such as atomic energies in the molecule.[9]

Experimental

Nitramide was synthesized following a conventional procedure by the reaction of $NaSO_3NH_2$ with concentrated HNO_3 ($\rho^{20\,°C} = 1.5$ g cm^{-3}).[10] Single crystals were obtained by high-vacuum sublimation at room temperature.

The X-ray diffraction study of compound **1** was performed at 100 K on a SMART APEX II CCD three-circle diffractometer (Mo-Kα, graphite monochromator, ω scanning, $\theta < 55°$). At 100 K, the crystals are monoclinic: $a = 7.7302(2)$, $b = 4.7342(1)$, $c = 6.4377(2)$ Å, $\beta = 111.173(1)°$, $V = 219.69(1)$ Å^3, space group $C2/c$, $Z = 4$ ($Z' = 0.5$), $M = 62.04$, $d_{calc} = 1.876$ g cm^{-3}, $\mu = 1.92$ cm^{-1}, F(000) = 128. Among 17782 reflections measured ($R_{int} = 0.0221$), 1403 independent reflections were used in subsequent calculations. The structure of compound **1** was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation against F^2_{hkl}. The H atoms were located by the difference Fourier syntheses of electron density and refined in the isotropic approximation. The final R factors for **1** were as follows: $R_1 = 0.0270$ over 1264 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0801$, and GOOF = 1.087 for all 1403 reflections. All calculations were carried out using the SHELXTL PLUS program package.[11]

The multipole refinement of the electorn density distribution function $\rho(\boldsymbol{r})$ in the crystal of compound **1** was performed within the Hansen—Coppens model using the XD program package.[12] In the multipole refinement, the coordinates, anisotropic displacement parameters, and multipole parameters up to the octupole level ($l = 3$) were refined for all non-hydrogen atoms against F_{hkl}. The positons of the H atoms and their isotropic displacement parameters remained fixed. Before the refinement, the N—H distance was normalized to 1.02 Å, which corresponds to optimization of the central molecule in the model cluster containing nine nitramide molecules (see below). For more correct description of hydrogen bonds, the electron density for the H atom was described by means of dipoles and hexadecapoles taking into account the cylindrical symmetry. The correctness of the anisotropic displacement parameters (ADP) obtained was estimated using the Hirshfeld test,[13] which was at most $1 \cdot 10^{-4}$ Å. The results of the multipole refinement for **1** are as follows: $R_1 = 0.0133$, $wR = 0.0133$, and GOOF = 1.526 over 1100 reflections with $I > 3\sigma(I)$.

The potential energy densities $v(\boldsymbol{r})$ were calculated from the X-ray diffraction data in terms of the Thomas—Fermi theory.[14] According to this approach, the kinetic energy density ($g(r)$) can be calculated from the equation $g(r) = 3/10(3\pi^2)^{2/3}[\rho(\boldsymbol{r})]^{5/3} + (1/72)|\nabla\rho(\boldsymbol{r})|^2/\mathrm{r}(\boldsymbol{r}) + 1/6\nabla^2\rho(\boldsymbol{r})$, which in combination with the local virial theorem $2g(\boldsymbol{r}) + v(\boldsymbol{r}) = 1/4\nabla^2\rho(\boldsymbol{r})$ allows one to calculate both the potential energy density and the local energy density $h_e(\boldsymbol{r})$. The corresponding topological characteristics ($\rho(\boldsymbol{r})$, $h_e(\boldsymbol{r})$, $g(\boldsymbol{r})$, and $v(\boldsymbol{r})$) at the (3, –1) critical points found were calculated using the WINXPRO 1.5.20 program.[15]

To reveal possible disordering of the N atom of the amino group, the ADP were estimated using the XDVIB1 and XDVIB2 programs of the XD suite.[16] The ADP values were estimated based on the atomic vibrations of nitramide at 100 K calculated for isolated molecule **1** (M062X/6-311+G**) within the framework of the density functional theory (DFT) and for the experimental geometry of the nitramide molecule in the crystal ignoring the contribution of the vibrations of the molecule as a whole (phonon vibrations) to ADP. No scale factors were used in conversion of the atomic displacements obtained from the DFT caclculations into ADP.

Details of quantum chemical calculations. Isolated molecule **1**, model compounds, and corresponding clusters were calculated using the GAUSSIAN 03 program. Perturbative calculations of molecular clusters are time-consuming and resource-intensive. Therefore, we performed a series of calculations of the isolated nitramide molecule using different functionals to select an optimal computational method for molecular assemblies with the use of the 6-311+G** split basis set. All functionals used (PBE1PBE, B3LYP, B3PW91, M05-2x, M06-2X) reproduce the GED data and the results of MP2/6-311+G** and CCSD/aug-cc-pVTZ calculations quite correctly. Formally, the least discrepancy between the calculated geometry of isolated molecule **1** and the GED data was obtained using the M06-2X functional (1.382 Å for N—N, $\Sigma_N = 337.2°$). In addition, this method enables a reasonably correct inclusion of dispersion interactions within the framework of DFT.[17] Therefore, in the present work all calculations were performed at the above-mentioned level of theory.[18]

Non-specific solvation was taken into account in the self-consistent reaction field (SCRF) approximation within the polarized continuum model.[19] The value of the dielectric constant (ε) corresponded to water (82), which usually correlates well with the polar environment in the crystal.[5,20] The standard convergence criteria were used upon optimization of molecular parameters.[5] To confirm unambiguously the type of the stationary points, atomic vibrational frequencies were calculated for all isolated molecules. No frequency calculations were performed for the cluster containing nine nitramide molecules.

The topological analysis of the calculated function ρ($\boldsymbol{r}$) was performed using the AIMAll program.[21] Upon integration of the atomic basins, the absolute value of $1/4\nabla^2\rho(\boldsymbol{r})$ was at most $2 \cdot 10^{-3}$ a.u., which, in turn, allowed us to obtain a good convergence of the total energy, charges, and the sum of atomic contributions. In particular, in the cluster containing nine molecules **1**, the loss of charge was $3 \cdot 10^{-3}$ e and the difference between the total energy of atoms and the energy of the system is 0.45 kcal mol^{-1}. For the isolated molecule, the above-mentioned values were ten times smaller.

As the potential energy of the interaction between particles in a molecule is proportional to the distance between them, the virial theorem for the total kinetic energy can be written as follows: $2T = V$ (T and V is the kinetic and potential energy, respectively). The appropriately scaled kinetic energy is equal in absolute value to the total energy of the system. Since for different conformations of molecule **1** and model compounds, the ratio of the potential energy to the kinetic energy (V/T) deviated slightly from 2, we used the unscaled kinetic energies (K) of atoms, which resulted in some increase in the energy differences. This increase did not change the qualitative and quantitative trends. For the sign of the kinetic energy be the same as that of the total energy of the system, the $-K$ values are given in the present work.

The structure of the nitramide molecule in the crystal was calculated using the PBESol exchange-correlation functional,[22] the plane wave basis set (the maximum kinetic energy is 545 eV), and the VASP 5.2.11 program.[23] The core electrons were described using the projected augmented waves[24] (nonlocal pseudopotentials). The atomic coordinates and unit cell vectors were optimized using the experimental data (atomic coordinates, unit cell parameters, and symmetry operations). The Kohn-Sham equations were integrated using the 4×4×4 k-point grid. After optimization, the maximum force on atoms was less than 0.01 eV Å^{-1} and the unit cell volume decreased by 0.58% as compared with the experimental value. Vibrational frequencies were calculated by the finite difference method using the 2×2×2 supercell (the volume is 1747.33 Å) obtained by duplication of the optimized unit cell parameters.

Results and Discussion

The spatial and electronic structures of the nitramide molecule in the crystal. When considering the molecular geometry of nitramide obtained in the precise X-ray diffraction study, it should be noted that the bond angle H—N—H (134.1°) is considerably larger than in the amino group linked to the tertiary C atom. An analysis of the Cambridge Structural Database (CSD) showed that, according to the neutron diffraction data, the typical value of the H—N—H angle for the sp^2-hybridized N atom is 120° (the maximum published value is 127°).[25] Such a large deviation of the value obtained for nitramide from the statistical one allows one to assume that this is due to superposition of two pyramidal configurations. Indeed, the projection of the H atomic positions in the isolated nitramide molecule calculated by the M06-2X/6-311+G** method (see below) on the plane of non-hydrogen atoms results in the geometry similar to that observed in the crystal with the H—N—H angle being close to 132°.

However, an attempt to separate the superposition of two pyramidal N—NH_2 fragments even by refining the model based on the data of the precise X-ray diffraction study has failed. The main geometry parameters (in particular, the N(1)—N(2) bond length equal to 1.3193(4) Å) and the type of supramolecular organization in the crystal of compound **1** (Fig. 1, Table 1) virtually do not differ from those described earlier (see Ref. 3). Therefore, to answer the question of disordering and its influence on the features of chemical bonding, hereafter we will pay attention to the analysis of thermal vibrations.

Earlier,[3] it was reported that the component of the atomic ellipsoid of N(1), directed along the axis perpendicular to the plane of the molecule, is noticeably greater than the other two components (Fig. 1, a). Since the promolecule model used in the standard structure refinement includes the contributions of not only atomic displace-

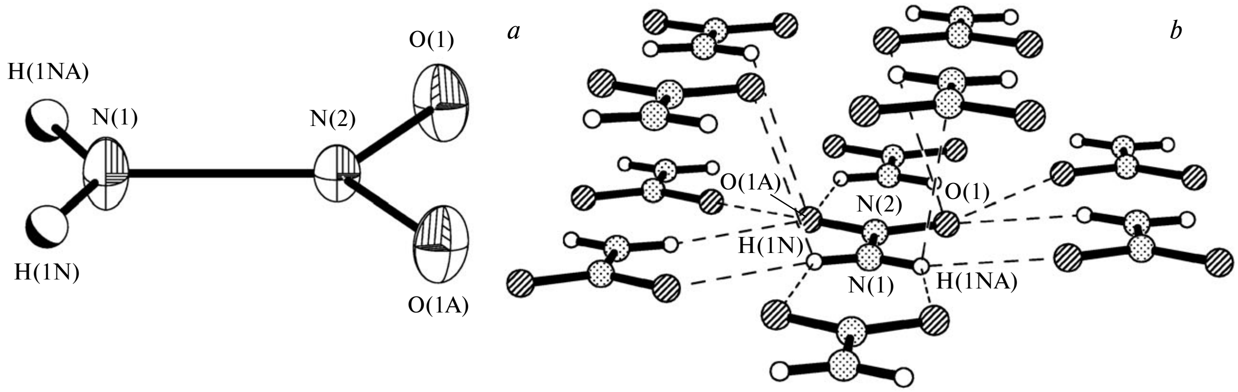

Fig. 1. General view of compound **1** with non-hydrogen atoms represented by thermal ellipsoids (p = 50%) (a) and the fragment of its crystal packing (b). The intermolecular interactions revealed by topological analysis of the experimental function ρ($\boldsymbol{r}$) are shown by the dashed lines.

Table 1. Geometric parameters and energy characteristics of molecule **1** obtained from M06-2X calculations of isolated molecular forms, determined within the SCRF theory, as well as from X-ray diffraction and gas-phase electron diffraction data[2]

Molecular forms	$-E_{tot}$	ZPE	N_{imag}	V/T	μ/D	N(1)—N(2) /Å	Σ_N /deg	N—O/Å	N—H/Å	*DI*
	a.u.									
					Isolated					
1 (C_s)	261.01220	0.0403	0	2.0027	3.78	1.382	337.2	1.208	1.012	1.14
1 (C_{2v})	261.00954	0.0389	1	2.0027	4.44	1.352	360.0	1.212	1.006	1.19
$\mathbf{1}_{perp}$ (C_s)	260.99509	0.0392	1	2.0027	3.63	1.456	312.0	1.195—1.209	1.020	1.01
$\mathbf{1}_{perp}$ (C_{2v})	260.97933	0.0376	2	2.0027	3.52	1.410	360.0	1.205	1.002	1.04
					Solvated (SCRF)					
1 (C_s)	261.02432	0.0399	0	2.0029	4.50	1.359	339.9	1.215	1.013	1.19
1 (C_{2v})	261.02262	0.0386	1	2.0029	5.52	1.330	360.0	1.22	1.008	1.26
1 (X-ray diffraction)	—	—	—	—	7.0	1.3193(4)	360.0	1.2376(2)	1.020	—
1 (GED)	—	—	—	—	—	1.381	340.3	1.232	—	—

Note. E_{tot} is the total energy of the molecule, ZPE is the zero-point vibrational energy, N_{imag} is the number of imaginary frequencies, V/T is the potential-to-kinetic energy ratio, μ is the dipole moment of the molecule, and *DI* is the delocalization index of the N—N bond. Molecule $\mathbf{1}_{perp}$ has perpendicular arrangment of the NH_2 and NO_2 groups; the longer N —O bond length in molecule $\mathbf{1}_{perp}$ (C_s) corresponds to the antiperiplanar-oriented orbital of the lone electron pair of the amine N atom. The dipole moment μ in the crystal was calculated based on the static function ρ(***r***) obtained in the multipole refinement.[2]

ments, but also the electron density distribution anisotropy to the ADP, we used the multipole model which allows one to obtain the static function ρ(***r***) contracted with the atomic displacement tensor. Although the ADP values obtained for molecule **1** met the Hirshfeld test,[13] one cannot exclude that the observed geometry of **1** can correspond to superposition of its two configurations with a small pyramidality caused by deviation of the N(1) atom from the plane of the molecule in the opposite directions. The magnitude of this deviation can be estimated by the root-mean-square displacement of the N(1) atom perpendicular to the plane of the molecule, which is 0.0197 Å at 100 K (see Ref. 2). Consequently, the deviation of the atom should not exceed half the ellipsoid eccentricity, *i.e.*, 0.07 Å. At such insignificant symmetry violation of the crystal, the Hirshfeld test[13] can be fulfilled even in the presence of dynamic and/or static disorder (see discussion of the analogous issue for hydromaleates[26,27]).

To estimate the influence of possible disordering on the root-mean-square amplitudes of atomic displacements in the nitramide crystal, we performed quantum chemical calculation of the harmonic vibrational frequencies of planar isolated molecule **1** followed by estimation of the corresponding anisotropic displacement parameters (see Experimental). The root-mean-square amplitudes of atomic displacements estimated according to the resulted ADP agree well with the experimental ones for the atoms of the NO_2 group (the difference between the maximum root-mean-square displacements for the N(2) and O(1) atoms is $4 \cdot 10^{-4}$ Å^2). For the N(1) atom of the amino group, the corresponding root-mean-square amplitudes are two orders of magnitude lower than the experimental ones and the maximum eccentricity is only 0.03 Å. Thus, a significant anisotropy for the N(1) atom in the crystal of compound **1** suggests superposition of nonplanar configurations of the molecule rather than characterizes intramolecular vibrations.

Vibrational frequency calculations for the crystal of compound **1** led to a similar conclusion (see *Details of quantum chemical calculations*). When using symmetry operations in the calculated Hesse matrix, three negative eigenvalues (−77.36, −111.85, and −244.44 cm^{-1}) were found. Their normal modes have a complex character and include displacement of the N(1) atom of the amino group from the plane in which both H atoms and the N(2) atom lie. In addition, distortion of the planar-trigonal configuration of bonds at the N(1) and N(2) atoms (the change in the positions of the H and O atoms) was observed. In this case, the lowest positive frequency is 75.35 cm^{-1} and corresponds to the changes in the positions of the N atoms. Vibrational frequency calculations using the same atomic coordinates but ignoring symmetry operations gave no negative eigenvalues (see above); the lowest frequency was 101.77 cm^{-1}. The normal mode of this vibration is associated with the changes in the positions of the O and N atoms.

One can conclude that the symmetry of molecule **1** in the crystal is other than C_2. This can either cause positional disordering of the N atom of the amino group or result from it. Based on the experimental values of the root-mean-square displacement amplitudes, a possible deviation of the N(1) atom from the plane passing through the atoms bonded to it is so small that two positions cannot be separated irrespective of the resolution used and the choice of the space symmetry group. In particular, a possible increase in the N—N bond length due to such a disorder will be at most 0.0019 Å.

Since molecule **1** is characterized by local disorder and its deviation from pyramidal shape is negligible, one can assume that the static function $\rho(\mathbf{r})$ obtained in the multipole refinement will allow one to correctly analyze the character of intermolecular interactions in the crystal and possible systematic errors can be observed only for the integral characteristics of the N(1) atom (see, for example, Ref. 28).

The deformation electron density (DED) distribution in molecule **1** is close to that to be expected. It is characterized by the presence of maxima in the regions of chemical bonds and lone electon pairs of the O atoms (Fig. 2, *a*). It should be noted that the DED maximum in the region of the N(1)—N(2) bond is considerably shifted toward the nitro group. The character of the electron density distribution in the regions of the N—H...O bonds is also quite typical and illustrates a certain directionality of interactions (Fig. 2, *b*).

The topological analysis of the function $\rho(\mathbf{r})$ in the crystal of compound **1** revealed the presence of the (3,–1) critical points (CP) corresponding, in terms of the AIM theory, to bonding interactions for all covalent bonds and for some intermolecular interactions from the hydrogen bonds N—H...O (N...O is 3.0241(4)—3.0612(4) Å, H...O is 2.24—2.50 Å, and the NHO angle is 120—165°) and interactions $NO_2...NO_2$ (O...O is 2.7701(4) Å) combining molecules into layers to the weaker interlayer hydrogen bonds N—H...O (N...O is 3.1952(4) Å, H...O is 2.80 Å, and the NHO angle is 110°), very weak interactions N—H...N (N...N is 3.4508(4) Å, H...N is 3.16 Å, and the NHN angle is 103°), and interactions between the nitro groups (O...O is 3.1532(4) Å) (see Fig. 1, *b*). An analysis of the topological parameters at the (3,–1) CP showed that all covalent bonds including N—N correspond to shared interactions ($\nabla^2\rho(\mathbf{r}) < 0$, $h_e(\mathbf{r}) < 0$) while intermolecular bonds correspond to the closed-shell type interactions ($\nabla^2\rho(\mathbf{r}) > 0$, $h_e(\mathbf{r}) > 0$).

The obtained integral parameters of the atoms are characterized by a sufficiently high accuracy. In particular, the loss of charge is at most 0.01 *e* and the error in the determination of the molecular volume is 0.6% compared to the unit cell volume. The nitro group bears a rather large negative charge of –0.39(1) *e* and the amino group has a positive charge of 0.40(1) *e*. Such a high polarity of the molecule agrees well with the high value of its dipole moment in the crystal (7 D) obtained in the multipole refinement.[29] It should be noted that this value is considerably higher than that of molecule **1** even calculated using the SCRF model (see Table 1).

For subsequent comparison of the strength of interatomic interactions in the crystal and in the model clusters and their role in the change in the electronic structure, we estimated the energies (E_{int}) of these interactions using a semi-quantitative correlation[30] which is successfully used to describe a wide range of weak interactions in crystals, including dispersion interactions.[31] We have found that all N—H...O bonds in the crystal are rather weak ($1 < E_{\text{int}} < 2.5$ kcal mol^{-1}), while the interaction energies between the O atoms of the nitro groups are 1.4 and 2.0 kcal mol^{-1} for the interlayer and intralayer contacts, respectively, and the energy of the N—H...N interlayer hydrogen bond between the amino groups is at most 0.7 kcal mol^{-1}. The overall energy of hydrogen bonds per

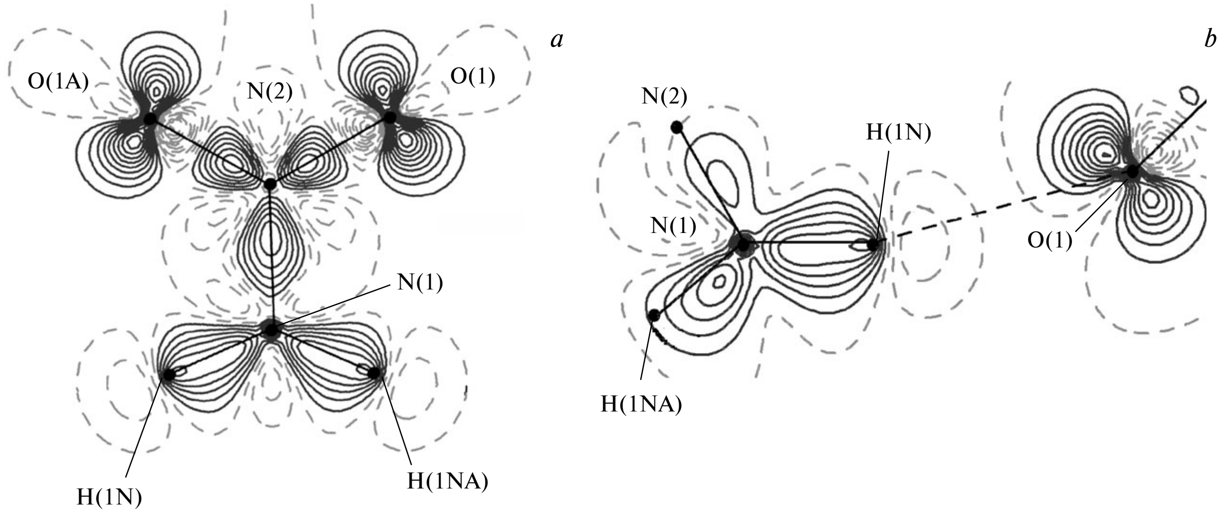

Fig. 2. DED distribution in the plane of molecule **1** (*a*) and in the region of the strongest N—H...O bond (distance N...O is 3.0241(4) Å) (*b*). The negative values are shown by the dashed lines. The contours are drawn at intervals of 0.05 *e* Å^{-3}.

Table 2. Charges (q/e) on atoms and functional groups in molecule **1** from M06-2X calculations of isolated molecular forms and calculated within the SCRF theory

Molecular forms	$q(\mathrm{N})_{\mathrm{NH_2}}$	$q(\mathrm{N})_{\mathrm{NO_2}}$	$q(\mathrm{H})$	$q(\mathrm{O})$	$q(\mathrm{NH_2})$	$q(\mathrm{NO_2})$
			Isolated			
1 (C_s)	−0.66	0.74	0.43	−0.47	0.21	−0.21
1 (C_{2v})	−0.71	0.75	0.46	−0.48	0.22	−0.22
$\mathbf{1}_{\mathrm{perp}}$ (C_s)	−0.63	0.74	0.39	−0.45*	0.16	−0.16
$\mathbf{1}_{\mathrm{perp}}$ (C_{2v})	−0.78	0.75	0.45	−0.44	0.13	−0.13
			Solvated (SCRF)			
1 (C_s)	−0.64	0.73	0.47	−0.51	0.29	−0.29
1 (C_{2v})	−0.67	0.73	0.49	−0.52	0.32	−0.32

* The atomic charges on oxygens in molecule $\mathbf{1}_{\mathrm{perp}}$ (C_s) differ due to the anomeric effect and are −0.42 and −0.47 *e*.

NH_2 or NO_2 group in the crystal of compound **1** is 11.9 and 10.5 kcal mol^{-1}, respectively. The integral energy values per molecule obtained in this work agree well with the published value of the sublimation enthalpy of nitramide (21.4 kcal mol^{-1}).[32]

The geometry and electronic structure of isolated nitramide molecule from quantum chemical calculations. Obviously, the geometry and electronic structure of molecule **1** change upon transition from the gas phase to the solid state accompanied by flattening of the molecule. It is logical to assume that flattening is caused by the change in the hybridization of the N atomic orbitals and by the onset of conjugation between the NO_2 and NH_2 groups. Since different molecular geometries in the gas phase and in the crystal evidence structural nonrigidity of the molecule, this assumption needs to be substantiated and the flattening process of the molecule requires a detailed study.

First, it it interesting to determine the differences in the spatial and electronic structures between the pyramidal (C_s symmetry) and planar (C_{2v}) configurations of isolated molecule **1** (see Tables 1—3). Irrespective of the computational method used, the nitramide molecule with C_{2v} symmetry corresponds to the transition state. Despite the fact that flattening of the molecule is accompanied by a significant decrease in the N—N bond length (by 0.03 Å), the energy difference between the forms **1** (C_s) and **1** (C_{2v}) with allowance for the zero-point vibrational energies is only 1.7 kcal mol^{-1}. In addition to the shortening of the N—N bond, flattening of the molecule causes a slight elongation of the N—O bond (1.212 *vs.* 1.208 Å) and shortening of the N—H bond by 0.006 Å.

An analysis of the atomic charges (see Table 2) shows that the above-mentioned shortening of the N—N bond does not lead to significant changes in the atomic charges of N (0.74 and 0.75 *e* for the N atom of the nitro group, −0.66 and −0.71 *e* for the N atom of the amino group of molecules **1** (C_s) and **1** (C_{2v}), respectively). A minor increase in the electron population of the N atomic basin of the amino group is accompanied by a decrease in the positive charges of the H atoms by 0.02 *e*. The overall electron population of the atomic basins of the nitro group increases slightly (by 0.01 *e*). Also, the dipole moment of the molecule changes a little (4.0 and 4.4 D for molecules **1** (C_s) and **1** (C_{2v}), respectively). In combination with slight changes in the atomic charges, this suggests an increase in the degree of charge transfer from the H atoms to the nitro group upon flattening of the molecule.

As can be seen from the data of Table 3, flattening of the molecule causes the energies of the NH_2 and NO_2 groups to change in opposite directions. For the amino group, redisribution of the atomic basin populations correlates with the change in the atomic contributions to the total energy of the molecule. Namely, the increase in the

Table 3. Atomic contributions (a.u.) to the kinetic energy[a] of molecule **1** from M06-2X calculations of isolated molecular forms and calculated within the SCRF theory

Molecular forms	$-K(\mathrm{N})_{\mathrm{NH_2}}$	$-K(\mathrm{N})_{\mathrm{NO_2}}$	$-K(\mathrm{H})$	$-K(\mathrm{O})$	$-K(\mathrm{NH_2})$	$-K(\mathrm{NO_2})$
			a.u.			
			Isolated			
1 (C_s)	−54.8550	−54.1140	−0.4453	−75.2226	−55.7457	−204.5591
1 (C_{2v})	−54.8944	−54.1074	−0.4287	−75.2196	−55.7519	−204.5466
$\mathbf{1}_{\mathrm{perp}}$ (C_s)	−54.8018	−54.1040	−0.4666	−75.2270[b]	−55.7349	−204.5580
$\mathbf{1}_{\mathrm{perp}}$ (C_{2v})	−54.8755	−54.0766	−0.4343	−75.2244	−55.7441	−204.5255
			Solvated (SCRF)			
1 (C_s)	−54.8562	−54.1172	−0.4271	−75.2270	−55.7104	−204.5711
1 (C_{2v})	−54.8877	−54.1168	−0.4123	−75.2229	−55.7122	−204.5625

[a] The V/T ratio is given in Table 1.

[b] The kinetic energies of the O atoms in molecule $\mathbf{1}_{\mathrm{perp}}$ (C_s) differ due to the anomeric effect and are 75.2255 and 75.2285 a.u.

basin population of nirogen results in its stabilization by 24.7 kcal mol^{-1}, whereas the descrease in the positive charges on the H atoms results in the increase in their overall energy by 20.8 kcal mol^{-1}. The reverse was found for the atoms of the nitro group, *viz*., its overall energy increases by 7.8 kcal mol^{-1} upon flattening of the molecule despite some increase in the negative charge.

Earlier,[3] it was reported that specific solvation, *viz*., intermolecular hydrogen bonds N—H...O, plays a significant role in flattening of the molecule. In addition, the geometry of structurally nonrigid molecules is ofted influenced by the polarity of the medium.[5,6] To estimate its effect on the spatial and electronic structures of nitramide, we performed quantum chemical calculations of solvated molecule **1**(C_s) using the SCRF model.

Despite the fact that the effect of the polarity of the medium leads to a significant decrease in the N—N bond length (to 1.359 Å), molecule **1** with C_s symmetry possesses a pyramidal configuration ($\Sigma_N = 339.9°$). Shortening of the N—N bond as a result of nonspecific solvation is accompanied by slight elongation of the N—O bonds (to 1.215 Å), the N—H bond lengths remaining unchanged. Thus, the effect of the polarity of the medium manifests itself only in the change in the N—N bond length without influencing other geometric parameters of the molecule.

Slight atomic charge redistribution upon increase in the relative dielectric constant of the medium mainly affects the H and O atoms (see Table 2), whereas the N atomic populations remain virtually unchanged despite a significant change in the N—N bond length. Shortening of the N—N bond caused by the increase in the polarity of the medium leads to an increase in the degree of intramolecular charge transfer from the H atoms to the O atoms, which agrees well with the increase in the dipole moment of form **1** (C_s). Thus, one can expect a stronger effect of the medium on the differences in the electronic structures between the molecules with C_s and C_{2v} symmetries. However, an analysis of the atomic charges and energies reveals only slight changes upon flattening of the molecule (see Tables 2 and 3), which reproduce the trend described above for $\varepsilon = 0$. An analysis of the atomic contributions to the energy of the molecule (see Table 3) demonstrates a similar trend, namely, taking account of the polarity of the medium leads to maximum changes for the H and O atoms. For example, the absolute energy of the amine N atom increases only by 5.5 kcal mol^{-1}, while that of the H atoms increases on the average by 11.5 kcal mol^{-1}. Stabilization of the NH_2NO_2 molecule in the crystal through nonspecific solvation occurs mainly due to the decrease in the energies of O atoms (9.1 and 9.5 kcal mol^{-1}).

The obtained data on the electronic structure of isolated molecule **1** do not allow one to conclude with certainty on the presence of conjugation in its planar configuration. Despite significant changes in the atomic energies upon flattening of the molecule, only a slight increase in the degree of charge transfer over the molecule was found, which can also be explained by the nonrigidity of the N—N bond in combination with the inductive effect of the nitro group.

Changes in the spatial and electronic structures of the nitramide molecule upon its flattening: a comparison with the model compounds NR_3. Taking into account the fact that flattening of the molecule can formally be described by the change in the orbital hybridization of the central N atom, we analyzed how the structure of the NR_3 molecule (R = H, Me, F) changes upon inversion of the N atom (Table 4).

A comparison of the bond lengths for the pyramidal (C_{3v}) and planar (D_{3h}) configurations of the molecules showed that in all cases, flattening is accompanied by shortening the N—R bonds by 0.014, 0.014, and 0.027 Å for NH_3, NMe_3, и NF_3, respectively. Thus, bond shortening in molecule **1** upon its flattening is quite expectable and can be explained without the use of the concept of conjugation. At the same time, the change in the bond in NF_3 is comparable in magnitude with shortening of the N—N

Table 4. Main geometric and energy[a] characteristics and atomic charges (q) for the NR_3 molecules obtained from M06-2X calculations[b]

Molecule	Symmetry	E_{tot}	V/T	$-K$(N)	$-K$(R)	q(N)	q(R)	N—R/Å
				a.u.		e		
NH_3	C_{3v}	−56.54590	2.0037	−54.8788	−0.48710	−1.03	0.34	1.013
	D_{3h}	−56.53900	2.0038	−54.9271	−0.46610	−1.17	0.39	0.999
NMe_3[b]	C_{3v}	−174.4283	2.0044	−55.0300	−39.5457	−1.02	0.34	1.451
	D_{3h}	−174.4135	2.0044	−55.1440	−39.5011	−1.15	0.38	1.436
NF_3	C_{3v}	−354.0706	2.0020	−53.6670	−99.8215	1.18	−0.29	1.355
	D_{3h}	−353.9509	2.0020	−54.0554	−99.7284	0.71	−0.24	1.328

[a] E_{tot} is the total energy of the molecule; K is the atomic contribution to the kinetic energy; V/T is the potential-to-kinetic energy ratio.

[b] For the methyl group (R), the overall energies and charges are given; the energies (charges) of the C atom bonded directly to the central atom are 37.6856 a.u. (0.36 e) and 37.6327 a.u. (0.41 e) for the C_{3v} and D_{3h} configurations , respectively.

bond in the isolated nitramide molecule (see Table 1), which suggests inapplicability of the term "structural nonrigidity" to the N—N bond upon flattening of the molecule.

An analysis of the atomic charges revealed slight differences between molecule **1** and the model compounds NR_3 (see Tables 2 and 4). For example, flattening of the NH_3, NMe_3, and NF_3 molecules causes an increase in the electron populations of the N atomic basin and their decrease on each substituent (see Table 4). Thus, irrespetive of the substituent electronegativity, flattening of the NR_3 molecule is always accompanied by a small charge transfer from the substituent R to the N atom, which is not realized for molecule **1** (*vide supra*). Upon flattening of the nitramide molecule, the basin population of the amine N atom changes to a lesser extent than for the NR_3 molecules considered above (0.05 *vs.* 0.12—0.15 *e*). This is likely due to a slight increase rather than decrease (as for NR_3) in the overall population of the atomic basins of the nitro group. Although all the above-mentioned values seem to be small, taking into accout a slight elongation of the N—O bonds and shortening of the N—N bond in molecule **1** (C_{2v}) as compared to molecule **1** (C_s), one can assume that the charge redistribution in molecule **1** compared to the compounds NR_3 can be considered as an indication of partial charge transfer from the amino group to the nitro one due to conjugation.

To a greater extent, the differences between molecule **1** and the model compounds NR_3 under consideration can be illustrated by the example of atomic contributions to its energy. Integration of the atomic energies showed that flattening of all nitramide molecules considered above results in significant increase in their absolute energies (see Table 3). At the same time, the energy of each substituent R in NH_3, NMe_3, and NF_3 decreases upon flattening (by 13.1, 27.5, and 58.5 kcal mol^{-1}, respectively, see Table 4). The C atoms in trimethylamine are destabilized by ~32.9 kcal mol^{-1}. In molecule **1**, the substituents at the N atom of the amino group are also destabilized upon flattening (see Table 3). The energy of the H atoms increases by the value comparable with that for ammonia (10.4 kcal mol^{-1}), while the nitro group is much less destabilized (7.8 kcal mol^{-1}) than the above-mentioned substituents R.

In the absence of conjugation, by analogy with the compounds NR_3, one can assume that the N atom bonded to the amino group will be destabilized to even greater extent than the C atom upon flattening of the molecule. However, a considerably smaller change in the energy of the N atom of the nitro group (4.1 kcal mol^{-1}) allows one to conclude that flattening of the molecule in the crystal is to a large extent caused by the conjugation effects. From this point of view, the above-mentioned increase in the overall population of the atomic basins of the nitro group accompanied by an increase in its energy upon flattening of the molecule is quite logical taking into account the increase in the charge transfer from the N atom of the amino group to the nitro group due to conjugation and the corresponding decrease in destabilization of the nitro group compared to the substituents in the compounds NR_3.

Thus, although the planar nitramide molecule with C_{2v} symmetry corresponds to a saddle point on the potential energy surface, flattening of the molecule is favored not only by the decrease in the energy of the amine N atom, but also by partial charge transfer from the amino group to the nitro group due to the conjugation effects.

Estimation of conjugation in isolated nitramide molecule. An obvious method of evaluating conjugation between fragments in molecule **1** is to compare the results obtained with the data for the *a priori* nonconjugated molecule, *i.e.*, the molecule with the perpendicular arrangement of funcitonal groups (*e.g.*, $\mathbf{1}_{perp}$, see Table 1). Unfortunately, this model has a big disadvantage. Planar molecule $\mathbf{1}_{perp}$ (C_{2v}) corresponds to the second-order saddle point with two imaginary vibrational frequencies (−883.15 and −561.12 cm^{-1}) corresponding to rotation of the nitro group and transition to the pyramidal molecule. The transition to the pyramidal molecule $\mathbf{1}_{perp}$ (C_s) is characterized by a saddle point with one imaginary frequency (−329.17 cm^{-1}) corresponding only to the U-turn of the functional groups relative to each other. On this basis, one can estimate the barrier to inversion of the N—NH_2 fragment in molecule $\mathbf{1}_{perp}$ and the barrier to rotation of the nitro group, which are respectively 10.7 and 11.4 kcal mol^{-1} (calculated with inclusion of zero-point vibrational energies). Thus, the barrier to inversion in molecule $\mathbf{1}_{perp}$ is 9 kcal mol^{-1} higher than in isolated molecule **1**, which can suggest the presence of conjugation in both its ground and transition states.

However, a rather strong anomeric interaction (*lp*N(1)—N(2)—O(1) = 180°) of the lone electron pair of the N atom with one N—O bond leading to elongation of this bond from 1.195 to 1.209 Å in the pyramidal molecule $\mathbf{1}_{perp}$ (C_s) should be noted. This does not allow one to relate directly the increase in the barriers to the conjugation effects, as well as to use the geometry, charges, and energies of the functional groups of molecule $\mathbf{1}_{perp}$ (C_s) for evaluation of the conjugation strength.

It is more correctly to compare the difference between the contributions to the total energies of molecules $\mathbf{1}_{perp}$ (C_{2v}) and **1** (C_{2v}); this can allow one to estimate the contribution of conjugation to the chemical bonding in nitramide (see Tables 2 and 3). For example, an analysis of atomic energies shows that, on going to the perpendicular arrangement of the functional groups relative to each other, the overall energies of the NO_2 and NH_2 groups increase differently (by 13.2 and 4.9 kcal mol^{-1}, respectively). Rotation of the amino group and the corresponding elongation of the N—N bond in molecule $\mathbf{1}_{perp}$ (C_{2v}) (1.410 Å) compared to molecule **1** (C_{2v}) (1.352 Å) (weakening of conjugation between the NO_2 and NH_2 groups) should lead to strengthening of conjugation within the nitro group (the N—O bond lengths are 1.212 and 1.205 Å, respectively).

Indeed, the O atoms in molecule $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) are stabilized in total by 6.1 kcal mol^{-1}; however, their atomic basin populations decrease by 0.04 *e* compared to molecule **1** (C_{2v}). This inverse relationship is quite expectable taking into account the absence of charge transfer in molecule $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}). At the same time, the atomic charge of the nitro N atom remains unchanged upon rotation of the amino group; however, its energy increases considerably (by 19.4 kcal mol^{-1}). Probably, such a large change in the energy is determined by not only the decrease in the contribution of conjugation of the nitro and amino groups, but also some charge transfer to the O atoms, which increases as the contribution of conjugation within the nitro group increases. When considering the amino group, it should be noted that its N atom in molecule $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) similarly to the nitro N atom is destabilized by 11.9 kcal mol^{-1} despite the increase in its atomic basin population by 0.07 *e*. The atomic charges of hydrogens in molecules $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) and **1** (C_{2v}) are virtually equal and the changes in their energies can be caused by the change in the atomic charge of nitrogen.

Based on the results obtained, we can estimate the degree of the charge transfer due to conjugation in isolated molecule **1** (C_{2v}) as the difference between the charges of the amino group in molecules $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) and **1** (C_{2v}); it equals 0.09 *e*. This is confirmed by the fact that the sum of this value (0.09 *e*) and the difference between the charges of the amino N atom in molecules **1** (C_{2v}) and **1** (C_s) (see Table 2) is equal to 0.14 *e*, *i.e.*, virtually does not differ from the corresponding atomic charge differences obtained upon flattening of the NR_3 molecules similar to molecule $\mathbf{1}_{\mathrm{perp}}$ in the lack of conjugation between the substituents and the N atom (see Table 4).

Unfortunately, from the results obtained for molecule $\mathbf{1}_{\mathrm{perp}}$ it is difficult to estimate the energy contribution of conjugation for molecule **1** (C_{2v}), because the changes in the energies of the atoms of the nitro group include the conjugation effects both within the group and between the functional groups and, for the amino group, the overall value includes the changes in the energies of H atoms, which are most likely not associated with conjugation. As a raw estimation, one can take the value of 11.9 kcal mol^{-1}, *i.e.*, the difference between the energies of the amino N atom in molecules $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) and **1** (C_{2v}), since conjugation effects mainly contribute to this value. One should keep in mind that the energy contribution of the increase in conjugation on going from molecule **1** (C_{2v}) to its analog in the crystal will be much smaller due to the difference in the corresponding bond lengths (see Table 1). It is obvious that the presence of conjugation between the NH_2 and NO_2 groups must result in weakening of conjugation within the nitro group and its partial destabilization despite the charge transfer to the nitro group due to the conjugation between the fragments. This is observed for the whole nitro group upon transition **1** (C_s) → **1** (C_{2v}) and for the O atoms upon transition $\mathbf{1}_{\mathrm{perp}}$ (C_{2v}) → **1** (C_{2v}).

Conjugation in nitramide from the results of molecular cluster calculations. An analysis of the results of quantum chemical calculations of isolated nitramide molecule using the polarized continuum model showed that the polarity of the medium influences the N—N bond shortening and causes no flattening of the molecule. These changes in the geometry can be due to "intention" of the molecule to increase its dipole moment in the polar medium. On this basis, one can conclude that the question on the mechanism of conjugation in the molecule (and, as a consequence, its flattening) on going from the gas phase to the crystal is still open. The role of specific intermolecular interactions (hydrogen bonds) in flattening of the molecule is undoubtful.

To estimate the influence of the number and nature of hydrogen bonds on the molecular geometry of **1**, we performed a series of quantum chemical calculations of model hydrogen-bonded nitramide clusters by successively increasing the number of molecules surrounding the central molecule (3, 5, and 9 molecules). Full geometry optimization of all clusters with increasing the number of neighbors led to gradual flattening of the central molecule, but the geometry of nitramide in the crystal (the distance N—N is 1.310 Å, the distances N—H are 1.019 and 1.020 Å, the distances N—O are 1.223 and 1.235 Å, and Σ_N is 357.9°) was quite accurately reprocuded only in the case of the cluster containing nine molecules. It should be noted that, taking into account the calculated vibrational amplitude (*vide supra*), the deviation of the N atom in the central molecule of the cluster (0.02 Å) is only slightly lesser than half the root-mean-square amplitude observed for the N(1) atom in the crystal of compound **1** according to the X-ray diffraction data.

Since optimization of geometric parameters of the above-mentioned cluster leads to a rather large scatter of their values from the viewpoint of the bond configuration of the amino N atom (Σ_N = 328.3—357.9°) and the N—N bond length (1.310—1.379 Å) while the virial value is constant, consideration of the nine-molecule cluster allows one to compare the energies of these molecules and their fragments, as well as to estimate the effect of intermolecular interactions on conjugation. On this basis and taking into account the fact that the spatial structures of the central molecule and its analog in the crystal almost match each other, hereafter, we will consider only the cluster built of nine molecules **1** (Fig. 3, Table 5).

The topological analysis of the function $\rho(\boldsymbol{r})$ revealed the (3,–1) CPs between the molecules in the cluster not only in the regions of hydrogen bonds, but also in the regions of some shortened contacts between the atoms of the nitro groups (both O...O and O...N), as well as

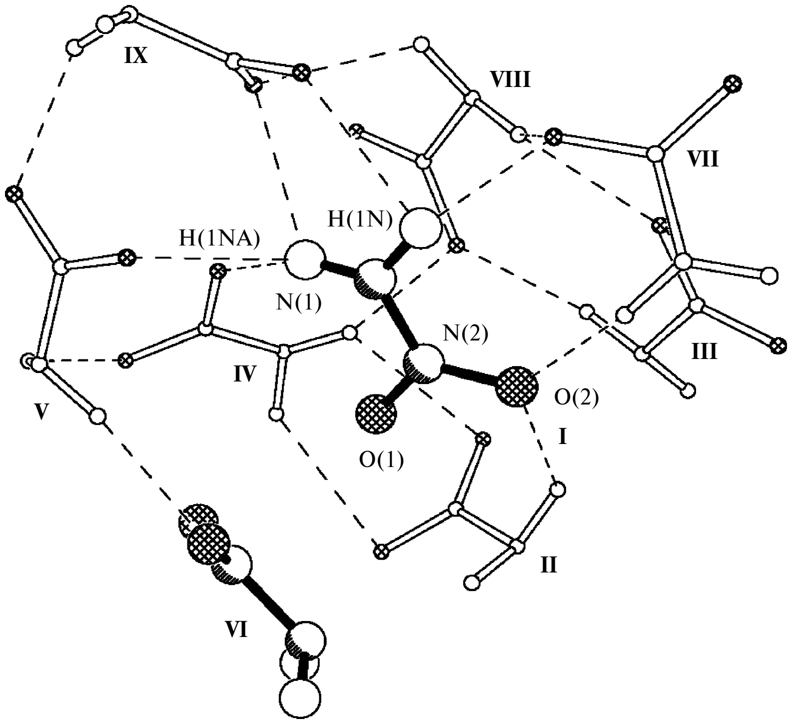

Fig. 3. The cluster containing nine nitramide molecules according to the M06-2X calculations. The intermolecular H-bonds found in the topological analysis of the theoretical function ρ(***r***) are shown by the dashed lines.

between the atoms of the nitro and amino groups (O...N). Estimation of the energies of the above-mentioned interactions based on the correlation[30] evidences that the H-bonds refer to the strongest interactions (the overall H-bond energies for the NH_2 and NO_2 groups are in the range 3.8—16.3 and 3.1—10.1 kcal mol^{-1}, respectively), while other intermolecular interactions in the cluster are characterized by the E_{int} values of at most 2.5 kcal mol^{-1}, being ~1 kcal mol^{-1} on the average. Moreover, from analysis of the atomic energies and charges it follows that in contrast to the H-bonds the nonvalence interactions mentioned above influence slightly the charge redistribution in

Table 5. Main geometric parameters, formal N—N bond orders, and intermolecular interaction energies in the cluster comprised of nine nitramide molecules

Molecule	N—N/Å	Σ_N /deg	*DI*	BO	H-bond energies		Intermolecular interaction energies	
					NH_2	NO_2	$E_{int}(NH_2)$	$E_{int}(NO_2)$
					kcal mol^{-1}			
I	1.310	357.9	1.32	1.34	16.3	7.2	16.3	25.5
II	1.367	345.6	1.17	1.17	7.6	3.8	7.6	12.8
III	1.362	343.4	1.18	1.18	3.8	7.5	3.8	14.2
IV	1.339	340.0	1.24	1.24	8.9	7.8	8.9	20.4
V	1.362	336.4	1.18	1.18	5.2	8.4	5.2	13.5
VI	1.379	335.4	1.14	1.14	0.0	3.1	0.0	11.0
VII	1.361	335.2	1.18	1.18	5.1	3.2	5.1	12.6
VIII	1.352	331.2	1.21	1.21	7.0	5.9	7.0	12.3
IX	1.350	328.3	1.22	1.22	8.8	10.1	8.8	18.4

Note. BO is the formal order of the N—N bond as a function of *DI* ($f(x) = 0.4274e^{0.8612x}$), *DI* is the delocalization index of the N—N bond. The intermolecular interaction energies E_{int} were estimated by correlation[30] (the summarized interaction energies of the nitro groups; for the NH_2 groups, the $E_{int}(NH_2)$ values coincide with the H-bond energies).

the molecule and cannot be related unambiguously to the changes in the atomic energies.

When considering the geometries of the nine molecules in the cluster, one can notice that the degree of flattening of the molecule (consequently, the N—N bond length) correlates qualitatively with the energy of hydrogen bonds formed by the amino group (see Table 5). For example, in molecule **I** whose geometric parameters are the closest to those in the crystal, the overall energy of the H bonds formed by the amino group is 16.3 kcal mol^{-1} (*cf.* 7.2 kcal mol^{-1} for the nitro group). Conversely, in molecule **VI** where the N—N bond length (1.379 Å) virtually does not differ from that in the isolated molecule, the amino group is not involved in the H bonds and the nitro group forms the H bond with the energy of 3.1 kcal mol^{-1}. A similar pattern was observed for molecule **V**, for which the overall energy of the H bonds formed by the nitro group (8.4 kcal mol^{-1}) has one of the highest values among all molecules of the cluster, whereas the corresponding value for the amino group is much lower (5.2 kcal mol^{-1}).

The geometric parameters of the molecules in the cluster change appreciably while the atomic charges of nitrogens in the NH_2 and NO_2 groups vary only slightly (from −0.67 to −0.63 *e* and from 0.71 to 0.74 *e*, respectively) and virtually do not differ from those in the isolated molecule **1** (see Tables 2 and 6). Conversely, the net charges of the NH_2 and NO_2 groups correlate with the degree of flattening of the molecule (the N—N bond shortening), indicating a significant increase in absolute value from ~0.30 *e* in molecule **VI** to ~0.40 *e* in molecule **I** (see Table 6). It should be noted that the latter value virtually coincides with that in the crystal (0.40 *e* according to the precise X-ray diffraction data) and, taking into account the twofold increase in the charges of the groups relative to isolated molecule **1**, can serve as an independent confirmation of its dipole moment value (7 D) in the crystal. The increase in the charge on the NO_2 group is independent of the method of calculations of the atomic charges, which is confirmed by the results of point-charge calculations by the natural bond orbitals (NBO) method. The calculated point charges correlate with the integral atomic charges obtained withing the framework of the AIM theory (correlation coefficient is ~0.9).

Based on the results obtained, we attempted to estimate to what extent the value of charge transfer (in particular, in molecule **I**) is caused exclusively by conjugation of the fragments in the cluster molecules. As noted above, the difference in the charges of the NH_2 group in molecules $\mathbf{1}_{perp}$ (C_{2v}) and **1** (C_{2v}) (0.09 *e*) corresponds to the charge transfer from the amino to nitro group due to conjugation. The degree of double bonding in molecule **1** (C_{2v}) was evaluated using the delocalization indices (*DI*)[33] of the N—N bond, which are equal to 1.04 and 1.19 for molecules $\mathbf{1}_{perp}$ (C_{2v}) and **1** (C_{2v}), respectively. In other words, the charge transfer (0.09 *e*) due to conjugation corresponds to an increase in the *DI* value by 0.15. In the cluster, the *DI* values for the N—N bonds vary in a wide range (from 1.32 to 1.14, see Table 5), the maximum value being observed for molecule **I** and the minimum value being observed for its analog **VI**. The value of charge transfer (0.17 *e*) due to conjugation in molecule **I** corresponds to the *DI* value for molecules **I** and $\mathbf{1}_{perp}$ (C_{2v}).

According to the value of charge transfer, conjugation in the cluster molecule **I** manifests itself to a greater extent than in isolated molecule **1**, which is confirmed by the N—N bond lengths (1.310 and 1.352 Å for molecules **I** and **1** (C_{2v}), respectively). In molecule **VI**, a charge of 0.06 *e* is also transferred due to conjugation between the fragments (see Table 6). Thus, the increase in the transferred charge by 0.11 *e* upon flattening of the molecule (**VI** → **I**) is not fully responsible for the polarization of nitramide. A significant role in the charge transfer is played by the hydrogen bonds whose influence is described below.

The most informative index of conjugation is the change in the length of a bond, which can be compared indirectly with the formal order of this bond (BO). The *DI*

Table 6. Charges (*q*/*e*) of the atoms and functional groups obtained by integration of the function ρ(***r***) over atomic basins in the cluster of nine nitramide molecules

Molecule	$q(N)_{NH_2}$	$q(N)_{NO_2}$	$q(H)^a$	$q(O)^a$	$q(NH_2)$	$q(NO_2)$	CT^b
I	−0.66	0.71	0.53	−0.56	0.40	−0.41	−0.17
II	−0.64	0.73	0.49	−0.53	0.33	−0.32	−0.08
III	−0.68	0.73	0.48	−0.50	0.28	−0.27	−0.08
IV	−0.64	0.72	0.48	−0.52	0.32	−0.31	−0.12
V	−0.67	0.74	0.45	−0.48	0.23	−0.22	−0.08
VI	−0.65	0.73	0.44	−0.52	0.31	−0.31	−0.06
VII	−0.65	0.74	0.46	−0.51	0.28	−0.27	−0.08
VIII	−0.63	0.73	0.46	−0.50	0.28	−0.28	−0.10
IX	−0.65	0.73	0.46	−0.51	0.27	−0.29	−0.11

[a] For the H and O atoms, the mean values per molecule are given.

[b] The charge transfer from the amino to the nitro group due to conjugation between them estimated by the change in the delocalization indices of the N—N bond upon charge transfer in isolated molecules $\mathbf{1}_{perp}$ ($C2_v$) and **1** (C_{2v}) (0.09 *e*).

of a chemical bond correlates with its length and their ratios can be used as reference points in the determination of bond order. To obtain the above-mentioned ratios, we performed quantum chemical calculations of the molecules N_2, N_2H_2, and N_2H_4 for which the formal nitrogen-nitrogen bond orders are known (bond lengths obtained from MP2/6-311+G** calculations are 1.12, 1.221, and 1.472 Å and the *DI* values are 2.27, 1.78, and 0.99, respectively).

It should be noted that the *DI* value for the N—N bond in N_2H_4 virtually does not differ from that (1.04) for molecule $\mathbf{1}_{perp}$ (C_{2v}) where the bond order is formally equal to one, *i.e.*, the *DI* value depends slightly on the nature of substituents and the observed correlations can be used to a high accuracy for estimation of the BO in nitramines with the carbon-containing substituents. By approximating the dependence of the BO on *DI* for these three molecules by the equation of a straight line or an exponential curve (in both cases, the correlation coefficient exceeded a value of 0.99) we estimated the N—N bond orders in the cluster molecules (see Table 5). In the cluster, for the *DI* range from 1.14 to 1.32, the N—N bond order almost linearly correlates with the bond length (the correlation coefficient is higher than 0.99); the difference between the BO values for molecules **I** (1.34) and **VI** (1.14) may reach a value of 0.2. One can see that this consideration suggests a certain contribution of conjugation between the NH_2 and NO_2 groups to the chemical bonding in molecule **VI**, which is evidenced by the N—N bond order being other than unity. Since the geometry of molecule **VI** virtually does not differ from that of isolated molecule **1** (C_s), one can also expect conjugation in the pyramidal configuration of molecule **1**. Indeed, the N—N bonds in molecules **1** (C_s) and **VI** are characterized by the same *DI* value equal to 1.14, which suggests the presence of conjugation between the functional groups in the gas phase.

It is interesting to compare the *DI* value for molecule **1** (C_s) with and without regard to the polarity of the medium (see Table 1). As mentioned above, when considering the polarity of the medium, the charge transfer from the amino group to the nitro group in molecule **1** (C_s) increases (see Table 2), which suggests an increase in conjugation between the fragments. The same conclusion can be drawn based on the *DI* values of the N—N bond, which increased slightly (to 1.19).

Let us consider why conjugation increases in the cluster (or in the crystal). The energies of the proton-donor and proton-acceptor atoms increase upon hydrogen bonding, whereas the basin population of the H atom decreases and, conversely, its energy increases (see Rev. 9 and references cited therein). Indeed, an analysis of the atomic charges and energies of hydrogens in the model cluster shows that H-bonding leads to a significant increase in their positive charges (see the average values for molecules **I** and **VI** in Table 6) and to their destabilization by ~28 kcal mol^{-1} (Table 7). An analogous conclusion can be drawn based on analysis of the properties of the atomic basins of oxygens, for which an increase in the populations (at most, by 0.16 *e*) causes the energies of these atoms to decrease by 26.5 kcal mol^{-1}.

It should be noted that high energies of the N atoms in both groups of molecule **1** cannot be explained based on the atomic charge values. Indeed, as noted above, the atomic charges of nitrogens change in a very narrow range (to 0.03 and 0.04 *e*) and their energies change by at most 9.4 and 30 kcal mol^{-1} (for the N atoms of the nitro and amino groups, respetively). Such energies can be due to the presence of the shortened contacts $NO_2...NO_2$, as well as to flattening of the molecule. For example, the energy difference between the N atoms in the cluster molecules **I** and **VI** (28 kcal mol^{-1}, see Table 7) virtually does not differ from that for isolated molecules **1** (C_s) and **1** (C_{2v}).

Probably, the hydrogen bonds of the amino group result in the charge transfer from the H atoms to the amine N atom of nitramide. Since accumulation of this charge can occur only in the region corresponding to the lone electron pair of the amino N atom, this kind of transfer favors its conjugation with the nitro group. Thus, virtually all charge "received" by the amino N atom is transferred to the nitro O atoms due to conjugation. As shown above,

Table 7. Kinetic energies of the atoms and functional groups in the cluster comprised of nine nitramide molecules (a.u.)

Molecule	$-K_{tot}$	$-K(N)_{NH_2}$	$-K(N)_{NO_2}$	$-K(H)$	$-K(O)$	$-K(NH_2)$	$-K(NO_2)$
I	−260.2898	−54.9005	−54.1091	−0.7826	−150.4976	−55.6831	−204.6067
II	−260.2961	−54.8572	−54.1091	−0.8620	−150.4678	−55.7192	−204.5769
III	−260.3008	−54.8524	−54.1208	−0.8639	−150.4636	−55.7163	−204.5845
IV	−260.2828	−54.8701	−54.1051	−0.8304	−150.4773	−55.7004	−204.5824
V	−260.2934	−54.8621	−54.1047	−0.8581	−150.4684	−55.7202	−204.5731
VI	−260.2906	−54.8566	−54.1023	−0.8712	−150.4605	−55.7278	−204.5628
VII	−260.3058	−54.8817	−54.1063	−0.8417	−150.4761	−55.7234	−204.5824
VIII	−260.2951	−54.8671	−54.1173	−0.8429	−150.4679	−55.7099	−204.5852
IX	−260.2836	−54.8638	−54.1058	−0.8403	−150.4736	−55.7042	−204.5794

Note. $V/T = 2.0028$, K_{tot} is the contribution of the molecule to the kinetic energy of the cluster.

this intramolecular process results in the charge transfer (0.17 *e*) and, in combination with charge accumulation by the O atoms through intermolecular hydrogen bonding, provides the observed polarization of the molecule which is accompanied by significant stabilization of the nitro group (27.6 kcal mol^{-1} for molecules **I** and **VI**). These features, as well as the energy gain of the amino N atom, are the only intramolecular effects stabilizing molecule **I**.

Considering the contributions of each molecule to the total energy of the cluster, one can see that molecule **I** is one of the most "unfavorable" despite the fact that the conjugation effects between the functional groups in it manifest themselves most pronouncedly. This apparent discrepancy is quite logical because the increase in the energy of molecule **I** by 55.6 kcal mol^{-1} compared to its analog **VI** (see Table 7) is due to exclusively the H atoms involved in strong hydrogen bonds. At the same time, our comparison of isolated molecules $\mathbf{1}_{\text{perp}}$ (C_{2v}) and **1** (C_{2v}) showed that the increase in the role of conjugation between the functional groups causes the contribution of conjugation within the nitro group to decrease, thus destabilizing the O atoms. However, in this case, the hydrogen bonds formed in the cluster stabilize the proton acceptors, which leads to accumulation of negative charge on them. Such a dual effect of hydrogen bonding should also be realized in the crystal; however, it seems likely that weaker hydrogen bonds in the condensed medium do not give such large increase in the energy of the H atoms, which results in stabilization of the less pyramidal configuration.

Thus, our detailed study of the spatial and electronic structures of nitramide NH_2NO_2 showed that the change in the molecular geometry on going from the gas phase to the condensed state is accompanied by an increase in conjugation between the nitro and amino groups. Despite the presence of conjugation in the crystal, the nitramide molecule has a nonplanar configuration and the observed molecular geometry is a result of superposition of two strongly flattened configurations. One cannot exclude that a similar situation can be observed for the crystal of any other compound; this requires a more thorough analysis of the atomic thermal motion, especially, if a molecule occupies a special position in the crystal.

We obtained a correlation between the formal N—N bond order and the delocalization index of this bond (as well as with its length) in nitramide, which can be extended to other nitramines. An increase in conjugation between the functional groups in nitramide is accompanied by an increase in the charge transfer from the amino group to the nitro group at virtually constant charges of the N atoms, which results in polarization of the molecule (increase in its dipole moment).

Conjugation between the functional groups is also observed in the gas phase. On going to the condensed state, the geometry and electronic structure of the nitramide molecule are influenced by both nonspecific and specific solvation. The former changes only slightly the electronic structure and mainly influences the N—N bond length, whereas the latter completely governs the charge distribution and the molecular geometry. Hydrogen bonds are the main impact factor and play different roles depending on their nature. For example, the H-bonds formed by the amino group lead to accumulation of the negative charge on the proton donor (N atom) and to a decrease in the basin population of the H atom. This considerably destabilizes the H atom, but favors greater stabilization of the N atom upon flattening of the molecule and the corresponding charge transfer to the N basin region reflecting conjugation with the nitro group.

The hydrogen bonds formed by the nitro group considerably stabilize the proton acceptor (O atom) whose energy in the isolated molecule increases as conjugation between the NH_2 and NO_2 groups increases due to the decrease in conjugation within the nitro group. The decrease in conjugation within the nitro group upon flattening of the molecule results in a significant increase in the O atomic charges. On going to the condensed state, this is embodied in the decomposition of nitramide under the action of bases, which is apparently due to the electrophilic attack of proton on the oxygen atom.[1]

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