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Electrical and Optical Properties of the Nitramine Group and Molecular Structure of Some *N*-Nitramines

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Abstract—The electrical and optical properties (dipole moment, electrooptical and optical Kerr constants, molecular polarizability anisotropy, polarizability tensor, molecular refraction) of *N*,*N*-dimethylnitramine as the simplest N–NO_2 derivative were studied by a set of experimental and theoretical methods with the aim to determine the components of the polarizability ellipsoid of the N–NO_2 group and develop a valence-optical scheme for calculating the optical and electrooptical parameters of N–NO_2 compounds. Conjugation of the *p* electrons of the imide nitrogen atom with the π electrons of the nitro group results in deviation of the properties of *N*,*N*-dimethylnitramine from the additive values. Comparative evaluation of the parameters of the C_{sp^3}–NO_2, C_{sp^2}–NO_2, and N–NO_2 groups was made.

N-Nitramines are used as propellants and explosives [1], which makes urgent studies of their physicochemical properties and molecular structure. Thanks to specific features of the N–N bond, these compounds are active in photochemical reactions [2]. The mechanism of the nitramine rearrangement is not yet understood [3]. *N*,*N*-Dimethylnitramine is the simplest nitramine; under standard conditions (T 298 K, P 1 atm) it is a solid (mp 331 K) and is not explosive, in contrast, e.g., to hexahydro-1,3,5-trinitro-1,3,5-triazine (hexogen) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen) [4]; therefore, the properties of this compound are a subject of numerous theoretical [5–9] and experimental [10, 11] studies. Also interesting are aromatic nitramines, which rearrange into *C*-nitro compounds under the action of acids or other external factors. Migration of the NO_2 group is intramolecular [1].

Experimental study of the molecular structure of *N*,*N*-dimethylnitramine showed that its core is planar both in the crystal [12, 13] and in the gas phase [14], in contrast to the nonplanar nitramine [15–17]. This difference is explained in [18, 19] by the different nature of the N–N bond in these molecules: The molecular structure correlates with the bond length, becoming more planar as the N–N bond length decreases [5]. According to early studies of the molecular structure of *N*,*N*-dimethylnitramine [20], the N–N bond length is 0.126 nm. Later more accurate measurements gave the bond length of 0.1331 nm, which is average between the length of the single N–N (0.1425 nm) and double N=N (0.1240 nm) bonds [13].

According to X-ray and neutron diffraction data [4, 13], the phase transition at 107 K is accompanied by minor changes in the molecular structure of *N*,*N*-dimethylnitramine. In the high-temperature crystalline phase, the *N*,*N*-dimethylnitramine molecule has a planar core with approximate C_{2v} symmetry, but its geometric parameters somewhat differ from those determined for the gas phase. On transition to the low-temperature crystal modification, the symmetry decreases from C_{2v} to C_s [4], the angle between the N–N bond and the C–N–C plane slightly changes, becoming 11.30°, and the nitro group turns around the N–N bond by an angle of 1.60°. The barrier to internal rotation around the N–N bond in the *N*,*N*-dimethylnitramine molecule was estimated experimentally at 9 kcal mol^{-1} [21] and theoretically at 4 to 13 kcal mol^{-1} [22, 23]. The turn of the NO_2 group by 90°, i.e., perpendicular to the C–N–C plane, increases (from 0.1341 to 0.1467 nm) the N–N bond length, with the arrangement of the C–N and N–N bonds around the imide nitrogen atom becoming tetrahedral [22]. Therefore, the experimental rotation barrier of 9 kcal mol^{-1}

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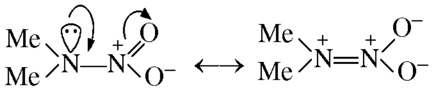
can be regarded as the “resonance energy of the nitramine group.”

The electronic structure of the *N*,*N*-dimethylnitramine molecule can be considered, in terms of the resonance theory, as a hybrid of the following canonical structures:



The lone electron pair of the imide nitrogen atom is shifted to the multicenter of the π orbital of the NO_2 group but is not fully delocalized. CNDO calculations with the minimal basis give for the N–N π bond an order of 0.394 [24]. However, some results complicate the simple resonance pattern. *Ab initio* calculations of the Mulliken charge distribution on atoms show that the nitrogen atom of the nitro group bears a large positive charge (+0.30), whereas the imide nitrogen atom is charged negatively (–0.20) [24]. The very low electron density on the nitrogen atom of the nitro group is also confirmed by the X-ray photoelectron spectra [25]. The specific features of charge distribution in the molecule should be reflected in its dipole moment μ; *ab initio* calculations, depending on the basis used, give the μ values ranging from 4.10 [24] to 5.727 D [22], which are consistent with the experiment (4.52–4.61 D [26–28]) and show that the nitramino group is strongly polar. The photoelectron spectra (He I, 21.22 eV) of the valence shell show that the very low ionization energies (9.91–11.63 eV) are due to interaction of four closely located orbitals. These external orbitals are delocalized over the molecular space and are largely nonbonding [25].

Thus, the experimental and theoretical studies of *N*,*N*-dimethylnitramine performed by now gave insight into the structural features of this molecule. However, studies of more complex molecules containing the $N–NO_2$ group require consideration of the whole set of properties of these compounds, including polarizability and its anisotropy, which, along with the geometric and energy parameters and electrical dipole moments, determine the structure and reactivity of substances. From the molecular anisotropies and Kerr constants, the bond polarizability anisotropies are calculated, which are used for calculating the additive parameters in elucidation of the steric structure of the molecules and analysis of interaction of nonbonded atoms. The additive scheme allowing for the effect of the bond surrounding can be principally constructed only if appropriate model compounds can be selected. In particular, for compounds containing the $N–NO_2$ group the best model compound is *N*,*N*-dimethylnitramine.

Procedure for determining the main semiaxes of the molecular polarizability ellipsoid. Usually the components of the molecular polarizability ellipsoid are determined from data on the molecular refraction, electrooptical Kerr effect, and degree of depolarization of the light scattering (or optical Kerr effect) [29–31]. These physical methods give three basic dependences between the measured parameters and the semiaxes of the molecular polarizability ellipsoids:

$$MR = \frac{4\pi N}{3}\frac{b_1 + b_2 + b_3}{3}, \tag{1}$$

$$\gamma^2 = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/2, \tag{2}$$

$$45k^2T^2\theta_2 = \mu_1^2(2b_1 - b_2 - b_3) + \mu_2^2(2b_2 - b_3 - b_1) + \mu_3^2(2b_3 - b_2 - b_1), \tag{3}$$

where *MR* is the molecular refraction; *N* is the Avogadro number; b_1, b_2, and b_3 are the main semiaxes of the molecular polarizability ellipsoid; γ^2 is the molecular polarizability anisotropy; θ_2 is the dipole term of the electrooptical Kerr constant; μ_1, μ_2, and μ_3 are the projections of the molecular dipole moment onto the axes of the chosen coordinate system; *k* is the Boltzmann constant; and *T* is the temperature, K.

The system of Eqs. (1)–(3) can be solved as a system of three equations with three unknowns (b_1, b_2, b_3):

$$b_1 + b_2 + b_3 \equiv A, \tag{4a}$$

$$(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 \equiv B, \tag{4b}$$

$$\Sigma\mu_i^2(2b_i - b_j - b_k) \equiv C. \tag{4c}$$

Combined analysis of data on the light scattering and electrooptical Kerr effect allows the dipole term to be separated out from the molecular Kerr constant mK [30]. Then,

$$C = \frac{405k^2T^2mK}{2\pi N} - \frac{2kP_d}{P_e}\gamma^2, \tag{5}$$

where P_e and P_d are the molar electronic and deformation polarizabilities of a substance, respectively.

The most general case accessible for total analysis is a molecule with a three-axis polarizability ellipsoid and the dipole moment directed along one of the axes (b_1); this is just the case for *N*,*N*-dimethylnitramine. Combination of Eqs. (4) gives the system (6a)–(6c):

$$b_1 = (A + C/\mu^2)^3, \tag{6a}$$

$$b_2 = A/3 - C/(6\mu^2) + (6B - 3C^2/\mu^4)^{1/2}/6, \tag{6b}$$

$$b_3 = A/3 - C/(6\mu^2) - (6B - 3C^2/\mu^4)^{1/2}/6. \tag{6c}$$

This method allows rigorous calculation of the main semiaxes of the molecular polarizability ellipsoids from the data of gas-phase measurements. All determinations in solutions or neat liquids give only apparent quantities [30]. Since a large set of data on the optical and electrical parameters of solids were obtained from measurements in benzene solutions [30, 32], in this work we performed all experimental studies in benzene at 25°C, taking also into account the solubility of the substances.

Refractometric measurements and measurements of the optical Kerr effect. The molecular polarizability anisotropy γ^2 was calculated from the experimental data on the optical Kerr effect in solutions, using the equation [30]

$$B_0 = \frac{6nN_1}{45kT\lambda_i\lambda_a}\left(\frac{n_i^2+2}{3}\right)^2\left(\frac{n_a^2+2}{3}\right)^2\gamma^2, \quad (7)$$

where B_0 is the optical Kerr constant; n is the refractive index of the medium; N_1 is the number of molecules in the unit volume; k is the Boltzmann constant; T is the temperature, K; λ_i is the wavelength of the light beam inducing the optical Kerr effect; λ_a is the wavelength of the analyzing beam; n_i is refractive index for the light beam inducing birefringence; and n_a is the refractive index of the medium for the analyzing beam. The quantities n_i and n_a are difficult to determine, since the inducing and analyzing beams are generated with a pulse laser (see Experimental); therefore, they are determined by measurement of the refractive index at experimentally accessible wavelengths (Table 1). The experimental refractive indices determined at various temperatures were used to obtain the dependences $n = f(T)$ in the form $n = a + bT$ for $\lambda_i = 1064$ and $\lambda_a = 532$ nm. The following dependences were obtained for various concentrations of the substance in solution c:

c, %	λ, nm	a	$-b \times 10^4$	r
1.4	532	1.5201276	6.2948983	0.9970
	1064	1.4773596	5.7072952	0.9959
2.6	532	1.5206487	6.5944395	0.9997
	1064	1.4767863	5.6412409	0.9938
4.5	532	1.5199812	6.4838437	0.9999
	1064	1.4775478	5.9250106	0.9971

The values of n_i and n_a determined from these dependences are listed in Table 2.

The molecular refraction of *N,N*-dimethylnitramine was calculated by the equation [33]

$$MR_2 = \frac{1}{N_2}\left[\frac{n^2-1}{n^2+2}\,\frac{M_1(2-N_2)+M_2N_2}{d} - MR_1(1-N_2)\right], \quad (8)$$

Table 1. Refractive indices of benzene solutions of *N,N*-dimethylnitramine

T, °C	656.3 nm	587.6 nm	546.1 nm	486.1 nm	435.8 nm
		1.4% solution			
22.8	1.4965	1.5013	1.5052	1.5129	1.5228
24.5	1.4953	1.4994	1.5040	1.5118	1.5216
25.7	1.4946	–	1.5032	1.5110	1.5207
27.7	1.4933	1.4981	1.5020	1.5097	1.5194
28.7	1.4929	1.4975	1.5015	1.5091	1.5189
30.2	1.4917	1.4964	1.5003	1.5080	1.5177
31.5	1.4909	1.4957	1.4995	1.5072	1.5169
32.7	1.4901	1.4948	1.4987	1.5063	1.5160
34.2	1.4891	1.4938	1.4978	1.5054	1.5150
35.5	1.4882	1.4929	1.4967	1.5045	1.5140
36.9	1.4875	1.4920	1.4960	1.5035	1.5131
38.6	1.4864	1.4911	1.4948	1.5026	1.5121
40.2	1.4854	1.4899	1.4937	1.5014	1.5109
41.9	1.4843	1.4889	1.4927	1.5002	1.5098
		2.6% solution			
20.6	1.4976	1.5021	1.5065	1.5138	1.5237
22.5	1.4962	1.5010	1.5052	1.5127	1.5227
23.8	1.4953	1.5002	1.5038	1.5118	1.5215
25.2	1.4945	1.4991	1.5032	1.5109	1.5207
26.4	1.4938	1.4985	1.5024	1.5102	1.5199
28.1	1.4926	1.4974	1.5013	1.5089	1.5188
29.7	1.4917	1.4965	1.5003	1.5080	1.5176
31.2	1.4908	1.4953	1.4992	1.5070	1.5167
32.8	1.4895	1.4942	1.4982	1.5058	1.5155
34.4	1.4886	1.4933	1.4971	1.5048	1.5144
36.0	1.4876	1.4923	1.4960	1.5037	1.5132
37.7	1.4867	1.4913	1.4950	1.5028	1.5123
39.1	1.4856	1.4902	1.4940	1.5016	1.5110
40.8	1.4846	1.4893	1.4930	1.5005	1.5100
42.6	1.4835	1.4881	1.4919	1.4995	1.5090
44.2	1.4823	1.4870	1.4907	1.4984	1.5079
		4.5% solution			
22.2	1.4961	1.5007	1.5046	1.5125	1.5223
24.6	1.4946	1.4995	1.5032	1.5105	1.5208
26.2	1.4936	1.4983	1.5023	1.5100	1.5200
27.9	1.4925	1.4973	1.5011	1.5088	1.5185
29.5	1.4916	1.4961	1.5002	1.5078	1.5175
31.0	1.4906	1.4953	1.4991	1.5068	1.5164
32.5	1.4895	1.4942	1.4980	1.5058	1.5154
33.9	1.4886	1.4933	1.4973	1.5049	1.5145
35.4	1.4877	1.4924	1.4962	1.5038	1.5133
36.8	1.4868	1.4913	1.4952	1.5028	1.5123
38.3	1.4859	1.4906	1.4943	1.5019	1.5114
40.0	1.4848	1.4894	1.4932	1.5009	1.5103
41.4	1.4839	1.4885	1.4923	1.4998	1.5094
43.2	1.4829	1.4874	1.4913	1.4988	1.5082

Table 2. Initial data for calculating the molecular refraction (MR_2) and molecular polarizability anisotropy (γ_2^2) of *N,N*-dimethylnitramine from solution data (benzene, 25°C, n_1 1.49864, d_1 0.87511 g cm^{-3}, γ_1^2 17.5 Å^6 [32])[a]

Concentration, wt %	N_2	n_D	d, g cm^{-3}	MR_2, cm^3	$N_1 \times 10^{23}$	n_i	n_a	$B_0 \times 10^8$, cm^2 erg^{-1}	γ^2, Å^6	γ_2^2, Å^6
1.4	0.01119	1.4992	0.87785	25.08	0.06766	1.4631	1.5044	3.90	17.414	11.5
2.6	0.02244	1.4991	0.88063	23.95	0.06776	1.4628	1.5042	4.64	14.596	16.1
4.5	0.03619	1.4990	0.88401	23.54	0.06788	1.4627	1.5038	5.83	14.807	25.4

[a] (N_2) Mole fraction of the solute, (n_D) refractive index of the solution at λ = 589.3 nm, (d) solution density, (n_i) refractive index of the solution for the beam inducing the birefringence, (n_a) refractive index of the medium for the analyzing beam, (N_1) number of molecules in 1 cm^3 of the solution, (B_0) optical Kerr constant of the solution, and (γ^2) molecular polarizability anisotropy of the solution.

Table 3. Dipole moments (μ, D), polarizability tensors (b_{ij}, Å^3), anisotropic (θ_1) and dipole (θ_2) terms of the Kerr constant, molar Kerr constant ($mK \times 10^{12}$), mean polarizabilities (α, Å^3), and molecular polarizability anisotropies (γ^2, Å^6) of *N,N*-dimethylnitramine, calculated by various quantum-chemical methods

Calculation method	μ_x	μ_y	μ_z	μ	b_{xx}	b_{yy}	b_{zz}	b_{xy}
RHF 6-31G*	0.0024	4.849	0.000	4.849	6.990	7.392	4.460	–0.001
RHF 6-311G**	0.0025	4.936	0.000	4.936	7.400	7.618	4.605	–0.001
MP2 6-31G*	0.0020	4.433	0.000	4.433	7.286	8.255	4.461	0.000
MP2 6-311G**	0.0020	4.393	0.000	4.339	7.812	8.572	4.692	0.000
CISD 6-31G*	0.0024	4.703	0.000	4.703	7.102	7.689	4.422	–0.001
AM1	–2.409	3.716	1.349	4.625	6.275	6.003	3.760	0.295

Calculation method	b_{xz}	b_{yz}	θ_1	θ_2	$mK \times 10^{12}$	α	γ^2
RHF 6-31G*	0.000	0.000	0.901	103.0	436.8	6.280	7.576
RHF 6-311G**	0.000	0.000	1.007	103.4	438.9	6.541	8.469
MP2 6-31G*	0.000	0.000	1.386	122.9	522.8	6.667	11.656
MP2 6-311G**	0.000	0.000	1.508	114.7	488.8	7.025	12.683
CISD 6-31G*	0.000	0.000	1.082	111.9	475.3	6.404	9.100
AM1	–0.875	1.430	1.713	–46.37	–187	5.346	14.410

where N_2 is the mole fraction of the solute; n is the refractive index of the solution; M_1 and M_2 are the molecular weights of the solvent and solute, respectively; d is the solution density, g cm^{-3}; MR_1 = 26.155 cm^3 is the molar refraction of benzene calculated from the experimental data. All the quantities required for calculating MR_2 and the calculation results are listed in Table 2. The mean value of MR_2 was compared with the values obtained by various additive schemes [33]. Naturally, none of the schemes contains the refraction of the N–NO$_2$ group; therefore, the refraction exaltation is as high as 0.93 to 4.11 cm^3, depending on the atomic and group refractions used [33].

The molecular polarizability anisotropy γ^2 of solutions was calculated by Eq. (7) from the optical Kerr constants B_0 of the solutions. The resulting values of γ^2 are listed in Table 2. Assuming that the molecular anisotropy of benzene solutions of *N,N*-dimethylnitramine is an additive quantity [$\gamma^2 = \gamma_2^2 N_2 + \gamma_1^2(1 - N_2)$], we calculated γ_2^2. This parameter increases with increasing concentration of *N,N*-dimethylnitramine, which may be due to association of *N,N*-dimethylnitramine molecules via dipole–dipole interactions (μ 4.52–4.61 D [33]). Indeed, the calculated molecular polarizability anisotropy γ^2 of the dimer with the antiparallel arrangement of the dipoles is 15.02 Å^6, and that of the head-to-tail dimer is 147.7 Å^6. Only the γ_2^2 value of 11.5 Å^6 obtained from the experimental data for the 1.4% solution is nicely consistent with the results of the quantum-chemical calculations (Table 3)

Table 4. Experimental dipole moments (μ, D) and molar Kerr constants ($mK_2 \times 10^{12}$, esu) of *N*,*N*-dimethylnitramine[a]

Solvent	α_H / α_L	β_H / β_L	γ_L	δ_L	$P_{2\infty}$, cm^3	P_d, cm^3	μ	$_\infty(sK_2) \times 10^{14}$	$_\infty(mK_2) \times 10^{12}$
Benzene	13.71	0.281			473.5	24.43	4.69	342.8	509
	11.90	0.244	–0.0221	84.23					
Tetrachloromethane	10.90	–0.428			436.6	24.43	4.50		
	–	–	–	–			4.61 [27]		535 [27]
Dioxane	–	–	–	–	–	–	4.52 [26]	–	546 [26]

[a] (α_H, β_H) Parameters of the Hedestrand extrapolation equation [34], (α_L, β_L, γ_L, δ_L) parameters of the Le Fevre extrapolation equation, ($P_{2\infty}$) solute polarizability at infinite dilution, (P_d) deformation polarizability, and $_\infty(sK_2)$ specific Kerr constant of the solute.

and can be therefore taken as the molecular anisotropy of *N*,*N*-dimethylnitramine. Attempts to measure B_0 in more dilute solutions failed because of small differences between the γ^2 values of the solvent and solute.

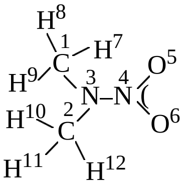
Dipole moment and molar electrooptical Kerr constant. To determine the main semiaxes of the polarizability ellipsoid of the *N*,*N*-dimethylnitramine molecule by Eqs. (1)–(6), the dipole moment μ and the molar Kerr constant *mK* of this compound should be known. Their experimentally determined values are listed in Table 4. Comparison with published data obtained with other solvents shows that μ and *mK* are solvent-dependent.

To compare with the experimental values, we calculated the Mulliken charge distribution on atoms of *N*,*N*-dimethylnitramine, its dipole moment, and the molar Kerr constant by various quantum-chemical methods. Since there is no unambiguous theoretical definition for the atomic charge in a molecule, only comparison of the calculated and experimental dipole moments can be a criterion for checking the adequacy of the calculated charge distribution. The results along with data of [5, 8] are listed in Tables 3 and 5. Comparison of the data calculated for the geometric parameters that were optimized in different approximations shows that, although the nitrogen atom of the nitro group bears a higher positive charge (from 0.831 in MP2/6–31G** to 0.216 in QCISD/STO-3G), in all the calculations this charge is compensated with an excess by the negative charges of the two oxygen atoms, so that the total charge of the nitro group is negative. The calculated negative charge on the imide nitrogen atom is insufficient for neutralization of the positive charges of the two methyl groups. Inclusion into the polarization basis of the *p* functions on hydrogen atoms in MP2 calculation appreciably decreases the charges of the methyl group, but its total charge is weakly sensitive to the basis set and geometric parameters [8]. The calculated dipole moments of *N*,*N*-dimethylnitramine are within 3.174–5.237 D. The experiment gives μ = 4.50–4.69 D (Table 4).

The fairly high values of the electrooptical molar Kerr constants of *N*,*N*-dimethylnitramine, both calculated (Table 3) and experimental (Table 4), are due to the large dipole moment of the molecule, so that the dipole term of the Kerr constant θ_2 is considerably greater than the anisotropic term (θ_1) (Table 3). The calculated values of *mK*, μ, γ^2, and α (mean molecular polarizability) reasonably agree with the experiment.

From the experimental values of *MR*, *mK*, μ, and γ^2, using Eqs. (4)–(6), we calculated the main semiaxes of the polarizability ellipsoid of the *N*,*N*-dimethylnitramine molecule: b_1 = 10.42, b_2 = 11.07, b_3 = 7.29 Å^3 and the mean molecular polarizability α = 9.59 Å^3 [$\alpha = (b_1 + b_2 + b_3)/3$]. The obtained values of b_1, b_2, and b_3 are somewhat higher than the values calculated quantum-chemically (see b_{xx}, b_{yy}, and b_{zz} in Table 3), which is also indicative of the solvent effect and the apparent character of the experimental values; however, they are consistent with the results obtained for dichloromethane solution (b_1 = 9.26, b_2 = 8.15, b_3 = 6.00 Å^3) [27]. From the b_1, b_2, and b_3 values obtained for the *N*,*N*-dimethylnitramine molecule, using the tensor-additive scheme, we subtracted the contributions from six C–H bonds believed to be isotropic [30] and obtained the values of the main semiaxes of the polarizability ellipsoid of the $C_2N–NO_2$ moiety: b_1 = 6.52, b_2 = 7.17, and b_3 = 3.39 Å^3. These apparent values can be used for constructing the valence-optical scheme for calculating the electrooptical and optical properties of various *N*-nitramines from data for benzene solutions. The nitramine group proper, $N–NO_2$, has the following axes of the polarizability ellipsoid: b_1 = 5.32, b_2 = 5.79, and b_3 = 2.01 Å^3. The somewhat different values obtained in [27] (b_1 = 4.04, b_2 = 3.05, and b_3 = 0.72 Å^2) are pro-

Table 5. Mulliken atomic charge distribution on atoms and dipole moments (μ, D) of *N*,*N*-dimethylnitramine, calculated by various quantum-chemical methods



Atom no.	AM1	CNDO	RHF STO-3G	RHF 6-31G*	RHF 6-31G** [8]	RHF 6-311G**	MP2 STO-3G	MP2 6-31G*	MP2 6-31G** [8]	QCISD STO-3G	MC-SCF [5]
1	–0.125	0.082	–0.079	–0.306	–0.139	–0.061	–0.088	–0.354	–0.286	–0.085	–0.408
2	–0.123	0.082	–0.061	–0.286	–0.138	–0.034	–0.070	–0.334	–0.286	–0.067	–0.408
3	–0.266	–0.123	–0.204	–0.428	–0.438	–0.406	–0.183	–0.296	–0.443	–0.179	–0.170
4	0.603	0.566	0.265	0.809	0.768	0.618	0.219	0.618	0.831	0.216	0.529
5	–0.358	–0.339	–0.231	–0.526	–0.483	–0.443	–0.184	–0.433	–0.508	–0.181	–0.377
6	–0.358	–0.339	–0.221	–0.511	–0.483	–0.428	–0.181	–0.420	–0.508	–0.175	–0.377
7	0.109	0.011	0.079	0.187	0.182	0.109	0.074	0.187	0.227	0.071	0.173
8	0.077	0.021	0.121	0.268	0.138	0.171	0.109	0.252	0.185	0.106	0.173
9	0.129	0.002	0.075	0.185	0.137	0.122	0.069	0.185	0.188	0.067	0.173
10	0.108	0.011	0.078	0.196	0.137	0.121	0.070	0.194	0.188	0.068	0.173
11	0.127	0.002	0.064	0.188	0.138	0.102	0.080	0.185	0.185	0.078	0.173
12	0.078	0.022	0.093	0.223	0.182	0.140	0.085	0.216	0.227	0.081	0.173
μ, D	4.63	4.47	3.85	5.14	4.85	5.24	3.17	4.74	4.82	3.08	–

Table 6. Dipole moments (μ, D) and molar Kerr constants ($mK_2 \times 10^{12}$, esu) of some substituted *N*-nitramines[a]

Comp. no.	$\frac{\alpha_H}{\alpha_L}$	$\frac{\beta_H}{\beta_L}$	γ_L	δ_L	P_d, cm^3	$P_{2\infty}$, cm^3	μ	$_\infty(sK_2) \times 10^{14}$	$(mK_2)_{exp} \times 10^{12}$	$(mK_2)_{calc} \times 10^{12}$
I	$\frac{14.04}{7.93}$	$\frac{0.562}{0.035}$	–0.010	40.63	24.28	485.6	4.75	393	456	459
II	$\frac{13.96}{8.42}$	$\frac{0.198}{0.029}$	–0.020	61.34	27.52	499.0	4.80	402	533	525
III	$\frac{13.58}{6.10}$	$\frac{0.934}{0.047}$	–0.034	79.61	59.79	497.3	4.63	413	719	730
IV	$\frac{11.89}{6.65}$	$\frac{0.354}{0.030}$	–0.096	28.09	44.51	429.1	4.34	161	245	240

[a] For the sense of α_H, β_H, α_L, α_L, γ_L, δ_L, $P_{2\infty}$, P_d, and $_\infty(sK_2)$, see the note to Table 4.

bably due to the fact that calculations in [27] were based on different values of the molecular polarizability anisotropy γ^2 (28.7 Å^6) and mean molecular polarizability α (7.80 Å^3) of *N*,*N*-dimethylnitramine (the source of these values was not given).

The thus determined polarizability parameters of the N–NO$_2$ group were used to calculate the Kerr constants of a series of nitramines: *N*-nitropyrrolidine $C_4H_8NNO_2$ (**I**), *N*-nitropiperidine $C_5H_{10}NNO_2$ (**II**), (i-$C_4H_9)_2NNO_2$ (**III**), and $C_6H_5(CH_3)NNO_2$ (**IV**). The calculated characteristics were compared with the experimental data (Table 6). The core of **I** was assumed to be in the *half-chair* (C_2) conformation, as suggested by the existing theoretical views (the planarity of the $C_2N–NO_2$ fragment suggests the *sp*^{2} hybridization of nitrogen, and on introduction of an *sp*^{2}-hybridized atom into a five-membered ring the *half-chair* C_2 becomes the equilibrium conformation

Table 7. Comparison of the electrical and optical properties of the C_{sp^3}–NO_2, C_{sp^2}–NO_2, and N–NO_2 groups, evaluated from the properties of the corresponding nitro compounds (benzene, 25°C)

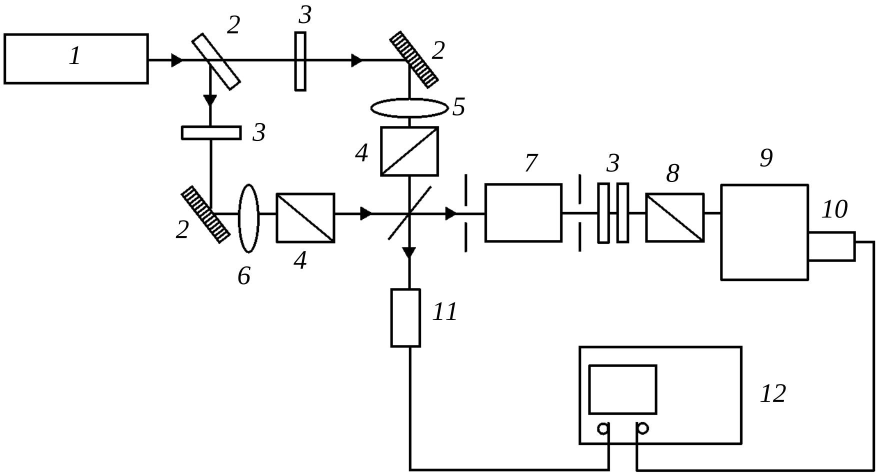
Parameter	N–NO_2 [$(CH_3)_2NNO_2$]	C_{sp^2}–NO_2 ($C_6H_5NO_2$)	C_{sp^3}–NO_2 (CH_3NO_2)
Dipole moment (μ, D)	4.69; 4.50; 4.52 [26]; 4.61 [27]	4.01 [36]	3.10 [36]
Mean polarizability (α, Å^3)	4.41	2.97	2.84
Molar Kerr constant ($mK \times 10^{12}$)	509, 535, 546 [32]	1332 [32]	54 [32]
Components of the polarizability tensor (Å^3):			
b_L (b_1)	5.26	5.23 [30]	3.56 [30]
b_T (b_2)	5.87	2.15 [30]	3.63 [30]
b_V (b_3)	2.09	1.52 [30]	1.33 [30]
Molecular polarizability anisotropy (γ^2, Å^6)	12.35	11.82	5.13

[35]). The interconversion between the two conformations of **I** occurs most probably via the planar form whose energy is higher by only ~10 kJ mol^{-1} [35]. The calculated molar Kerr constant (mK 459 × 10^{-12} esu) reasonably agrees with the experiment (Table 6). For **II**, based on data of [35], we assumed the *chair* $\rightleftarrows$ *boat* equilibrium and obtained mK_{calc} = 525 × 10^{-12} esu, which is close to the experimental value (533 × 10^{-12} esu). Rotation around the C–N bonds in **III** does not affect the dipole moment but affects the constituents of the molecular polarizability tensor on which the Kerr constant is dependent. The calculations were performed for equal angles θ of the turn of the $(CH_3)_2CH$ group relative to the initial planar structure with the *trans* orientation of the C–C bonds relative to the C_2N–NO_2 plane. The experimental value corresponds to θ = 120°, i.e., to the usual *gauche–gauche* conformation of the C–C–N–C–C moiety. Single crystal X-ray diffraction study of **IV** showed that the dihedral angle θ between the Me–N–NO_2 plane and the aromatic ring of the molecule for different *p*-substituted derivatives varies from 65.6° [36] to 72.3° [37]. Assuming θ_d = 70°, from the obtained semiaxes of the molecular polarizability ellipsoid of the N–NO_2 group and the corresponding parameters of the other fragments [30] we obtained mK_{calc} = 245 × 10^{-12} esu. As seen from Table 6, all the experimental and calculated mK values are reasonably consistent, and the obtained semiaxes of the polarizability ellipsoid of the N–NO_2 group can be used for calculating the optical and electrooptical properties of molecules.

Comparison of the electrical and optical characteristics of the C_{sp^3}–NO_2, C_{sp^2}–NO_2, and N–NO_2 groups. Comparison of the spectral characteristics of the C_{sp^3}–NO_2, C_{sp^2}–NO_2, and N–NO_2 groups determined from studies of CH_3NO_2, $C_6H_5NO_2$, and $(CH_3)_2NNO_2$, respectively, showed [6] that all the parameters [$\nu_{as}(NO_2)$, $\nu_s(NO_2)$, $\delta(ONO)$, $\omega(NO_2)$, $\rho(NO_2)$, $\chi(NO_2)$] of the N–NO_2 group appreciably differ from those of the C_{sp^3}–NO_2 and C_{sp^2}–NO_2 groups. The same conclution can be made from a comparison of the electrical and optical characteristics. However, the parameters of the N–NO_2 group are closer to those of the C_{sp^2}–NO_2 group than to those of the C_{sp^3}–NO_2 group (Table 7). This fact suggests that the planar (or nearly planar [8]) structure of the *N,N*-dimethylnitramine molecule is the most favorable for the *p*–π interaction between the imide nitrogen atom and the nitro group. The calculated values of both the mean polarizability and the semiaxes of the polarizability ellipsoids of the C_{sp^3}–NO_2, C_{sp^2}–NO_2, and N–NO_2 bonds differ considerably. As in analysis of the refraction exaltation, it is impossible to distinguish the contributions from the conjugation and bond nature; the semiaxes considered separately (b_1, b_2, b_3) vary to a greater extent than the mean polarizabilities α. Therefore, we cannot conclude that the exaltation is directed along the X–NO_2 axis. Along with increase in b_L (b_1), the aryl derivatives are, as a rule, characterized by depression along the b_T (b_2) and b_V (b_3) axes, so that the whole polarizability ellipsoid significantly rearranges. The main semiaxes of the polarizability ellipsoid of the N–NO_2 group calculated by the tensor-additive scheme (b_1 5.84, b_2 3.94, b_3 1.43 Å^2) substantially differ from the experimental values (b_1 5.38, b_2 5.79, b_3 2.01 Å^3) and the values calculated quantum-chemically using data in Table 5 (b_1 4.00–3.17, b_2 4.76–3.58, b_3 0.88–0.82 Å^3), which also shows that interaction of the imide nitrogen atom with the nitro group causes rearrangement of the whole polarizability ellipsoid of the N–NO_2 group.

EXPERIMENTAL

Synthesis of *N,N*-dimethylnitramine. Several routes to secondary nitramines are known. For example,



Scheme of a unit for observing the optical Kerr effect: (*1*) Nd:YAG laser, (*2*) dichroic mirror, (*3*) filter, (*4*) polarizer, (*5*) lense with the focal length *f* = 30 cm, (*6*) lense with the focal length *f* = 50 cm, (*7*) Kerr cell, (*8*) analyzer, (*9*) monochromator, (*10*) photomultiplier, (*11*) photodiode, and (*12*) digital oscilloscope.

N,*N*-dimethylnitramine can be prepared by nitration of dimethylamine with acetone cyanohydrin nitrate [38]. However, the use of gaseous dimethylamine and formation of hydrogen cyanide as a by-product require serious precautions in the course of the synthesis. The better route to *N*,*N*-dimethylnitramine is oxidation of the corresponding nitroso derivative. As oxidant was used trifluoroperoxyacetic acid prepared *in situ* by the reaction of trifluoroacetic anhydride or trifluoroacetic acid with 90% hydrogen peroxide [39]. In this study we oxidized dimethylnitrosamine with dimethyldioxirane, which was used previously for oxidation of amines to *C*-nitro compounds [40] and of pyridine to pyridine *N*-oxide [41]. *N*,*N*-Dimethylnitramine was prepared as follows. To a solution of 7.5 g of *N*,*N*-dimethyl-*N*-nitrosamine in 100 cm^3 of acetone we added 500 cm^3 of a buffer solution (pH 7–8.5) containing 120 g of K_2HPO_4 and 13.6 g of KH_2PO_4 and then, in portions over a period of 8 h, 61.4 g of OXONE ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). Dimethyldioxirane formed *in situ* by the reaction of acetone with the OXONE [41]. The mixture was stirred for an additional 4 h. The product was extracted with methylene chloride (4 × 100 cm^3). The extract was dried over anhydrous sodium sulfate, the solvent was evaporated, and the residue was recrystallized from *n*-hexane. Yield of *N*,*N*-dimethylnitrosamine 5.1 g (57%), mp 54–55°C. *N*-Nitropiperidine and *N*-nitropyrrolidine were prepared similarly from the corresponding *N*-nitroso derivatives. Yield of *N*-nitropyrrolidine 88%; the product was crystallized from *n*-hexane (mp 56–57.5°C). Yield of *N*-nitropiperidine 83%; the product was isolated by vacuum distillation, bp 63–65°C (2 mm), and then crystallized from *n*-hexane cooled with dry ice. The other *N*-nitramines were prepared as described in [42].

Determination of the dipole moments and electrooptical molar Kerr constants. Dielectrometric studies were performed with a Dipol' apparatus (OKBA, Angarsk). The dielectric permittivity ε and density ρ of dilute (up to 10^{-3} M) solutions of *N*,*N*-dimethylnitramine in benzene were measured. The molar polarizability of the solute extrapolated to infinite dilution $P_{2\infty}$ was calculated by the Hedestrand procedure [34]. The resulting values of $\alpha_H = d\varepsilon/dN_2$ (N_2 is the mole fraction of the solute), $\beta = d\rho/dN_2$, and also $P_{2\infty}$, $P_D = 1.1R_D$ (R_D is the molar refraction), and μ_{exp} are listed in Table 4. Calculation of the dipole moment by the vector-additive scheme was based on data in [43]. The electrooptical Kerr constants of *N*,*N*-dimethylnitramine solutions *B* were determined on the apparatus and by the procedure described in [44]. To calculate the molar Kerr constants *mK*, the measurement results were processed according to [45]. The concentration dependences of the measured solution parameters were expressed as $\varepsilon = \varepsilon_1(1 + \alpha_L\omega_2)$, $\rho = \rho_1(1 + \beta_L\omega_2)$, $n = n_1(1 + \gamma\omega_2)$, and $B = B_1(1 + \delta\omega_2)$, where ω_2 is the weight concentration of the solutions and ε_1, ρ_1, n_1, and B_1 are the corresponding solvent parameters. Extrapolation to infinite dilution was performed graphically. The values of α_L, β_L, δ, and *mK* are listed in Table 4. The molar Kerr constants were calculated by the tensor-additive scheme using data in [30].

Study of the optical Kerr effect and refractive indices. In the measuring unit for determining the optical Kerr constant (see figure), we used an Nd:YAG pulse laser operating in the subnanosecond mode (τ 0.4 ns) and generating the polarized light with a wavelength of 1064 nm and the second harmonic with a wavelength of 532 nm. The birefringence in the cell was induced by the light with λ_i 1064 nm (E 40 mJ), and the wavelength λ_a of the analyzing beam was 532 nm. The beams were focused with long-focus lenses to obtain the highest pulse energy and the best geometry in the cell with a sample. At the analyzer outlet, a set of filters was arranged to transmit the analyzing light only; this light, after passing a monochromator, was received by a photomultiplier, whereas the beam inducing the birefringence was recorded with a photodiode. The signals from both beams were registered with an oscilloscope.

The refractive indices of solutions were measured with a Pulfrich–Refraktometr-PR2 device (Carl Zeiss, Jena) using various light sources (656.3, 587.6, 546.1, and 435.8 nm).

The *ab initio* quantum-chemical calculations were performed with GAUSSIAN 94 programs [46].

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