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Synthesis, Properties, and Molecular Structure of Nitro-Substituted *N*-Methyl-*N*-nitroanilines

V. V. Prezhdo, A. S. Bykova, O. V. Prezhdo,
Z. Daszkiewicz, J. B. Kyziol, and J. Zaleski

Kharkov Polytechnical Institute, ul Frunze 21, Kharkov, 61002 Ukraine
Institute of Chemistry, Jan Kochanowski Technical Universitety of Kielce, Kielce, Poland
Institute of Chemistry, Technical University of Opole, Opole, Poland
G. Washington University, Seattle WA, USA

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Abstract—Ten mono-, di-, and trinitro derivatives of *N*-methyl-*N*-nitroaniline were synthesized and studied by spectral, electrooptical, and quantum-chemical methods. Three of these derivatives, *N*-methyl-*N*,2,3-trinitroaniline, *N*-methyl-*N*,2,5-trinitroaniline, *N*-methyl-*N*,3,5-trinitroaniline, were also examined by the X-ray diffraction method. The *N*-nitroamino group in their molecules is almost planar, the $N^7–N^8$ bond is shortened, and the N^8 atom is characterized by a strong deficit of electron density. The dihedral angle between the planes of the *N*-nitroamino group and the benzene ring is 56°–92°, which makes conjugation between these fragments impossible. The *N*-nitroamino group in the examined compounds acts as a weak electron donor with respect to the nitro groups in the aromatic ring; the mechanism of this effect is inductive.

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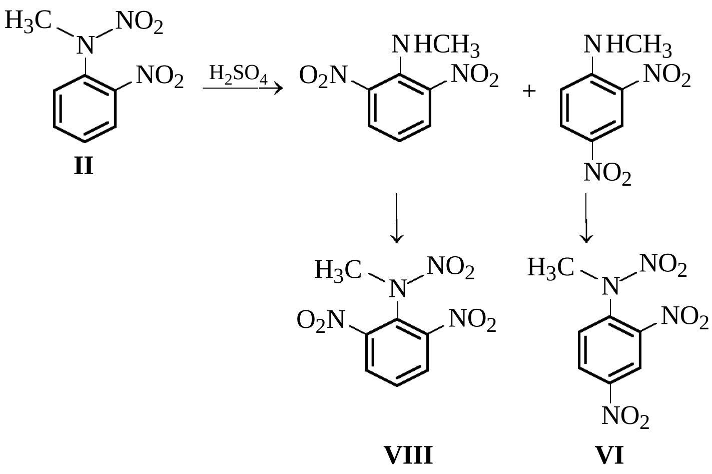
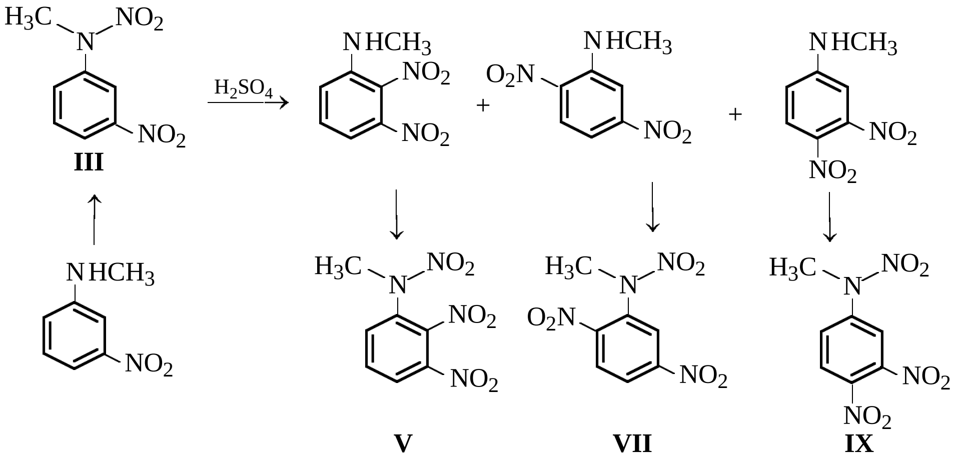
Rearrangement of aromatic N-nitro amines into C-nitro compounds can be promoted be various factors, including acid catalysis. Depending on the *N*-nitro amine structure, different acidities of the medium are required. *N*-Methyl-*N*-nitroaniline (**I**) undergoes such rearrangement by the action of dilute (0.1 M) sulfuric acid solution [1], while the rearrangement of *N*-methyl-*N*,2,3-trinitroaniline occurs only in concentrated (78%) sulfuric acid at room temperature [2]. The difference in the reaction conditions originates from the presence of nitro groups in the aromatic ring. Presumably, substituents in the aromatic ring and their position affect migration of the nitro group, which should be reflected in properties of secondary *N*-nitroarylamines. On the other hand, the results of X-ray diffraction study of N-nitro amine **I** and its substituted derivatives showed that π-electron system of the nitroamino group is not involved in conjugation with the benzene ring [3, 4]. Formalistically, this means that lone electron pair on the amino nitrogen atom is delocalized toward the nitro group and that it does not interact with π-electrons of the ring. As a result, *para*-substituted *N*-methyl-*N*-nitroanilines are characterized by considerably lower interaction moments $\Delta\vec{\mu} = \vec{\mu}_{exp} - \Sigma\vec{\mu}$ [5] than those intrinsic to, e.g., *para*-substituted *N*,*N*-dimethylanilines in which *n*-electrons on the amino nitrogen atom are conjugated with the aromatic ring. For example, $\Delta\mu$ values for *N*-methyl-*N*,4-dinitroaniline and *N*,*N*-dimethyl-4-nitroaniline are 0.28 [5] and 1.48 D [6], respectively.

It was interesting to estimate the effect of introduction of nitro groups (which are strong electron acceptors) into the aromatic ring on charge distribution in the molecule, specifically to elucidate whether accumulation of nitro groups in the *N*-methyl-*N*-nitroaniline molecule will lead to competition for lone electron pair on the amino nitrogen atom. These effects should be reflected in the dipole moments, molar Kerr constants, spectral parameters, and molecular structure. Therefore, we synthesized mono-, di-, and trinitro derivatives **II**–**IX** and examined their properties (Table 1).

In the IR spectra of *para*-substituted derivatives of **I**, absorption band due to asymmetric stretching vibrations of the N-nitroamino group was located at 1520–1570 cm^{-1} [7]. The nitro group attached to the aromatic ring is more sensitive to *para* substituent: The corresponding absorption band appears in the region 1490–1579 cm^{-1}, depending on the electronic properties of the other substituent [10]. In the IR spectra of compounds **II**–**XI**, absorption bands belonging to N-nitro and C-nitro groups either overlap or





are displaced by 20–30 cm^{-1} with respect to each other (Table 1).

The stretching vibration frequency of C-nitro groups ranges from 1520 to 1560 cm^{-1}, indicating that the $N(CH_3)NO_2$ group is a stronger electron acceptor than, e.g., halogen atom [10]. Symmetric stretching vibrations of N- and C-nitro groups have different frequencies (1280–1300 and 1340–1350 cm^{-1}, respectively). It is well known [11] that N-nitro groups absorb at lower frequencies (by about 50 cm^{-1}) than C-nitro groups. An exception is compound **XI** which shows in the IR spectrum a strong absorption band at 1315 cm^{-1}, i.e., beyond the typical range. Nevertheless, we can conclude that the number and position of C-nitro groups do not affect vibration frequencies of the N-nitro group, which occupy different regions, 1280–1300 and 1520–1560 cm^{-1}.

The electronic absorption spectra of almost all of the examined compounds contained a strong band ($3.96 < \log\varepsilon < 4.40$) with its maximum at λ 240–250 nm. Only in the spectrum of **IV** the corresponding maximum is displaced to the red region (λ_{max} = 283 nm). Even if this weak red shift would result from interaction between the *para* substituents, it cannot be compared with that observed, e.g., for *N*,*N*-dimethyl-4-nitroaniline which absorbs in the visible region [12]. A conclusion can be drawn that the C-nitro and N-nitroamino groups are not involved in donor–acceptor interaction with each other.

Table 2 contains the experimental dipole moments and molar Kerr constants of compounds **II**–**XI** together with those calculated according to the vector- and tensor additive schemes. Molecules **II**–**XI** are strongly polar; the dipole moments of some compounds exceed 6 D. In these cases, molecular conformation is to be known to analyze intramolecular interaction effects. The principal structural data for aromatic nitro compounds were obtained by the X-ray diffraction method [13]. These data together with the results of theoretical calculations of the energy of intramolecular interactions indicated that the dihedral angle φ between the aromatic ring plane and the nitro group is equal to ~0° provided that no *ortho* substituents are present [14]. Molecular conformations of ortho-substituted nitrobenzenes are determined by steric interactions which can be estimated on the basis of their physical properties [15–17]. It is important that sterically hindered nitroaromatic compounds whose steric and mesomeric interaction energies are related to each other may be conformationally labile [15]. Presumably, electronic effects of remote substituents (if they are capable of affecting the angle of rotation of nitro groups) should be pronounced just in such sterically hindered molecules [15].

While studying nitro derivatives of *N*-methyl-*N*-nitroaniline, the main problem is to elucidate intramolecular interactions between functional groups in their

Table 1. Melting points and IR and UV spectra of nitro-substituted *N*-methyl-*N*-nitroanilines **II**–**XI**

Comp. no.	Substitution pattern	mp, °C	IR spectrum, ν, cm^{-1}		UV spectrum, λ_{max}, nm (ε)
			$\nu_s(NO_2)$	$\nu_{as}(NO_2)$	
I	–	44.5	–	–	258 (2770), 265 (2070)
II	2-NO_2	65–66	1295, 1345	1530	245 (11 200)
III	3-NO_2	72–73[a]	1292, 1351	1529	251 (13 400)
IV	4-NO_2	138–140[b]	1294, 1344	1521	283 (9100)
V	2,3-$(NO_2)_2$	102–104	1297, 1347	1549, 1564	239 (10 600)
VI	2,4-$(NO_2)_2$	113–114[c]	1284, 1346	1522, 1540	234 (16 600)
VII	2,5-$(NO_2)_2$	162–165	1303, 1346	1525, 1555	249 (14 500)
VIII	2,6-$(NO_2)_2$	111–112	1292, 1348	1536	227 (18 500)
IX	3,4-$(NO_2)_2$	97–99	1315, 1347	1524, 1545	252 (9200)
X	3,5-$(NO_2)_2$	110–111	1285, 1352	1544	244 (19 400)
XI	2,4,6-$(NO_2)_3$	131–132[d]	1286, 1351	1541, 1556	227 (25 400)

Published data, mp, °C: [a] 71–73 [7]; [b] 139 [8]; [c] 111–113 [9]; and [d] 127 [9].

Table 2. Experimental (benzene, 25°C) and calculated by the vector and tensor additive schemes dipole moments (μ) and molar Kerr constants (*mK*) of nitro-substituted *N*-methyl-*N*-nitroanilines **II**–**XI**

Comp. no.	$\frac{\alpha_H}{\alpha_L}$[a]	$\frac{\beta_H}{\beta_L}$	γ	δ	$P_{2\infty}$, cm^3	P_D, cm^3	μ_{exp}, D	$-sK_2 \times 10^{14}$	$-mK_{exp} \times 10^{12}$
II	27.01	1.082	–	–	131.8	50.76	6.55	–	–
	10.34	0.040	0.0407	0.732	–	–	–	109.6	215.8
III	12.31	0.965	–	–	452.3	50.76	4.43	–	–
	4.739	0.274	0.0393	0.0523	–	–	–	35.46	69.85
IV	10.56	1.466	–	–	373.2	50.76	3.97	–	–
	4.195	0.582	0.0435	3.280	–	–	–	53.42	105.2
V	29.15	1.126	–	–	1026	57.01	6.88	–	–
	9.434	0.160	0.0317	0.269	–	–	–	67.75	164.0
VI	17.39	1.361	–	–	614.8	57.01	5.22	–	–
	5.497	1.728	0.0218	–0.171	–	–	–	51.19	123.9
VII	9.751	0.866	–	–	384.9	57.01	4.00	–	–
	3.151	0.492	0.0522	–0.159	–	–	–	30.70	74.29
VIII	23.01	1.298	–	–	816.3	57.01	6.09	–	–
	7.466	0.343	0.0354	–0.644	–	–	–	60.24	145.8
IX	17.73	1.238	–	–	641.3	57.01	5.35	–	–
	5.745	0.624	0.0388	0.229	–	–	–	41.95	101.5
X	9.764	1.235	–	–	350.9	57.01	3.79	–	–
	3.321	0.400	0.0511	–0.365	–	25.35	61.35		
XI	9.116	2.258	–	–	352.0	61.92	3.74	–	–
	2.374	1.585	0.0613	–0.573	–	–	–	35.93	103.2

Table 2. (Contd.)

Comp. no.	μ_{calc}, D	$-mK_{calc} \times 10^{12}$	$\Delta\mu$, D	$\Delta\mu_1$,[b] D	$\Delta mK \times 10^{12}$	Comp. no.	μ_{calc}, D	$-mK_{calc} \times 10^{12}$	$\Delta\mu$, D	$\Delta\mu_1$,[b] D	$\Delta mK \times 10^{12}$
II	6.60	–	0.45	0.45	–	**VII**	4.34	–	0.57	0.28	–
	–	236.0	–	–	20.25		–	89.56	–	–	15.27
III	5.11	–	0.20	0.20	–	**VIII**	7.27	–	0.60	0.30	–
	–	71.33	–	–	1.48		–	171.0	–	–	25.18
IV	4.18	–	0.28	0.28	–	**IX**	6.90	–	1.05	0.52	–
	–	107.7	–	–	2.55		–	129.0	–	–	27.47
V	8.18	–	0.79	0.40	–	**X**	4.18	–	0.34	0.17	–
	–	199.1	–	–	35.12		–	62.69	–	–	1.34
VI	5.11	–	0.70	0.35	–	**XI**	4.34	–	0.81	0.40	–
	–	142.6	–	–	18.73		–	122.4	–	–	19.17

[a] For definitions of α_L, α_H, β_H, β_L, δ, $P_{2\infty}$, P_D, μ_{calc}, mK_{calc}, $\Delta\mu$, and ΔmK, see text. [b] Variation of the dipole moment per one nitro group in the aromatic ring.

molecules. Therefore, in the calculations of the dipole moments and molar Kerr constants of compounds **II**–**IX** we used molecular conformations determined on the basis of the X-ray diffraction data and dihedral angles calculated by the B3LYP/6-31G* method (Table 3). As a rule, the calculated dihedral angles

Table 3. Experimental (numerator, according to the X-ray diffraction data) and calculated (denominator, B3LYP/6-31G*) dihedral angles used in the calculation of the dipole moments (μ_{calc}, D) and molar Kerr constants ($mK \times 10^{12}$) of compounds **II**–**XI** by the vector and tensor additive schemes, respectively

Angle	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI** [18]
$C^1N^7N^8O^{10}$	–	–	–	–161.97(18)	–	178.12(16)	–	–	–179.5(2)	–
	168.4	167.0	168.5	–171.9	168.0	168.6	180.0	173.4	–166.7	180.0
$C^{11}N^7N^8O^{10}$	–	–	–	–8.1(3)	–	3.4(3)	–	–	10.5(4)	–
	14.2	8.8	7.3	–12.3	13.8	13.6	0.0	7.7	9.2	0.0
$C^1N^7N^8O^9$	–	–	–1.7(2)	20.4(3)	–	–3.0(2)	–	–	1.3(4)	–
	–14.0	–14.5	–6.9	9.8	–14.6	–13.6	0.0	–13.0	14.7	0.0
$C^{11}N^7N^8O^9$	–	–	–	174.3(2)	–	–177.7(2)	–	–	–168.8(3)	–
	–168.3	–172.6	–173.8	169.5	–168.8	–168.6	–180.0	–168.1	–172.1	180.0
$N^8N^7C^1C^6$	–	–	–	66.7(3)	–	116.89(2)	–	–	–140.5(3)	65
	60.4	60.2	–55.8	67.0	–56.2	123.4	–92.3	–53.5	–121.8	87.8
$C^{11}N^7C^1C^6$	–	–	–	–86.6(3)	–	–86.6(3)	–	–	29.0(4)	–
	–92.4	–143.2	–144.3	–86.8	–82.5	–82.4	–87.7	–147.5	34.2	–87.7
$N^8N^7C^1C^2$	–	–	–72.3(2)	–115.9(2)	–	116.89(2)	–	–	43.6(4)	–
	–120.4	–122.9	–52.5	–114.7	–124.6	124.0	–92.3	–129.3	55.2	–92.2
$C^{11}N^7C^1C^2$	–	–	–	90.8(3)	–	109.9(3)	–	–	–147.0(3)	–
	92.4	33.9	32.5	91.6	96.6	97.0	87.7	29.7	–148.8	87.7
$C^1C^2N^{12}O^{13}$	–	–	–	–91.0(3)	–	149.27(2)	–	–	–	–
	158.4	–	–	–128.9	152.4	150.2	154.9	–	–	–153.8
$C^1C^2N^{12}O^{14}$	–	–	–	86.3(2)	–	–30.2(2)	–	–	–	25
	–23.5	–	–	52.9	–25.2	–28.8	–25.7	–	–	25.6
$C^2C^3N^{15}O^{16}$	–	–	–	10.2(3)	–	–	–	–	–	–
	–	178.7	–	–31.8	–	–	–	–137.0	–178.2	–

Table 3. (Contd.)

Angle	II	III	IV	V	VI	VII	VIII	IX	X	XI [18]
$C^2C^3N^{15}O^{17}$	–	–	–	–171.7(2)	–	–	–	–	–	–
	–	–	–	–150.7	–	–	–	39.9	1.8	–
$C^3C^4N^{15}O^{16}$	–	–1.0	–	–	–	–	–	–	–	23
	–	–	–	–	0.0	–	–	36.0	–	0.4
$C^3C^4N^{15}O^{17}$	–	–	179.2	–	–	–	–	–	–	–
	–	–	–	–	180.0	–	–	–147.0	–	179.4
$C^4C^5N^{15}O^{16}$	–	–	–0.8	–	–	–5.3(3)	–	–	–9.2(4)	–
	–	–	–	–	–	–1.2	–	–	–0.9	–
$C^4C^5N^{15}O^{17}$	–	–	–	–	–	174.61(18)	–	–	168.5(3)	–
	–	–	–	–	–	178.4	–	–	179.4	–
$C^5C^6N^{15}O^{16}$	–	–	–	–	–	–	–	–	–	44
	–	–	–	–	–	–	25.7	–	–	25.6
$C^5C^6N^{15}O^{17}$	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	–	–	–154.9	–	–	–153.8

Table 4. Selected structural parameters: bond lengths (Å) and bond angles (deg) (experiment[a]/calculation[b]) of compounds **I, IV, V, VII, X**, and **XI**

Bond or angle	I	IV	V	VII	X	XI
$N^7–N^8$	1.345(3) 1.3925	1.346(3) 1.3946	1.360(2) 1.3948	1.352(2) 1.3936	1.358(2) 1.3940	1.348 1.3935
$C^1–N^7$	1.435(2) 1.4306	1.431(2) 1.4276	1.427(2) 1.4272	1.422(2) 1.4265	1.417(2) 1.4203	1.497 1.4830
$C^{11}–N^7$	1.445(3) 1.4600	1.498(4) 1.4607	1.457(3) 1.4632	1.445(3) 1.4603	1.459(2) 1.4627	1.466 1.4725
$C^1N^7C^{11}$	121.8(2) 122.03	122.0(2) 121.88	120.2(2) 110.74	122.3(2) 121.56	121.8(1) 122.09	118.8 119.02
$C^1N^7N^8$	118.1(2) 119.04	118.8(2) 119.03	116.4(2) 117.27	117.8(1) 118.07	120.4(1) 121.11	117.8 118.33
$C^{11}N^7N^8$	118.6(2) 115.41	119.1(2) 116.01	118.0(2) 115.62	119.6(2) 116.67	117.0(1) 115.00	118.8 115.90
$N^7N^8O^9$	118.1(2) 117.93	117.8(3) 117.32	116.9(2) 116.72	117.6(2) 117.32	118.5(1) 118.30	117.5 117.22
$N^7N^8O^{10}$	117.6(2) 117.93	117.1(3) 115.68	117.3(2) 117.63	117.0(2) 117.22	117.6(1) 116.34	116.8 115.90
$O^9N^8O^{10}$	124.39(2) 126.12	125.1(2) 126.25	125.7(2) 126.00	125.3(2) 125.96	123.9(1) 125.70	125.7 126.00

[a] Data of [3, 18, 20, 21]. [b] Calculated by the B3LYP/6-31G* method.

were in a satisfactory agreement with the data of crystallographic data. Some deviations are likely to result from packing effects, as follows, e.g., from comparison of the *p*-dinitrobenzene structures in crystal [13] and in the gas phase [19]. Figure 1 shows the molecular structures of compounds **IV**, **VI**, and **XI**. Selected structural parameters (bond lengths and bond angles) of nitro-substituted *N*-methyl-*N*-nitroanilines are given in Table 4.

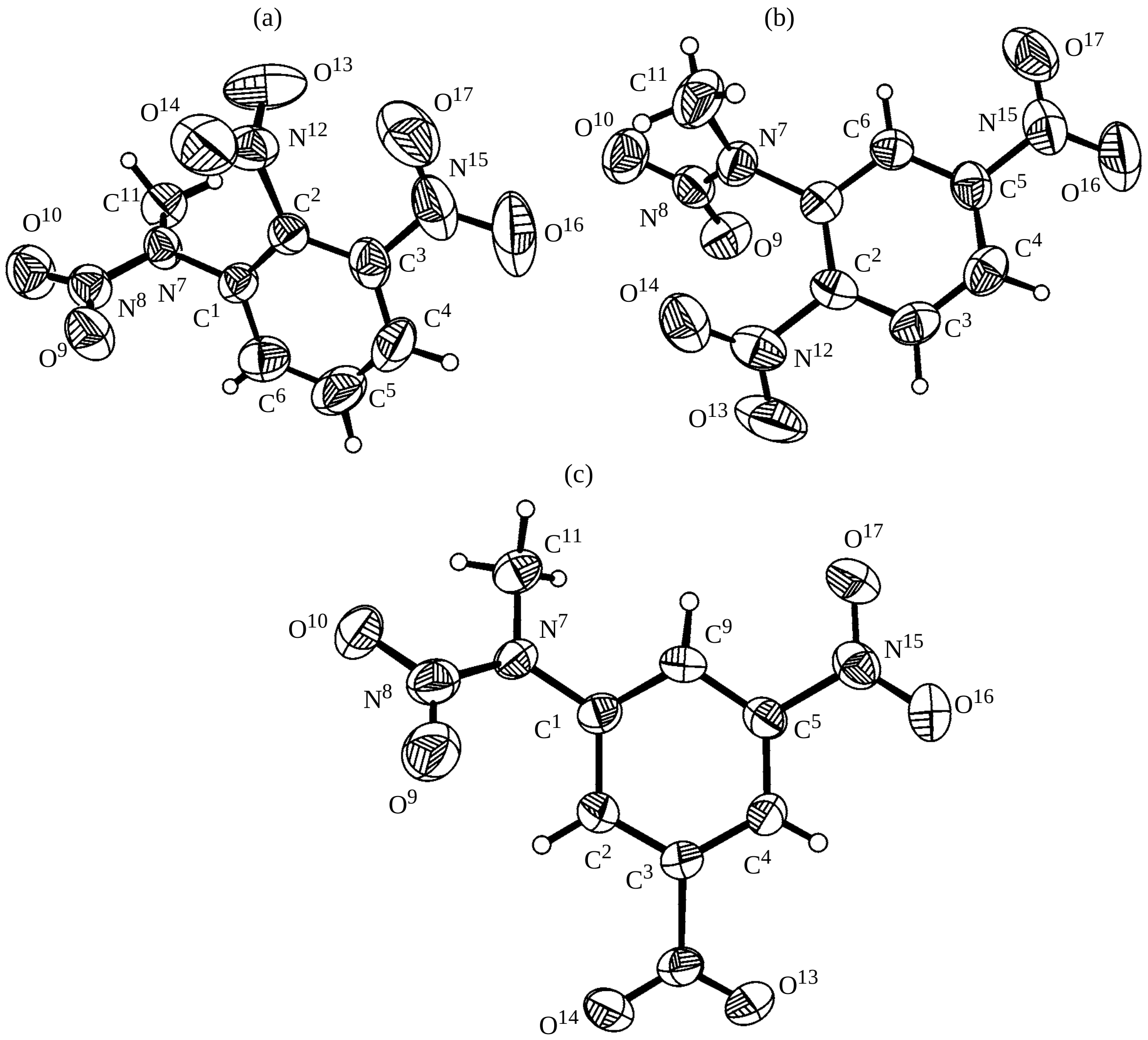


Fig. 1. Structure of the molecules of (a) *N*-methyl-*N*,2,3-trinitroaniline, (b) *N*-methyl-*N*,2,5-trinitroaniline, and (c) *N*-methyl-*N*,3,5-trinitroaniline.

The data in Tables 3 and 4 indicate that the nitroamino group is almost planar, i.e., atoms of the $C_2N–NO_2$ fragment lie in one plane. The $N^7–N^8$ bond in both unsubstituted *N*-methyl-*N*-nitroaniline (**I**) (as well as in its chloro-substituted derivatives [22]) and in all nitro derivatives is shortened [1.345(3)–1.360(2) Å] as compared to the standard single N–N bond (1.48 Å) but is considerably longer that the nitrogen–nitrogen bond in nitrous acid esters and azo compounds (1.25 Å) [23]. This means that one couple of π electrons among six electrons occupying a set of four-center π orbitals is transferred to an antibonding orbital and that the aromatic sextet and π electrons of the nitroamino group give rise to two sets of multicenter orbitals which are not conjugated with each other. The dihedral angle between the planes of the $N–NO_2$ fragment and the aromatic ring ($N^8N^7C^1C^6$ and $N^8N^7C^1C^2$) varies over a wide range: from 50.7° for the least sterically hindered compound **IX** to 87.8° for compounds **VIII** and **XI**; i.e., the $N–NO_2$ group in arylnitroamines possessing two nitro groups in the *ortho* positions is arranged orthogonally to the benzene ring plane. Although molecules **III**, **IV**, **IX**, and **X** lack nitro groups in the *ortho* positions, the corresponding dihedral angles therein suggest the existence of steric interaction between the $(CH_3)NNO_2$ group and the aromatic ring and the absence of conjugation between their π-electron systems. This is consistent with the $C_{arom}–NO_2$ bond length which ranges from 1.417(2) to 1.435(2) Å and thus approaches the standard ordinary $C_{arom}–N$ bond length equal to 1.45 Å [24].

The bond lengths and bond angles characterizing the nitro groups in the aromatic ring are typical of aromatic nitro compounds [21]. The C_{arom}–NO_2 bonds range from 1.466(3) to 1.476(2) Å, i.e., they are longer by 0.05 Å than the C_{arom}–N bond between the aromatic ring and the nitroamino group. The dihedral angles formed by the C_{arom}–NO_2 groups are given in Table 3. The *para*-nitro groups in molecules **IV**, **VI**, and **XI**, which suffer no steric effect from the neighboring groups, lie in the benzene ring plane; the same applies to the *meta*-nitro groups in molecules **III** and **X**.

The structure of compounds possessing C_{arom}–NO_2 bonds was studied in detail by Holden and Dickinson [25]. In most cases, deviation of the nitro group from the aromatic ring plane was attributed to low energy of conjugation between the nitro group and aromatic π system. Depending on the nature, number, and position of the other substituents, the dipole moment of the nitro group varies over a wide range, from 3.16 to 4.03 D [26]).

Taking into account the above structural features of nitro compounds **II**–**XI**, we calculated their dipole moments (μ_{calc}) by the vector additive scheme [6] and molar Kerr constants (mK_{calc}) by the tensor additive scheme [27] (Table 2). The parameters for *N*-methyl-*N*-nitroaniline (**I**) [7] having no nitro groups in the aromatic ring were taken as initial parameters for the calculation of dipole moments and molar Kerr constants. As in [28, 29], we presumed that the anisotropic polarizability of a nitro group attached to an aromatic ring changes with variation of the degree of acoplanarity (i.e., degree of conjugation between the NO_2 group and aromatic π-electron system). The polarizability parameters of the nitro group in a completely conjugated system were derived from the data for nitrobenzene. In the calculation of molar Kerr constants for conformers with orthogonal orientation of the NO_2 group and aromatic ring planes, the parameters for nitromethane were used [27]. Therefore, exaltations and dispersions of the polarizability ellipsoid axes b_i in going from "aliphatic" to "aromatic" nitro group resulted only from the conjugation effect. Taking into consideration a small magnitude of that effect in nitrobenzene molecule [30] and the pattern of variation of the nitro group polarity [31], we presumed that the difference in the polarizability ellipsoid axes of the NO_2 group originates from different modes of hybridization of the corresponding carbon atoms, and that this difference remains constant for different steric orientations of aromatic NO_2 group. Thus, in the calculation of molar Kerr constants of compounds **II**–**XI** we used the NO_2 polarizability ellipsoids derived from the data for nitrobenzene: $b_1 = 5.04$ (along the symmetry axis of the NO_2 group), $b_2 = 2.60$ (in the O–N–O plane), and $b_3 = 1.31$ Å (orthogonal to the O–N–O plane) [27]. The parameters of the N–NO_2 group were determined by us recently [32], Å^3: $b_1 = 5.28$, $b_2 = 5.79$, $b_3 = 2.01$. The parameters of other bonds and groups were taken from [27]. Table 2 lists the dipole moments and molar Kerr constants determined on the basis of the above considerations and molecular conformations defined by the dihedral angles given in Table 3.

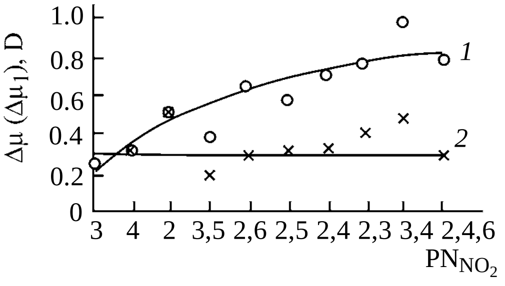


Fig. 2. Plots of (*1*) the interaction moment (Δμ) between the C–NO_2 and nitroamino groups through the aromatic ring and (*2*) the interaction moment per C–NO_2 group ($\Delta\mu_1$) vs. the number and position of C–NO_2 groups (PN_{NO_2}).

Analysis of the data in Table 2 shows that the contribution of the dipole moment of the C-nitro group to the total dipole moment of sterically hindered molecules **II**, **V**–**IX**, and **XI** as a rule decreases, presumably due to reduction of the degree of conjugation between the nitro group and aromatic ring. Depending on that factor, the dipole moment of the nitro group may change from to 3.97 to 3.10 D [26], which affects in turn the total dipole moment of mono-, di-, and trisubstituted benzene derivatives. The nitro group in molecules **III**, **IV**, and **X** lies in the benzene ring plane (Table 3); therefore, the corresponding Δμ are small, reflecting only a weak interaction between the C-nitro and nitroamino groups. This interaction is mainly inductive since the nitroamino group is forced out from conjugation with the benzene ring. In molecules **II**, **V**–**VIII**, and **XI**, one or two nitro groups are partially turned out from the aromatic ring plane (the dihedral angle is 23.5°–25.7°). In this case, conjugation between the nitro group and aromatic ring is disrupted, which affects the total dipole moment (Table 2): The Δμ value is larger than that found for molecules **III**, **IV**, and **X**. The effect of the *para*-nitro group in molecules **VI** and **XI** may interpreted in terms of competing conjugation which makes the interaction between the 2-NO_2 and 6-NO_2 groups and the aromatic ring weaker, thus facilitating their rotation due to steric repulsion [27]. The maximal Δμ value is observed for compound **IX**; both nitro groups in molecule **IX** are turned through an angle of ~40° with respect to the benzene ring plane. Figure 2 illustrates the dependence of Δμ on the

Table 5. Calculated dipole moments (μ, D) and molar Kerr constants ($mK \times 10^{12}$) of compounds **II**–**XI**

Comp. no.	Calculation method	μ_x, D	μ_y, D	μ_z, D	μ, D	b_{xx}, Å^3	b_{yy}, Å^3	b_{zz}, Å^3	b_{xy}, Å^3	b_{xz}, Å^3	b_{yz}, Å^3	$mK \times 10^{12}$
II	HF/6-31G*	5.299	–5.052	2.980	7.905	18.739	15.113	8.862	–0.204	–1.642	–0.578	1325
	B3LYP/6-31G*	4.419	–4.552	2.636	7.134	20.763	16.594	9.547	–0.663	–1.516	–0.676	1745
III	HF/6-31G*	0.488	2.386	4.146	4.771	18.969	15.751	8.432	–1.336	0.707	0.024	–1498
	B3LYP/6-31G*	0.506	1.045	2.941	3.162	22.752	17.705	8.046	–1.023	0.247	0.247	–1007
IV	HF/6-31G*	–1.978	3.081	2.698	4.548	20.590	13.996	9.041	–0.759	–0.596	–2.014	–595.2
	B3LYP/6-31G*	–2.299	3.169	1.735	4.282	26.027	16.059	8.091	–0.516	–0.326	–1.426	305.7
V	HF/6-31G*	0.803	6.310	4.527	7.807	19.876	17.213	11.412	–1.173	1.507	–0.495	–1335
	B3LYP/6-31G*	0.276	7.468	2.919	8.023	22.530	18.902	12.068	–1.049	2.104	–0.283	10.16
VI	HF/6-31G*	–0.384	–5.156	–3.323	6.146	22.567	17.232	9.449	–0.201	–1.366	0.680	–516.3
	B3LYP/6-31G*	–0.236	–4.805	–2.836	5.584	26.654	18.646	10.094	0.016	–1.203	0.799	–598.0
VII	HF/6-31G*	2.336	0.500	3.449	4.195	21.148	18.356	9.596	1.383	–0.784	–1.566	–1077
	B3LYP/6-31G*	–2.070	0.184	–2.991	3.642	24.989	19.690	10.224	–0.981	–0.594	1.514	–769.7
VIII	HF/6-31G*	6.626	2.552	0.000	7.100	20.740	10.076	17.632	–0.570	0.000	0.000	2410
	B3LYP/6-31G*	5.858	2.430	0.000	6.342	22.892	10.782	20.190	–0.697	0.000	0.000	1838
IX	HF/6-31G*	4.108	–0.576	3.889	5.686	21.860	17.345	10.293	0.931	1.006	1.311	367.0
	B3LYP/6-31G*	–4.039	0.339	–2.627	4.830	27.445	19.587	9.828	–0.915	0.481	–1.171	1619
X	HF/6-31G*	1.999	1.188	3.920	4.558	21.767	18.119	9.371	0.369	1.339	0.201	–928.9
	B3LYP/6-31G*	–1.994	–2.571	2.518	4.114	25.548	21.669	8.804	0.427	–0.748	–0.548	175.2
XI	HF/6-31G*	–3.632	1.349	0.000	3.874	10.776	24.170	19.740	–0.129	0.000	0.000	–1359
	B3LYP/6-31G*	–3.355	1.150	0.000	3.547	11.579	28.894	22.117	–0.081	0.000	0.000	–1409

number and position of nitro groups in molecules of the compounds under study. The general tendency is that accumulation of nitro groups increases $\Delta\mu$ (curve *1*). On the other hand, $\Delta\mu_1$ values (i.e., $\Delta\mu$ per nitro group) for different compounds oscillate about 0.3 D, reflecting a weak interaction between C-nitro and nitroamino group.

Molar Kerr constants are more sensitive to intramolecular interactions than dipole moments, for the former are determined not only by variations in the dipole moments but also by transformation of the bond polarizability ellipsoids, which accompanies such interactions [27, 33]. One of the most important parameters characterizing interactions between atoms which are not linked through a covalent bond is deviation of the polarizability parameter of a molecule from that calculated by the additivity scheme, i.e., without taking into account these interactions. In the general case, the existence of such interactions follows from exaltation of the molar Kerr constant: $\Delta mK = mK_{\text{exp}} - mK_{\text{calc}}$, where mK_{exp} is the experimental molar Kerr constant, and mK_{calc} is that calculated by the tensor-additivity scheme from known molecular conformation [34]. The molar Kerr constants of all the examined nitro-substituted *N*-methyl-*N*-nitroanilines are negative, i.e., the directions of the largest polarizability axis and the dipole moment of their molecules do not coincide but form a considerable angle [33]. Small exaltations of the molar Kerr constants (ΔmK) may be rationalized in terms of small $\Delta\mu$ values and change of the anisotropic polarizability of the C_{arom}–NO_2 group due to variation of the degree of its conjugation with the aromatic π-electron system. The C–NO_2 groups in molecules **III**, **IV**, and **IX** are coplanar to the aromatic ring (Table 3), and the corresponding ΔmK values are minimal (Table 2). The maximal ΔmK values were obtained for compound **IX**, in the molecule of which both C-nitro groups deviate from coplanarity by an angle of 40°, and for compound **V** where the C-nitro group is completely forced out from conjugation with the aromatic ring (the dihedral angle $C^1C^2N^{12}O^{13}$ is 91°); therefore, the polarizability ellipsoid parameters of the nitro group in **V** are similar to those of the C_{sp^3}–NO_2 group in nitromethane ($b_1 = 3.4$, $b_2 = 2.8$, $b_3 = 2.3$ Å^3) [27], and the polarizability exaltation attains is maximal value: $\Delta b_1 = 1.64$, $\Delta b_2 = -0.2$, $\Delta b_3 = -0.99$ Å^3).

Table 5 contains the dipole moments and molar Kerr constants of compounds **II**–**XI**, calculated by the HF/6-31G* and B3LYP/6-31G* quantum-chemical methods with full geometry optimization; the principal geometric are given in Tables 3 and 4. The calculated dipole moments (Table 2) agree satisfactorily with the experimental data. For compounds **II**, **IV**, **VI**,

VIII, and **X**, the experimental data matched best those calculated by the B3LYP/6-31G* method, and for the other compounds, by HF/6-31G*. While comparing experimental and calculated dipole moments, it should be kept in mind that the dipole moments measured in nonpolar solvents are always smaller by 0.3–0.5 D than the data obtained for the gas phase (so-called solvent effect) [35]. Just the same pattern was observed with the experimental and calculated dipole moments of compounds **II**–**XI**. Compound **V** was characterized by the largest difference (>1 D) between the experimental and calculated dipole moment, and differences were also found between the geometric parameters (specifically dihedral angles) determined experimentally and calculated by quantum-chemical methods. Differences in the angles of rotation of the 2-NO_2 and 3-NO_2 groups with respect to the benzene ring plane ranged from 21.0 to 37.9°. Taking into account the fan-like structure of such sterically hindered molecules [21], the error in determination of the moment of conjugation between the nitro group and benzene ring may be fairly large.

An analogous pattern was observed for the calculated (Table 5) and experimental molar Kerr constants (Table 2) of compound **V**. In this case, the difference is even greater since the dipole moment contribution to the molar Kerr constant is supplemented by the anisotropic polarizability contribution which is especially sensitive to the molecular geometry. Comparison of the angles of rotation of the C–NO_2 and N–NO_2 groups in the 2,5- and 3,5-dinitro derivatives, determined from the crystallographic data and calculated by quantum-chemical methods (Table 3), shows that the difference for sterically unhindered positions 3 and 5 attains 11°. The nitro group not only is strongly polar, but also is characterized by a fairly high anisotropic polarizability (γ = 0.6–3.08 $Å^3$) [27]; therefore, even a small angle (5°–10°) of rotation of that group strongly affects the molar Kerr constant [15]. Moreover, the experimental molar Kerr constants depend to a considerable extent on the solvent nature. As a rule, molar Kerr constants measured in a solvent are lower than in the gas phase even if donor–acceptor interaction between the solvent and the solute is lacking (i.e., there are only universal interactions) [36]. The above reasons make it impossible to compare the calculated (Table 5) and experimental molar Kerr constants (Table 2).

The nitroamino group is strongly polar. According to the results of quantum-chemical calculations, a large positive charge resides on N^7 while all neighboring atoms possess a negative charge (Table 6). Analysis of the charge distribution pattern over the N^7, N^8, C^1, C^{11}, O^9, and O^{10} atoms shows that the aromatic ring exerts some effect on the N–NO_2 group, which leads to variation of the charge on N^7, depending on the number and position of C–NO_2 groups in the molecule: The charge on N^7 is minimal in absolute value if one or two C–NO_2 groups are present in the *ortho* position with respect to the N–NO_2 group. Decrease of the charge on N^7 is accompanied by increase of the charge on N^8, the latter attaining its maximal value for the 2,4,6-trinitro derivative. The charge on C1 is also fairly sensitive to the nitro substitution pattern in the aromatic ring: It changes from 0.2685 for compound **II** to 0.3288 for **IV** (B3LYP/6-31G* calculations). HF/6-31G* calculations give a different series of charge variation on C^1: The minimal value is obtained for compound **III** (0.2532), and the maximal, for **XI** (0.3916). The charges on C^{11}, O^9, and O^{10} turned out to be less sensitive to the effect of C-nitro groups; as a rule, variations only in the second decimal point were observed, regardless of the number and position of nitro groups in the aromatic ring. These data support our previous conclusion [20] that *n* electrons on the amino nitrogen atom are involved mainly in conjugation with π electrons of the N-nitro group rather than with the aromatic ring; as a result, the nitroamino group becomes less sensitive to various interactions.

Thus, the nitroamino group can be regarded as an independent functional group possessing a four-center π-orbital system. It acts as a weak electron donor with respect to C_{arom}–NO_2 groups according to the inductive mechanism. No conjugation exists between π electrons of the nitroamino group and the aromatic ring. The presence of nitro groups in the aromatic ring of *N*-methyl-*N*-nitroaniline derivatives almost does not affect the geometric parameters of the nitroamino group. The moment of interaction between the C- and N-nitro groups through the aromatic ring depends on the number and position of the former. Nitro groups in the aromatic ring weakly affect charge distribution over the nitroamino group. Taking into account the weak effect of aromatic nitro groups on the nitroamino group, we presume that the ability of nitro-substituted *N*-methyl-*N*-nitroanilines to undergo acid-catalyzed rearrangement weakly depends on the interaction of the nitroamino group with other substituents in the aromatic ring.

EXPERIMENTAL

Dielcometric measurements were performed at 25°C using a WTW DMO-1 setup (Germany). The dielectric constants (ε) and densities ρ) of dilute solutions (up to 5×10^{-3} M) of compounds **II**–**XI** in benzene were measured. The $P_{2\infty}$ values (molar

Table 6. Charges on atoms in the molecules of nitro-substituted *N*-methyl-*N*-nitroaniline, calculated by the HF/6-31G* (numerator) and B3LYP/6-31G* methods (denominator)

Atom	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
C^1	0.2655	0.2971	0.3288	0.2671	0.2924	0.2774	0.2754	0.3294	0.3061	0.2950
	0.2991	0.2532	0.2966	0.2925	0.3251	0.2973	0.3654	0.2870	0.2386	0.3916
C^2	0.3161	–0.1842	–0.1699	0.3100	0.3100	0.3300	0.2840	–0.1894	–0.1705	0.2790
	0.2330	–0.1600	–0.2055	0.2519	0.2269	0.2621	0.1989	–0.1764	–0.1247	0.1893
C^3	–0.1590	0.2685	–0.1599	0.2636	–0.1873	–0.1676	–0.1346	0.2698	0.2659	–0.1619
	–0.1768	0.1490	–0.1752	0.2190	–0.1456	–0.1904	–0.1440	0.2308	0.1347	–0.1090
C^4	–0.1295	–0.1423	0.2858	–0.1336	0.2791	–0.1499	–0.1420	0.2798	–0.1723	0.2742
	–0.2068	–0.1595	0.1599	–0.1621	0.1477	–0.1704	–0.2213	0.2377	–0.1234	0.1393
C^5	–0.1196	–0.1550	–0.1655	–0.1394	–0.1369	0.2930	–0.1346	–0.1632	0.2549	–0.1619
	–0.1793	–0.2272	–0.1785	–0.2114	–0.1437	0.1740	–0.1440	–0.1907	0.1339	–0.1090
C^6	–0.1533	–0.0918	–0.1259	–0.1256	–0.1677	–0.1912	0.2840	–0.1088	–0.1214	0.2700
	–0.2075	–0.1348	–0.1768	–0.1337	–0.2232	–0.1820	0.1989	–0.1456	–0.1050	0.1893
N^7	–0.3712	–0.3859	–0.3884	–0.3839	–0.3759	–0.3769	–0.3699	–0.3967	–0.3944	–0.3729
	–0.5415	–0.5483	–0.5543	–0.5700	–0.5435	–0.5462	–0.5633	–0.5597	–0.5471	–0.5636
N^8	0.6618	0.6435	0.6440	0.6560	0.6639	0.6638	0.7016	0.6479	0.6492	0.7040
	0.8638	0.8492	0.8494	0.8588	0.8668	0.8657	0.9111	0.8504	0.8534	0.9138
O^9	–0.4259	–0.4175	–0.4133	–0.4192	–0.4187	–0.3997	–0.4137	–0.3959	–0.3962	–0.4049
	–0.5128	–0.5053	–0.5028	–0.4970	–0.4787	–0.4903	–0.4957	–0.4874	–0.4890	–0.4845
O^{10}	–0.4096	–0.4076	–0.4061	–0.4046	–0.3981	–0.4217	–0.4377	–0.4090	–0.4082	–0.4333
	–0.4913	0.4990	–0.4995	–0.4852	–0.5094	–0.5112	–0.5176	–0.5016	–0.5023	–0.5167
C^{11}	–0.3092	–0.3163	–0.3163	–0.3081	–0.3128	–0.3127	–0.3190	–0.3224	–0.3208	–0.3224
	–0.2772	–0.2837	–0.2829	–0.2759	–0.2829	–0.2804	–0.2811	–0.2913	–0.2868	–0.2847
N^{12}	0.3649	0.3840	0.3795	0.3564	0.3696	0.3659	0.3590	0.3969	0.3901	0.3647
	0.5016	0.5221	0.5215	0.5183	0.5079	0.5005	0.4905	0.5010	0.5275	0.4956
O^{13}	–0.3943	–0.3926	–0.3905	–0.3636	–0.3868	–0.3810	–0.3736	–0.3777	–0.3736	–0.3567
	–0.4451	–0.4636	–0.4663	–0.4210	–0.4688	–0.4310	–0.4316	–0.4424	–0.4609	–0.4265
O^{14}	–0.3729	–0.3775	–0.3933	–0.3399	–0.3542	–0.3592	–0.3629	–0.3758	–0.3862	–0.3611
	–0.4744	–0.4671	–0.4626	–0.4390	–0.4330	–0.4606	–0.4535	–0.4309	–0.4513	–0.4426
N^{15}	–	–	–	0.3664	0.3875	0.3863	0.3541	0.3655	0.3911	0.3930
	–	–	–	0.5058	0.5274	0.5238	0.4905	0.5008	0.5262	0.5318
O^{16}	–	–	–	–0.3650	–0.3762	–0.3772	–0.3629	–0.3629	–0.3777	–.3687
	–	–	–	–0.4468	–0.4526	–0.4533	–0.4535	–0.4359	–0.4560	–0.4469
O^{17}	–	–	–	–0.3624	–0.3821	–0.3790	–0.3736	–0.3862	–0.3758	–0.3687
	–	–	–	–0.4465	–0.4592	–0.4544	–0.4316	–0.4347	–0.4532	–0.4469
N^{18}	–	–	–	–	–	–	–	–	–	0.3647
	–	–	–	–	–	–	–	–	–	0.4966
O^{19}	–	–	–	–	–	–	–	–	–	–0.3567
	–	–	–	–	–	–	–	–	–	–0.4426
O^{20}	–	–	–	–	–	–	–	–	–	–0.3611
	–	–	–	–	–	–	–	–	–	–0.4265

polarization of a solute, extrapolated to infinite dilution) were calculated according to Hedestrand [37]. The values of $\alpha_N H = d\varepsilon/dN_2$ (where N_2 is the mole fraction of a solute), $\beta = d\rho/dN_2$, $P_{2\infty}$, $P_D = 1.1R_D$ (R_D is molar refraction), and μ_{exp} are given in Table 2. The dipole moments were calculated (μ_{calc}) according to the vector additive scheme using the data of [6, 28, 29]. The Kerr constants of solutions (B) were determined using a setup and procedure described in [33]. The refractive indices (n_D) were measured on an IRF-23 refractometer. To calculate molar Kerr constants (mK), the measured data were treated by the procedure described in [38]. Concentration dependences of the measured parameters of solutions were expressed in the following forms: $\varepsilon = \varepsilon_1(1 + \alpha_L\omega_2)$, $\rho = \rho_1(1 + \beta_L\omega_2)$, $n = n_1(1 + \gamma\omega_2)$, $B = B_1(1 + \delta\varepsilon_2)$, where ω_2

is the weight concentration of a solution, and ε_1, ρ_1, n_1, and B_1 are the corresponding solvent parameters. The data were extrapolated to infinite dilution by graphical methods. The values of α_L, β_L, γ, δ, and mK are given in Table 2. Tensor additive calculations of the molar Kerr constants (mK_{calc}) were performed using the data of [27, 32]. *Ab initio* quantum-chemical calculations were performed with the aid of the GAUSSIAN-98 software.

The IR spectra were recorded in KBr on a Philips PU-9804FTIR spectrometer. The electronic absorption spectra were measured from solutions in methanol on a Beckman DU-640B spectrophotometer. X-Ray diffraction studies were performed at room temperature on a KUMA KM-4 diffractometer (MoK_α radiation); the experimental conditions and crystallographic data were reported in detail previously [21]. The dihedral angles are given in Table 4.

N-Nitro amines **II**–**X** were synthesized from the corresponding nitro-substituted *N*-methylanilines by nitration with a mixture of nitric acid and acetic anhydride. This procedure was successfully used previously to obtain *N*-nitroazoles [39]. The progress of reactions and the purity of products were monitored by gas–liquid chromatography. Nitro amines **I** and **II** were subjected to rearrangement in concentrated sulfuric acid, and the products were separated by thin-layer chromatography and subjected to nitration as shown in Scheme 1. *N*-Methyl-*N*,3,5-trinitroaniline (**X**) was synthesized by methylation of 3,5-dinitroaniline, followed by nitration in acetic anhydride. *N*-Methyl-*N*,2,4,6-tetranitroaniline (**XI**) was synthesized by nitration of *N*-methyl-2,4-dinitroaniline with fuming nitric acid (d_4^{25} = 1.52 g cm^{-3}) in 80% sulfuric acid. As an example, the procedure for the preparation of *N*-methyl-*N*,3,5-trinitroaniline (**X**) is given below. *N*-Methyl-3,5-dinitroaniline (mp 158–160°C), 1.58 g, was dissolved in 1 ml of 100% nitric acid, a solution of 1.00 g of hydroxamic acid in 20 ml of acetic anhydride was added, and the mixture was kept for 2 h at room temperature and was distilled under reduced pressure. The nonvolatile residue was recrystallized from benzene–hexane to obtain 1.73 g of compound **X** with mp 94–98°C. The product was recrystallized once more from methylene chloride–*n*-hexane. Yield 1.68 g (87%), slightly yellowish sticks with mp 111–112°C. Some crystals were suitable for X-ray analysis. Mass spectrum, m/z (I_{rel}, %): 240 (1) $[M]^+$, 196 (100), 150 (54), 104 (95), 91 (1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.89 (3H, H_{arom}), 3.77 (3H, NCH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 148.3 (C^3, C^5), 141.7 (C^1), 127.9 (C^2, C^6), 118.6 (C^4).

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