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# Structure and properties of some nitro derivatives of *N*-methyl-*N*-phenylnitramine

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#### Abstract

Ten mono-, di- and tri-nitro derivatives of *N*-methyl-*N*-phenylnitramine were prepared and investigated using spectral and electrooptical methods. Three of them, viz. *N*-(2, 5-dinitrophenyl)-*N*-methylnitramine (monoclinic,  $P2_1/c$ , a = 8.248(2), b = 11.655(2), c = 10.404(2) Å,  $\beta = 102.57(2)^\circ$ ), *N*-(2,3-dinitrophenyl)-*N*-methylnitramine (monoclinic,  $P2_1/c$ , a = 9.224(2), b = 7.222(2), c = 15.458(4) Å,  $\beta = 101.08(2)^\circ$ )) and *N*-(3,5-dinitrophenyl)-*N*-methylnitramine (monoclinic,  $P2_1/c$ , a = 9.814(2), b = 12.000(2), c = 8.865(2) Å,  $\beta = 114.94(2)^\circ$ ) were examined by the X-ray diffraction method. The nitramino group is nearly planar with the short N(7)–N(8) bond and strongly electron deficient N(8) atom. The nitramino group is twisted vs. the aromatic ring, there is no conjugation between the nitro and nitramino groups across the ring. The nitramino group is an electron withdrawing substituent due to the inductive effect. The number and positions of the Ar-nitro groups have no influence on the *N*-nitro group. Its migration ability cannot be explained in terms of the interaction between the migration origin and the ring substituents. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nitramines; Dipole moments; X-ray diffraction; FTIR spectra

## 1. Introduction

The rearrangement of aromatic nitramines is an acid catalysed reaction, however, requirements of acidities are strongly dependent on the substrate. *N*-Methyl-*N*-phenyl-nitramine can be rearranged in dilute (0.1 M) sulphuric acid [1], while the rearrangement of N-(2,3-dinitrophenyl)-nitramine only occurs in a concentrated (78%) acid at room temperature [2]. Such a difference suggests that the nitramino group is strongly influenced by the ring substituents. This interaction, which determines the migration ability of the *N*-nitro group, should be reflected with some spectral and electrooptical properties of the secondary

arylnitramines. On the other hand, rentgenostuctural analyses of N-methyl-N-phenylnitramine and its ring substituted derivatives indicated that nitramine  $\pi$ electron system is not conjugated with the aromatic sextet [3,4]. That means that the formally unshared electron pair on the amido nitrogen is delocalised towards the N-nitro group and does not interact with the  $\pi$ -electrons of the ring. Consequently, we have observed that the dipole moments of the series of nitramines obey the additivity rule, i.e. they are vector sums of the contributions coming from the substituted ring and the nitramino group [5]. Therefore, it may be reasonably assumed that introduction of 1-3 nitro groups, strong electron-withdrawing substituents, to the aromatic ring, would change the charge distribution within the molecule. The shift of the nitrogen

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Table 1

Identification code	6	4	9
Empirical formula		CH <sub>3</sub> NNO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub>	
Formula weight		242.16	
Temperature		293(2) K	
Wavelength		0.71073 Å	
Crystal system,		Monoclinic	
Space group	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/n$
Unit cell dimensions $a$ (Å)	8.248(2)	9.224(2)	9.814(2)
<i>b</i> (Å)	11.655(2)	7.222(2)	12.000(2)
<i>c</i> (Å)	10.404(2)	15.458(4)	8.865(2)
$\beta$ (°)	102.57(2)	101.08(2)	114.94(2)
Volume (Å <sup>3</sup> )	976.2(3)	1010.6(3)	946.7(3)
Calculated density (Mg/m <sup>3</sup> )	1.648	1.592	1.699
Ζ	4	4	4
Absorption coefficient (mm <sup>-1</sup> )		0.14(1)	
F(000)		496	
Theta range for data collection (°)	2.5-30.1	2.5-25.1	2.5-30.0
Index ranges	$-11 \leq h \leq 11$	$-10 \le h \le 9$	$-12 \leq h \leq 13$
	$0 \le k \le 16$	$0 \le k \le 7$	$0 \le k \le 16$
	$0 \leq l \leq 14$	$0 \le l \le 18$	-11 < =1 < =0
Reflections collected/independent	2955/2836	1670/1609	2859/2701
Refinement method	Full-matrix least-square	s on $F^2$	
Number of parameters	178	178	178
Goodness-of-fit on $F^2$	1.106	1.060	1.023
Final R indices $(I > 2\sigma(I)) R_1$	0.0375	0.0370	0.0354
$wR_2$	0.0997	0.1022	0.1126
$R$ indices (all data) $R_1$	0.1203	0.0492	0.0714
$wR_2$	0.1299	0.1110	0.1341
Largest diff. peak and hole $(e.\text{\AA}^{-3})$	0.181/-0.144	0.197/-0.186	0.251/-0.232

Crystal data and structure refinement for *N*-methyl-*N*-(2,3-dinitrophenyl)-nitramine (**4**) *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (**6**) and *N*-methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**)

lone pair towards the ring should be reflected in values of dipole moments of the compounds, their spectral properties and the overall geometry of the molecules. We have prepared and examined ten one, two and trinitro derivatives of *N*-methyl-*N*-phenylnitramine. We present the results that have been obtained in this article.

## 2. Experimental

The dipole moments were determined at 25°C with the use of Dipolmeter DM 01 (WTW, Germany). The measurements of dielectric constants and densities were performed in diluted solutions (to 0.005 mole fraction of the solute) in benzene. The polarisation of the molecules was extrapolated to the infinite dilution by the Halvestrand method [6]. The infrared spectra were recorded on the Philips PU9804 FTIR spectrometer in KBr pellets. The electronic spectra were registered in methanolic solutions ( $c = 0.4 \times 10^{-4}$  to  $1.4 \times 10^{-4}$  M) at 25°C using Beckman DU 640B Spectrometer. The calculations of the dipole moments were performed employing WINMOPAC 2.0 molecular orbital program [7].

The X-ray data collection were carried out on a single crystal KM4 KUMA diffractometer using Mo K $\alpha$  radiation at room tempreature. Lattice parameters were refined from setting angles of 20–34 reflections in the  $12^{\circ} < 2\theta < 28^{\circ}$  range. During data collections, the  $\omega - \theta$  scan technique was used. Two control reflections measured after the interval of 50 reflections indicated that the intensity variations were negligible. The structures were solved by direct

Atomic coordinates  $[\times 10^4]$  and equivalent isotropic displacement parameters  $[\mathring{A}^2 \times 10^3]$  for *N*-methyl-*N*-(2,3-dinitrophenyl)-nitramine (**4**) *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (**6**) and *N*methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**).  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	у	z	$U_{\rm eq}$
6				-1
C(1)	3238(2)	4264(2)	1692(2)	39(1)
C(2)	1875(2)	4857(2)	1937(2)	42(1)
C(2)	288(2)	4446(2)	1537(2) 1524(2)	51(1)
C(4)	29(2)	3408(2)	880(2)	57(1)
C(5)	1382(2)	2828(2)	651(2)	45(1)
C(6)	2978(2)	3234(2)	1036(2)	43(1)
N(7)	4909(2)	4643(1)	2109(2)	46(1)
N(8)	5346(2)	5629(1)	1589(2)	50(1)
O(9)	4292(2)	6109(1)	749(2)	63(1)
O(10)	6775(2)	5959(1)	1984(2)	72(1)
C(11)	6090(4)	4069(3)	3137(3)	75(1)
N(12)	2079(2)	5961(2)	2627(2)	57(1)
O(13)	941(3)	6641(2)	2333(2)	98(1)
O(14)	3345(2)	6153(1)	3435(2)	72(1)
N(15)	1135(2)	1727(2)	-63(2)	61(1)
O(16)	-258(2)	1333(2)	-339(2)	101(1)
O(17)	2337(2)	1273(1)	-339(2)	80(1)
4				
C(1)	7977(2)	53(3)	6868(1)	42(1)
C(2)	7368(2)	-1671(3)	6932(1)	40(1)
C(3)	6997(2)	-2217(3)	7719(1)	49(1)
C(4)	7293(3)	-1073(5)	8443(2)	68(1)
C(5)	7963(3)	606(5)	8382(2)	76(1)
C(6)	8282(3)	1188(4)	7598(2)	1(1)
N(7)	8224(2)	655(3)	6029(1)	49(1)
N(8)	9654(2)	935(2)	5959(1)	51(1)
O(10)	9878(2)	1870(2)	5343(1)	70(1)
O(9)	10602(2)	171(2)	6505(1)	66(1)
C(11)	7084(3)	1686(4)	5439(2)	64(1)
N(12)	7174(2)	-2848(3)	6142(1)	55(1)
O(13)	6033(3)	-2763(3)	5630(1)	100(1)
O(14)	8216(2)	-3776(3)	6050(2)	94(1)
N(15)	6292(2)	-4013(4)	7793(2)	68(1)
O(16)	5840(2)	-4327(4)	8461(2)	107(1)
O(17) 9	6230(3)	-5118(3)	7190(2)	98(1)
C(1)	-3214(2)	7208(1)	10.223(2)	32(1)
C(2)	-1929(2)	6741(1)	$10\ 223(2)$ $10\ 182(2)$	32(1) 33(1)
C(2)	-1041(2)	7414(1)	9706(2)	32(1)
C(3)	-1357(2)	8511(1)	9700(2) 9243(2)	34(1)
C(5)	-2643(2)	8928(1)	9285(2)	33(1)
C(6)	-3578(2)	8314(1)	9772(2)	35(1)
N(7)	-4238(1)	6564(1)	10,603(2)	38(1)
N(8)	-3727(2)	5833(1)	$11\ 894(2)$	40(1)
O(9)	-2373(1)	5747(1)	12 710(2)	55(1)
O(10)	-4659(2)	5291(1)	12 156(2)	55(1)
C(11)	-5848(2)	6794(2)	9847(3)	47(1)
N(12)	312(1)	6925(1)	9650(2)	36(1)

Table 2 (continued)

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	x	у	z	$U_{ m eq}$
O(13)	853(1)	7400(1)	8814(2)	50(1)
O(14)	811(1)	6073(1)	10 427(2)	54(1)
N(15)	-3063(2)	10 084(1)	8753(2)	40(1)
O(16)	-2151(2)	10 667(1)	8528(2)	60(1)
O(17)	-4313(2)	10 393(1)	8534(2)	56(1)

methods and refined by a full-matrix least squares method using the SHELX97 program [8]. The Lorentz and polarisation corrections were applied. All hydrogen atoms were located from the difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically. The temperature parameters for the hydrogen atoms were freely refined. The details of the data collection and processing are listed in Table 1, whereas the atomic coordinates and the equivalent atomic displacement parameters are presented in Table 2. A list of the calculated and observed structure factors may be obtained from authors on request.

The nitramines were prepared from the corresponding nitro derivatives of *N*-methyl-aniline using the well-known methods. The procedure of *N*-nitration is exemplified below.

N-(3,5-Dinitrophenyl)-N-methylnitramine. 3,5-Dinitro-N-methylaniline (1.58 g, 8.0 mmol, mp 158-160°C) was dissolved in the solution of absolute nitric acid (1.0 ml, 22 mmol) and hydroxamic acid (1.00 g) in acetic anhydride (20 ml). The mixture was left at room temperature for 2 h and evaporated in vacuum. The residue was dissolved in methanol (20 ml) to get rid of the residual anhydride, and evaporated. The non-volatile residue was crystallised from the benzene-hexane mixture yielding the crude product (1.73 g, mp 94-98°C). It was recrystallised from the methylene chloride-n-hexane mixture. N-(3,5-Dinitrophenyl)-N-methylnitramine (1.68 g, 87%) was obtained as light yellow rods melting at 111-112°C. The crystals were suitable for the X-ray analysis. MS, m/z (int.): 240 (M<sup>+</sup>, 1), 196 (100), 150 (54), 104 (95), 91 (1), 75 (38), 63 (95). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): 8.89, s, 3H (aromatic protons, overlapped); 3.77, s, 3H (N-methyl group). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): 148.3 (C-3, C-5); 141.7 (C-1); 127.9 (C-2, C-6); 118.6 (C-4).

No	Substituents	Melting point (°C)	IR, $\nu$ (NO <sub>2</sub> ), cm	-1	UV (MeOH) $\lambda_{\text{max}}$ , nm ( $\epsilon$ )
			Symmetric	Asymmetric	
1	2-NO <sub>2</sub>	65-66	1295, 1345	1530	245 (11 200)
2	3-NO <sub>2</sub>	72–73 <sup>a</sup>	1292, 1351	1529	251 (13 400)
3	4-NO <sub>2</sub>	138–140 <sup>b</sup>	1294, 1344	1521	283 (9100)
4	$2,3-(NO_2)_2$	102-104	1297, 1347	1549, 1564	239 (10 600)
5	$2,4-(NO_2)_2$	113–114 <sup>°</sup>	1284, 1346	1522, 1540	234 (16 600)
6	$2,5-(NO_2)_2$	162-165	1303, 1346	1525, 1555	248 (14 500)
7	$2,6-(NO_2)_2$	111-112	1292, 1348	1536	227 (18 500)
8	$3,4-(NO_2)_2$	97–99	1315, 1347	1524, 1545	252 (9200)
9	$3.5 - (NO_2)_2$	110-111	1285, 1352	1544	244 (19 400)
10	2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	131-132 <sup>d</sup>	1286, 1351	1541, 1556	227 (25 400)

Characteristics of the nitro derivatives of N-methyl-N-phenylnitramine

<sup>a</sup> Ref. [5] mp 71–73°C.

<sup>b</sup> Ref. [10] mp 139°C.

<sup>c</sup> Ref. [11] mp 111–113°C.

<sup>d</sup> Ref. [11] mp 127°C.

#### 3. Results and discussion

#### 3.1. Preparations

The compounds 1-10 are collected in Table 3. The nitramines 1-9 were obtained from the corresponding *N*-methylanilines by nitration with the mixed anhydride (HNO<sub>3</sub>/Ac<sub>2</sub>O). The method, successfully employed in the preparations of *N*-nitroazoles [9], provides nitramines contaminated with *N*-acetyl derivatives. The syntheses and purification of our compounds were controlled using HPLC technique. The nitramines 1 and 2 were rearranged in concentrated sulphuric acid, the isomers were separated employing the flesh-chromatography method and *N*-nitrated, as shown in Scheme 1.

*N*-Methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**) was obtained from 3,5-dinitroaniline by the methylation. and *N*-nitration in acetic anhydride. Tetryl (**10**) was prepared from 2,4-dinitro-*N*-methylaniline by the nitration with fuming nitric acid (d 1.52) in 80% sulphuric acid.

# 3.2. Spectra

In the *para*-substituted *N*-methyl-*N*-phenylnitramines, the asymmetric stretching vibration of the *N*nitro group lies in the narrow range of  $1520-1540 \text{ cm}^{-1}$  [5]. The nitro group attached to the benzene ring is more sensitive to para-substituents: the asymmetric band occurs at 1490–1570 cm<sup>-1</sup> depending on the electronic properties of the second group [12]. In the spectra of the compounds 1-10, the frequencies of the N-nitro and C-nitro groups overlap or are separated for  $20-30 \text{ cm}^{-1}$  only (see Table 3). The equivocal assignment is not possible without <sup>15</sup>N labelling, however, the appearance of the  $C-NO_2$ band within  $1520-1560 \text{ cm}^{-1}$  indicates that the Nmethylnitramino group has the electron withdrawing properties, comparable with those of halogens (cf. Ref. [12]). In the region of the symmetric stretching vibrations, the frequencies of the N-nitro (1280- $1300 \text{ cm}^{-1}$ ) and *C*-nitro (1340–1350 cm<sup>-1</sup>) groups can be distinguished according to the general rules; this is well known that the bands of the former are shifted towards lower wave numbers in respect to the latter for ca. 50 cm<sup>-1</sup> [13]. The only exception is the nitramine 8, which displays the strong band at  $1315 \text{ cm}^{-1}$ , i.e. outside of the typical region. In spite of that, the final conclusion is that the number and positions of the C-nitro groups do not influence the frequencies of the N-nitro group which appear invariably in the narrow regions of 1280-1300 and 1520- $1560 \text{ cm}^{-1}$ .

In the UV spectra, a strong  $(3.96 < \log \epsilon < 4.40)$  band with the maximum at 240–250 nm appears in almost all cases; the only exception is the nitramine **3**, where we observe a weak batochromic shift to

Table 3



Scheme 1.

283 nm. Even if this weak batochromic shift is the result of interaction between the *parasubstituents*, it is not comparable with that observed in, e.g. *N*,*N*-dimethyl-4-nitroaniline which absorbs in the visible region. Consequently, we must conclude that the nitro and nitramino groups are not the complementary (donor and acceptor) ones.

## 3.3. Dipole moments, experimental

The experimental and calculated values of the dipole moments of the title compounds are collected in Table 4. The molecules (1-10) are intensely polar, and their dipole moments exceed in some cases to

6 Debye, the values calculated as the vector sum of contributions from the *C*-nitro and nitramino groups are even higher. The numbers collected in column A were obtained assuming perpendicular conformation of the nitramino group, with respect to the ring, and the contribution of the *C*-nitro groups such as in nitrobenzene [14]. In the case of sterically hindered substituents, it can be presumed that the contribution of the *C*-nitro groups is decreased, due to the elimination of the resonance interaction. In fact, the values in column B are closer to the experimental ones; they were obtained assuming that contributions of the *C*-nitro groups are such as in nitromethane [15]. In the case of **4** and **8**, the agreement, between the calculated

Table 4

Dipole moments (in benzene, 25°C) of *N*-methyl-*N*-phenylnitramines substituted with the nitro groups (A: these values were calculated assuming that the contribution from the *N*-methyl-*N*-phenylnitramine moiety is 4.34 Debye and that of the nitro group amounts 4.01 Debye, the nitramino group is planar and perpendicular to the aromatic ring. B: the contribution of the nitro group in the vicinal position to the nitramino or conjugated Ar-nitro group was diminished to 3.10 Debye due to the steric hindrance excluding conjugation [14])

No	Substituents	α	β	$P_2 ({\rm cm}^3)$	$\mu_{exp}$ (Debye)	μ <sub>calc</sub> (]	μ <sub>calc</sub> (Debye)		$\Delta\mu_{calc}$ (Debye)		
						А	В	AM1	A	В	AM1
1	2-NO <sub>2</sub>	27.01	1.008	928.7	6.55	6.60	5.93	6.77	-0.05	+0.62	-0.22
2	3-NO <sub>2</sub>	12.31	0.965	452.3	4.43	5.11	_	2.96	-0.68	_	+1.47
3	$4-NO_2$	10.56	1.470	373.2	3.97	4.18	_	4.13	-0.21	_	-0.16
4	2,3-(NO <sub>2</sub> ) <sub>2</sub>	29.15	1.126	102.6	6.88	8.18	7.41	7.62	-1.30	-0.53	-0.74
5	$2,4-(NO_2)_2$	17.39	1.361	614.8	5.22	5.11	4.63	5.81	+0.11	+0.59	-0.59
6	2,5-(NO <sub>2</sub> ) <sub>2</sub>	9.751	0.866	384.9	4.00	4.34	4.20	3.88	-0.34	-0.20	+0.12
7	$2,6-(NO_2)_2$	23.01	1.298	816.3	6.09	7.27	6.47	6.90	-1.18	-0.38	-0.81
8	3,4-(NO <sub>2</sub> ) <sub>2</sub>	17.73	1.238	641.3	5.35	6.40	5.78	5.07	-1.05	-0.43	+0.28
9	$3,5-(NO_2)_2$	9.764	1.235	350.9	3.79	4.18	_	4.17	-0.39	_	-0.38
10	2,4,6-(NO <sub>2</sub> ) <sub>3</sub>	8.716	2.258	352.0	3.74	4.34	3.96	3.56	-0.60	-0.22	+0.18

and experimental values, can be better (6.90 vs. 6.88 Debye) and 5.22 vs. 5.35 Debye) assuming that both vicinal nitro groups are not conjugated with the ring.

The experimental dipole moment of **1** is nearly the same as the value calculated, assuming perpendicular conformation of the molecule, i.e. that the torsion angle along the Ar–N bond amounts 90°. The result seems to be reasonable for the first sight, considering the steric hindrance around the nitramino group. The high values of  $\Delta \mu$  in the case of **7** and **10** (the compounds substituted in positions 2 and 6) indicate, that the agreement between the experimental and calculated values maybe rather incidental.

The calculated dipole moment of 2 exceeds the experimental value for 0.68 Debye; in such a molecule, the dipole moment must be very sensitive to its conformation. Rotation of the methylnitramino group by 10° from its perpendicular position decreases the calculated value to 4.57 Debye (3.33 Debye when the torsion angle along the Ar-N bond decreases from 90 to  $60^{\circ}$  placing the nitramino group far off the C-nitro substituent). On the contrary, in the para substituted nitramine 3, rotation along the C-N does not influence the dipole moment since the vector of the C-nitro group is collinear with the rotation axis. The value  $\Delta \mu = -0.21$  Debye may be, therefore, considered as the moment of interaction between the nitro and nitramino groups. However, the dipole moment of symmetrically substituted 9 should be also insensitive to the C-C-N-N torsion angle. Considering that  $\Delta \mu = -0.39$  Debye in this case, we must conclude that the interaction between substituents in **3** and **9** must be of inductive nature, if any.

The results indicate the lack of any strong interactions between the nitro and nitramino groups across the ring, however, the  $\Delta\mu$  values are very large in most cases. It prompted us to examine the molecular structure of selected nitramines from the series, employing the X-ray diffraction method. Our aim was to calculate the dipole moments basing on the factual geometry of these molecules.

# 3.4. Crystal structure

The following compounds have been selected for crystal structure determination:

- *N*-methyl-*N*-(2,3-dinitrophenyl)-nitramine (4), characterised by the largest dipole moment;
- *N*-methyl-*N*-(3,5-dinitrophenyl)-nitramine (9), which possesses the second smallest experimental dipole moment since the crystal structure of tetryl (10) is known [15];
- *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (6), to compare its geometry with that of 4.

The molecular structures of **4**, **6** and **9**, showing the atomic numbering scheme, are presented in Fig. 1(a)–(c). The bond lengths and angles within the aromatic rings and the nitramino groups are collected in Table



V(12)

(c)

0(13)

0(14)

5. The Table 6 contains the data on the geometry of the *C*-nitro groups.

In further discussion we will compare mainly the geometry of fist four compounds. The structure determination of tetryl has been carried out over 20 years ago and before such a comparison it should be redetermined on modern facilities. The nitramino group is almost planar, the atoms of the  $C_2N-NO_2$  group are situated on the same plane. The N(7)-N(8) bond is short (1.346(3)-1.360(2) Å), indicating a high bond order which is not influenced with the ring substituents. Consequently, the aromatic sextet and the nitramine  $\pi$ -electron sextet are two independent sets of multicenter orbitals, which are not conjugated to each other. The mean torsion angle along the Ar-NNO<sub>2</sub> bond varies between 42.6 and 72.3°. In crystal lattice, the nitramino group is therefore twisted from the perpendicular position to the ring for ca.  $18-47^{\circ}$ . Considering that the length of the Ar-NNO<sub>2</sub> bond, 1.417(2)-1.431(2) Å, is close to the typical C<sub>ar</sub>-NN single bond (1.43 Å [16]); it may be concluded that the C-C-N-N torsion angle is determined by the weak intermolecular interactions in the crystal lattice.

The bond lengths and angles within the C-nitro groups are typical of aromatic nitro compounds [16]. The  $C-NO_2$  bond length equals to 1.466(3)-1.476(2) Å and it is for ca. 0.05 Å longer than the analogous C-N bond between the aromatic ring and the nitramino group. Another interesting feature is the torsion angle along the C-N bond of the Ar-NO<sub>2</sub> group, as shown in Table 6. The para-nitro group in 3 is almost coplanar with the aromatic ring, so is the *meta*-nitro group in 6. In the 9 molecule, both metha nitro groups are slightly more twisted to the ring plane: for 10.4 and 18.8°. The most overcrowded nitramine 4 presents a rather peculiar geometry. The C-nitro group in the orthoposition is perpendicular to the ring while the meta nitro group is nearly coplanar with the ring  $(9.3^{\circ})$ .

The problem of conjugation between an aromatic ring and the nitro substituents was studied by Holden and Dickinson [17]. They have found that in most cases, the nitro groups are deviated from coplanarity

Fig. 1. Molecular structure of: (a) *N*-methyl-*N*-(2,3-dinitrophenyl)nitramine (**4**); (b) *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (**6**); (c) *N*-methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**); showing atomic numbering scheme. Thermal ellipsoids at 50% probability.

Table 5

Selected structural parameters of the nitro derivatives of *N*-methyl-*N*-phenyl-nitramine; *N*-methyl-*N*-(4-nitrophenyl)-nitramine, *N*-methyl-*N*-(2,3-dinitrophenyl)-nitramine (**4**), *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (**6**), *N*-methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**) and *N*-methyl-*N*-(2,4, 6-trinitrophenyl)-nitramine The geometry of the aromatic ring and the C-nitro groups

	Bond lengths (Å) and angles (°) in the <i>N</i> -methyl- <i>N</i> -phenylnitramine derivatives						
	4 [4]	2,5 (6)	2,3 (4)	3,5 (9)	2,4,6 [15]		
Aromatic ring							
C(1)– C(2)	1.383(3)	1.390(2)	1.378(3)	1.394(2)	1.397		
C(2)– C(3)	1.387(4)	1.372(3)	1.382(3)	1.378(2)	1.393		
C(3)- C(4)	1.379(4)	1.377(3)	1.375(4)	1.375(2)	1.365		
C(4)- C(5)	1.377(4)	1.368(3)	1.373(4)	1.373(2)	1.377		
C(5)- C(6)	1.389(4)	1.374(2)	1.368(4)	1.381(2)	1.393		
C(6)– C(1)	1.377(3)	1.375(2)	1.379(3)	1.388(2)	1.385		
Nitramino groups							
C(1)– N(7)	1.431(2)	1.422(2)	1.427(2)	1.417(2)	1.497		
N(7)- N(8)	1.346(3)	1.352(2)	1.360(2)	1.358(2)	1.348		
N(7)- C(11)	1.448(4)	1.445(3)	1.457(3)	1.459(2)	1.466		
N(8)- O(9)	1.238(3)	1.225(2)	1.224(2)	1.220(2)	1.232		
N(8)- O(10)	1.225(2)	1.223(2)	1.216(2)	1.222(2)	1.230		
C(1)- N(7)- N(8)	118.8(2)	117.8(1)	116.4(2)	120.4(1)	117.8		
C(1)- N(7)- C(11)	122.0(2)	122.3(2)	120.2(2)	121.8(1)	118.8		
C(11)- N(7)- N(8)	119.1(2)	119.6(2)	118.0(2)	117.0(1)	118.8		
N(7)- N(8)- O(9)	117.8(2)	117.6(2)	116.9(2)	118.5(1)	117.5		
N(7)- N(8)- O(10)	117.1(3)	117.0(2)	117.3(2)	117.6(1)	116.8		
O(9)- N(8)- O(10)	125.1(2)	125.3(2)	125.7(2)	123.9(1)	125.7		
C-C-N-N (average)	72.3	63.9	65.4	42.6	65		

Table 6

Selected structural parameters of the nitro derivatives of *N*-methyl-*N*-phenyl-nitramine; *N*-methyl-*N*-(4-nitrophenyl)-nitramine, *N*-methyl-*N*-(2,3-dinitrophenyl)-nitramine (**4**), *N*-methyl-*N*-(2,5-dinitrophenyl)-nitramine (**6**), *N*-methyl-*N*-(3,5-dinitrophenyl)-nitramine (**9**) and *N*-methyl-*N*-(2,4, 6-trinitrophenyl)-nitramine. The geometry of the Ar-nitro groups

	Bond lengths (Å) and angles (°) in the N-methyl-N-phenylnitramine derivatives						
	4 [4] para	2,5 (6) meta	2,3 (4) meta	3,5 ( <b>9</b> ) meta	2,4,6 [15] para		
C–N	1.472(2)	1.476(2)	1.466(3)	1.467(2)	1.488		
N-O	1.221(2)	1.212(2)	1.207(3)	1.217(2)	1.216		
N-O	1.218(2)	1.212(2)	1.220(3)	1.216(2)	1.211		
C-N-O	118.1(2)	118.0(2)	117.7(3)	118.0(1)	116.8		
C-N-O	118.6(2)	117.9(2)	118.4(2)	117.8(1)	117.9		
O-N-O	123.2(2)	124.1(2)	123.9(3)	124.1(1)	125.4		
O–N–C–C (av.)	2.5	4.8	9.3	10.4	23		
	_	ortho	ortho	meta	ortho, ortho		
C–N	_	1.465(2)	1.470(3)	1.472(2)	1.497, 1.485		
N–O	_	1.216(2)	1.203(3)	1.220(2)	1.214, 1.216		
N-O	-	1.211(2)	1.191(2)	1.214(2)	1.202, 1.213		
C-N-O	-	119.5(2)	118.3(2)	117.7(1)	116.9, 115.9		
C-N-O	_	116.7(2)	116.6(2)	118.0(1)	118.6, 117.2		
O-N-O	_	123.8(2)	125.0(3)	124.3(1)	124.5, 126.9		
O–N–C–C (av.)	_	29.9	90.0	18.8	25, 44		

with the aromatic ring due to the small value of the stabilisation energy, emerging from the conjugation between the nitro group and the aromatic sextet. Consequently, the aromatic nitro substituent is not so rigid as it used to be considered and some distortions must be expected not only in a crystal lattice, but also in solutions.

#### 3.5. Dipole moments, calculated by the AM1 method

Considering large values of  $(\Delta \mu)$  (Table 4, columns A and B), we have calculated the dipole moments of the nitramines 1-10 using the AM1 method [7]. The compounds 3, 4, 6, 9 and 10, which molecular structures are known from the X-ray diffraction studies, were examined first. We have assumed that the conformations of the molecules in crystal lattices are similar to those existing in diluted solutions in a non-polar solvent. Consequently, the geometry optimisation of, e.g. nitramine 3, was started from the conformation with the twisted nitramino group and slightly distorted C-nitro groups, as given in Tables 5 and 6. It turned out that the optimal conformation of the isolated molecule (3) is that with coplanar C-nitro groups and the nitramino group twisted for 72° from the ring plane. Its calculated dipole moment amounted 4.17 Debye and exceeded the experimental value for 0.38 Debye. The calculations of the remaining nitramines were carried out assuming analogous geometry of their molecules; the compound 8 is an exemplification. It was presumed that the nitramino group and either of the C-nitro groups were perpendicular to the aromatic ring, while the second one remained coplanar. The results of the calculations were the same in both cases. The geometry optimisation established the torsion angle along the C(1)-N(7) bond as ca.  $65^{\circ}$  and demonstrated that both C-nitro groups are arranged in a fan-like manner, twisted for ca. 40° from the ring plane. The calculated dipole moment was the same (5.07 Debye), and was smaller by 0.28 Debye from the experimental value. The mean deviation of the calculated from the experimental values is 0.2 Debye for ten compounds. The 2, 4 and 7 molecules require a special consideration.

The semiempirical AM1 calculations point out the source of large values of dipole moments of the nitramines as well as the reasons of differences between the calculated and measured values in some cases.



There is a strong separation of charges  $(\pm 0.6e)$  in the N-nitro group. Contrary to the mesomeric forms presented above, the N(7) nitrogen atom is negatively (-0.25e) charged on the expense of both substituents. Such a charge distribution is consistent with the results of more advanced QM studies carried out on a simple model molecule [18,19]. It is responsible for the contribution of the N-methyl-N-phenylnitramine moiety into the dipole moments. The other source of the dipole is the aryl nitro substituents, in which the charge distribution is similar to that in the N-nitro groups. It is not influenced with the torsion angles, i.e. the partial charges on the nitrogen and oxygen atoms are the same in coplanar and twisted groups. The orientation of these vectors determines the magnitude of the dipole moment. The estimated value for 2 is significantly lower than calculated, presuming perpendicular conformation, but much higher than the dipole moment predicted (AM1) for the optimised structure with the torsion angle of 118° along the C(1)-N(7) bond. The result indicates that the orientation of the nitramino group with respect to the ring is statistical without any preferable conformation.

Rotation along the C–N bonds cannot account for the large  $\Delta \mu$  values in the case of overcrowded nitramines **4** and **7**. There is a difference between the optimised geometry of the **4** molecule and its conformation in the crystal lattice. The *C*-nitro groups are not twisted in parallel for ca. 45° (fan-like conformation) as predicted by AM1, but the more hindered one (at C-2) is perpendicular to the ring. This effect cannot be responsible for the differences between the calculated and estimated values of dipole moments. Probably, in diluted solutions in non polar solvents, the separation of positive and negative charges is smaller when all the local dipoles are situated on the same side of the molecule.

## 4. Conclusions

1. The nitramino group must be considered as the

individual functional group with the four-center system of  $\pi$ -orbitals. It displays the electron withdrawing properties due to the inductive effect. There is no tendency to the conjugation between the nitramine  $\pi$ -electrons and the aromatic sextet.

- 2. The presence of nitro groups bound to the ring does not significantly influence the geometry of the nitramino moiety. The moment of the interaction do not increase with the increasing number of nitro groups. The electron withdrawing substituents on the ring do not disturb the charge distribution within the nitramino group.
- 3. Comparison of the calculated and estimated by AM1 method dipole moments indicates small energy barrier for the rotation of the nitramino group in the absence of *ortho* substituents.
- 4. There is no sight of strong interaction of the nitramino group with another NO<sub>2</sub> substituent across the aromatic ring. Consequently, the influence of the NO<sub>2</sub> substituents on the susceptibility of the derivatives of *N*-methyl-*N*-phenylnitramine to the acid catalysed rearrangement cannot be explained as the result of the interaction of the migration origin with the another group bonded to the ring.

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