Polish J. Chem., **75**, 707–718 (2001)

Dipole Moment, Molar Kerr Constant, Crystal and Molecular Structure of 3-Chloro-N-methyl-N-nitroaniline

by V.V. Prezhdo[1], A.S. Bykova[2], T. Glowiak[3], O.V. Prezhdo[4], Z. Daszkiewicz[5] and J.B. Kyziol[5]

[1]*Institute of Chemistry, Pedagogical University, Chęcińska 5, 25-020 Kielce, Poland*
[2]*Kharkov State Polytechnic University, Frunze 21, 61-002 Kharkov, Ukraine*
[3]*Department of Chemistry, University of Wrocław, Joliott-Cuire 14, Wrocław, Poland*
[4]*Department of Chemistry, University of Washington, WA 98915, USA*
[5]*Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland*

(Received June 14th, 2000; revised manuscript December 8th, 2000)

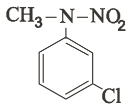
Dipole moment, molar Kerr constant, crystal and molecular structure of *m*-$ClC_6H_4N(CH_3)NO_2$ (or $C_7H_7ClN_2O_2$) are studied. Comparison the data obtained by dipole moment and molar Kerr constant measurement, X-ray crystallographic investigation and quantum-chemical calculation show that the molecule contains a planar NNO_2 nitroamino group which is twisted around the $N–C_{phenyl}$ bond by *ca* 61.4° from the plane of the aromatic ring. The structural data are compared with the data for *p*-$ClC_6H_4N(CH_3)NO_2$ and the influence of the substituent on the structural parameters of the molecule is established.

Key words: N-nitroamino group, N-methyl-N-nitro-chloranilines, crystal structure, dipole moment, molar Kerr constant, quantum chemical calculation

Properties and molecular structure of compounds containing N-nitroamino group are studied, in particular since these compounds are used in rocket fuels and as explosive substances [1]. Due to the presence of the N–N bond, these compounds are very active in photochemical reactions [2]. The crystal and molecular structures of N,N-dimethylnitramine and some cyclic and aliphatic nitramines were investigated previously [3,4]. Within the aromatic series: tetryl [5], N-methyl-N-nitro-4-nitroaniline [6], N-methyl-N-nitro-4-chloroaniline [7], 2,4-N-trinitroanilinoacetic acid [8], N(β,β,β-trifluoroethyl)-N-2,4,6,-tetranitroaniline [9], bis-(2,6-dimethoxyphenyl)nitramine [10], and several compounds with the nitramino group connected to the pyridine ring: 4-(nitramino)pyridyl nitrate [11], 1-methyl-4-(N-methyl-nitramino)pyridyl bromide [12], 4-(N-methylnitramino)pyridyl 1-oxide [13] and N,N′-dinitro-N,N′-bis-(2-pyridyl)-1,4-diaminocubane [14] were investigated. An interesting feature of N-methyl-N-nitroaniline and its derivatives is their ability to rearrange. Migration of the nitro group, three or five nodes far from the amino nitrogen is acid catalysed, however, some N-nitro compounds can rearrange without interference of an acid but under increased temperature or during photolysis [15].

Sensitivity of nitramines to acids is various: N-phenylnitramine and most its derivatives can be obtained only in alkaline conditions, since under influence of acids they rearrange immediately [16]. N-Nitroazoles can be effectively prepared by nitration with the mixed anhydrides (*e.g.* acetyl nitrate) [17], while N-nitration of aminopyridines and picramine required mixed acids [18] or nitronium salts [19]. In particular it concerns derivatives of N-methyl-N-phenylnitramine, which are used as model compounds in investigations on the mechanism of nitramine rearrangement [20]. Only recently [21] the products of the N-methyl-N-nitroaniline rearrangement reaction were identified. However, the mechanism of the rearrangement is still not established.

The nitramine group is a complex substituent for which substituent parameters such as σ constants [6] also the dipole moment [22] and the main half-axes of anisotropy of polarizability [23] were established recently. Undoubtedly the nitro group substituted at the nitrogen atom of the amino group increases its electronegativity [6]. In addition, it should be taken into account that the lone pair at the amino group may be involved in co-operative interactions with π-electron system of the nitro group. These kinds of interactions are usually reflected in geometry of the molecule [6]. Dipole moments and molar Kerr constants of polar compounds are sensitive to changes in molecular geometry [24]. Therefore, in the present work the dipole moment, the molar Kerr constant, crystal and molecular structure of N-methyl-N-nitro-3-chloraniline (compound I) were investigated.


I

The molecular and crystal structure of N-methyl-N-nitro-4-chloraniline (compound II) has been reported [7]. Presently we are interested in the effect of the change of the position of the chlorine substituent on the structural parameters of molecules.

EXPERIMENTAL

Preparation of the compound: The title compound was obtained by the action of *n*-butylnitrate on the Grignard compound generated *in situ* from 3-chloro-N-methylaniline and ethylmagnesium bromide as described in [25]. The crude product was crystallized from *n*-hexane. Crystals suitable for X-ray studies were obtained by slow cooling of the methylene chloride solution to 253 K.

Physical methods: Dipole moments (*DM*) were measured in benzene at 25°C using "Dipole" apparatus, produced by the Experimental Design Office of Automation, Angarsk, Russia. The "Dipole" apparatus allowed us to obtain the dielectric constant and the density of the solution, both to the fourth place accuracy. Refractive indices of the same solutions were measured using the IRF-23 refractometer. Molar Kerr constants (*MKC*) were determined with the help of the apparatus described in [26]. The vector and tensor addition schemes used in the calculation of *DM* and *MKC* are described in [24,27]. The quantum-chemical calculations were carried out with the Gaussian 98 suite of programs [28]. Molecular geometries were fully optimised with standard accuracy. The calculated values of *DM* were taken directly from the Gaussian output. *MKC* were calculated from the values of *DM* and polarizability tensors according to [24]. X-ray measurements were performed at room temperature using *Kuma KM-4* four-circle diffractometer [29] and graphite-monochromated CuKα radiation. The structures were solved by direct methods with SHELXS-86 [30] and refined by the full-matrix least-squares methods using the SHELXL-93 [31] with anisotropic parameters for all non-hydrogen atoms. The hydrogens were located from geometries of the molecules, their isotropic temperature factors fixed at 1.2 U_{eq} of their parent atoms. The atomic scattering factors were those of neutral atoms incorporated in SHELXL-93 [24]. Details of the measurements, crystal data and refinement parameters are given in Table 1. The crystal structure of 3-chloro-N-methyl-N-nitroaniline has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 144472.

Table 1. Crystal data and structural refinement for compound I.

$C_7H_7ClN_2O_2$	Cu Kα radiation
$M_r = 186.60$	$\lambda = 1.5418$
Orthorhombic	Cell parameters from 25 reflection
$P2_12_12_1$	$\mu = 3.87$ mm^{-1}
$a = 3.993(2)$	$\theta = 10–18°$
$b = 17.845(4)$	$T = 293(2)$ K
$c = 11.364(3)$	Parallelepiped
$V = 809.7(3)$	0.15 × 0.15 × 0.20 mm
$Z = 4$	
$D_x = 1.531$ Mg m^{-3}	
Data collection	
Kuma KM-4 diffractometer	$\theta_{max} = 81.3°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 4$
Absorption correction: none	$k = 0 \rightarrow 22$
1696 measured reflection $I > 2\sigma(I)$	$l = –14 \rightarrow 14$
1458 independent reflection $I > 2\sigma(I)$	2 standards reflections
$R_{int} = 0.0081$	every 50 reflections intensity decay: 2.0%
Refinement	
Refinement on *F2*	
$R_1[I > 2\sigma(I)] = 0.0333$	$\Delta\rho_{max} = 0.209$ e Å^{-3}
$wR_2 = 0.0849$	$\Delta\rho_{min} = –0.165$ e Å^{-3}
$S = 1.092$	Extinction correction:
111 parameters	*SHELXL93* (Sheldrick, 1993)
All H atoms refined	Extinction coefficient: 0.0198(12)
$w = 1/(\sigma(F_0^2) + (0.0365P)^2 + 0.3640P)$ where $P = (F_0^2 + 2F_c^2)/3$	Scattering factors from *International Tables for*
$(\Delta/\sigma)_{max} < 0.001$	*Crystallography* (Vol. C)

Data collection: *Kuma KM-4 Users Guide* (Kuma, 1997).
Cell refinement: *Kuma KM-4 Users Guide.* Data reduction: *Kuma KM-4 Users Guide.*
Program(s) used to solve structure: *SHELXS-86* (Sheldrick, 1990).
Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).
Software used to prepare material for publication: *SHELXL*93.

RESULTS AND DISCUSSION

The molecular structure of compound I is given in Fig. 1. The nitroamino group in (I) is planar. The bond lengths and bond angles agree with the corresponding values in N,N-dimethylnitramine [4] and N-methyl-N-nitro-4-chloraniline [7]; the differences do not exceed 0.03 Å and 2°, respectively. The carbon skeleton of the aromatic ring is planar, the deviations do not exceed 0.012 (2) Å. The nitrogen atom N(1) also practically stays in the plane of the benzene ring, the deviation being only 0.024 (3) Å. This is in contrast to compound II, where the observable deviation is 0.0653 (6) Å [7]. Strong interaction of atom N(1) with the NO_2 group is supported by the fact that NNO_2 in (I) is planar. The greatest deviation from the plane is observed for atom N(2) and equals only 0.002 (2) Å. The bond lengths and bond angles in (I) correspond to the values in (II) [7]; the differences in the bond lengths do not exceed 0.020 (2) Å. The largest difference in the angles is observed for angle O1–N2–N1 and equals 3.3°. This difference must be related to the change in the position of the chlorine atom from 4 to 3. The N–N bond in N-nitramines is significantly longer [1.341 Å in $(CH_3)_2NNO_2$ [4], 1.350 Å in (II) [7] and 1.338(3) Å in (I)] than in hyponitrites and azo compounds (1.25 Å [32]), but is shorter than a single bond (1.48 Å [33]). This indicates that one π-electron pair from the sextet, occupying the set of the four-centre π-orbitals, goes to an anti-bonding level [7].

In molecule (II), as well as in molecules of other 4-derivatives of N-methyl-N-nitroaniline, the steric interaction between the nitramino group and substituents in the aromatic ring is not possible. Nevertheless, the magnitude of the N2–N1–C1–C2 torsion angle which equals 66.5° [18] indicates that there is no conjugation between the two π-electronic systems. This is also the case for N-methyl-N-nitro-4-nitroaniline, where the angle equals 72.3° [6]. In arylnitramines containing two NO_2

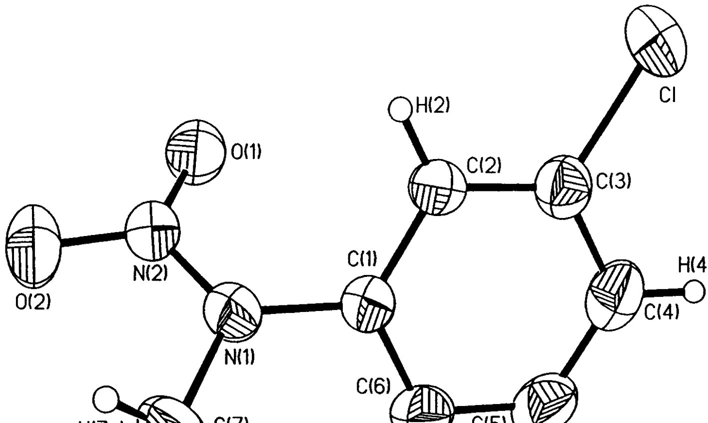


Figure 1. Molecular structure of 3-chloro-N-methyl-N-nitroaniline.

groups situated *ortho* to the NNO_2 group the latter is nearly perpendicular to the aromatic ring [5]. In molecule (I) the steric interaction between the NNO_2 group and *meta* chlorine atom is not possible as well. As a result, the 61.4(3)° magnitude of N2–N1–C1–C2 torsion angle is close to that for (II) and is compatible with the N2–N1–C1–C2 torsion angle obtained for compound (I) (Fig. 2). The calculation of the potential energy (E, kcal/mol) as a function of the rotation angle of the N-methyl-N-amino group around the N(1)–C(1) bond is performed by the AM1 method with full optimization of the remaining variables (Fig. 2) as well as *ab initio* with using the Gaussian 98 program by the B3LYP method in the 6-31g* basis. This mutual agreement between the molecular fragments of (I), (II) and other 4-substituted N-methyl-N-nitroanilines supports the fact that ring substituents do not influence spectral and electric properties of these compounds [12]. The nitroamino group is polar, and the interaction of the N–O dipoles plays a role in the crystal structure, however, the shortest intermolecular N···O distances (3.10 Å) are longer than those predicted from the van der Waals radii of the interacting atoms.

Atomic coordinates are listed in Table 2, whereas bond lengths and angles are listed in Table 3. The magnitude of the torsion angles, bond length and valence angles (Table 1) testify to the absence of symmetry elements in molecule (I). Closeness of torsion angles C7–N1–N2–O1 and C1–N1–N2–O2 to 180° and C1–N1–N2–O1 and C7–N1–N2–O2 to 0°, the largest deviation being 7.4(4)° for C7–N1–N2–O2 in molecule (I), testify that the molecular fragments formed by these atoms stay in plane. This is also the case for the 4-substituted N-methyl-N-nitroaniline [6].

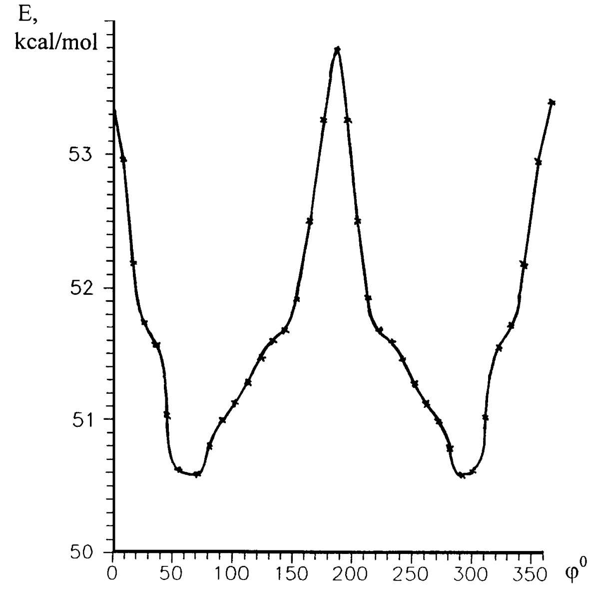


Figure 2. Potential energy (E, kcal/mol) of the 3-chloro-N-methyl-N-nitroaniline molecule as a function of the rotation angle (φ°) of the $N(CH_3)NO_2$ group around the N(1)–C(1) bond relative to the benzene ring.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for compound I.

	x	y	z	$U_{(eq)}$
Cl	0.2193(2)	0.6930(3)	0.3854(6)	0.0556(2)
O(1)	0.6673(6)	0.9530(1)	0.4599(15)	0.0583(6)
O(2)	0.4775(7)	1.0643(1)	0.4216(2)	0.0699(7)
N(1)	0.3624(6)	0.9728(1)	0.2997(2)	0.0440(5)
N(2)	0.5092(6)	0.9971(1)	0.3984(2)	0.0450(5)
C(1)	0.4103(6)	0.8966(1)	0.2635(2)	0.0378(5)
C(2)	0.3038(6)	0.8390(1)	0.3356(2)	0.0379(5)
C(3)	0.3483(7)	0.7663(1)	0.2963(2)	0.0407(6)
C(4)	0.4895(8)	0.7512(2)	0.1883(2)	0.0506(6)
C(5)	0.5845(8)	0.8095(2)	0.1183(2)	0.0541(7)
C(6)	0.5457(8)	0.8829(2)	0.1547(2)	0.0475(6)
C(7)	0.2161(9)	1.0286(1)	0.2219(2)	0.0551(7)

Compounds (I) and (II) are different only in the positions of the substituents in the aromatic ring. The change of valence angles in (I) in comparison with (II): N2–N1–C1 (119.4(2)° > 118.0(2)°), N2–N1–C7 (117.6° < 118.8(3)°) and C1–N1–C7 (121.9(2)° < 123.3(3)°) is noticeable. Position of the substituent is important in this case. At the same time, change of the substituent to the *para* position produces very small changes in the valence angles. For example, the replacement of the NO_2 group [6] by Cl [18] does not lead to notable changes: N2–N1–C1: 118.8(2)° ≈ 118.4(3)°; N2–N1–C7: 119.1(4)° ≈118.8(3)° and C1–N1–C7: 121.9(2)° ≈122.0(2)°.

Table 4 presents the experimental values of *DM* and *MKC* for compounds I, II and N-methyl-N-nitroaniline (III), together with the corresponding values calculated by the vector (*DM*) and tensor (*MKC*) addition schemes using parameters obtained for the crystallographic structure. The similarity between the experimental values of *DM* and *MKC* that were measured in benzene solutions and *DM* and *MKC* calculated by the addition schemes indicates that compound (I) maintains its molecular structure in solution.

In compounds II and III the rotation of molecular fragments around C1–N1, N1–N2 and N1–C7 bonds has no influence on *DM*, but it changes components of molecular polarizability tensor determining *MKC* (except for N1–C7 bond). The rotation of aromatic ring around C1–N1 bond has an influence on *DM*, so on *MKC* in the molecule of the compound I. In response to strong interaction of the nitro group with nitrogen atom of the amino group, leading to shortening N1–N2 bond and increasing of double character of the bond [20], the free rotation the nitro group around N1–N2 bond does not take place in the compounds I–III molecules [20]. Therefore, the calculation of *MKC* of compounds I–III was carried out for different angles of rotation of aromatic ring around N1–C1 bond (the rotation angle θ). Theoretical value of *MKC* for the compound I falls in the range between $-193\cdot10^{-12}$ ($\theta = 0°$) and $-23\cdot10^{-12}$ ($\theta =$

180°), and theoretical value of *DM* falls in the range between 5.36 D ($\theta = 0°$) and 3.08 D ($\theta = 180°$). The experimental values of *MKC* and *DM* of the compound I (Table 4) are most close to the theoretical ones at $\theta = 60°$ (Fig. 3).

Comparison of the experimental (Table 4) and quantum-mechanically calculated values of *DM* and *MKC* (Table 5) indicate the importance of electron correlation effects. The best agreement for compound (I) is achieved with the MP2 method. Compounds (II) and (III) are better described by the B3LYP density functional. The higher level MP2 and B3LYP approaches outperform the mean-field HF method. Quantum chemical calculations predict a large positive charge on the N(2) atom of molecules (I), (II) and (III) as well as large negative charges on all adjacent atoms. The Mulliken charges computed by MP2/3-21g*, HF/6-31g* and B3LYP/6-31g* with full geometry optimization are presented in Table 6. Analysis of the charge distribution on atoms N(1), N(2), O(1), O(2), C(1) and C(7) of compounds (I), (II) and (III) in comparison with the charges in N,N-dimethylnitroamine, compound (IV), Table 7 shows that the aromatic ring influences the NNO_2 group. In the sequence (IV)–(III)–(II)–(I) the absolute magnitude of the charge on the N(1) atom increases, while the magnitude of the charge on the oxygens decreases. For example, the changes according to the B3-LYP/6-31g* data are $-0.238007 \rightarrow -0.375733 \rightarrow -0.377768 \rightarrow -0.379531$ for the nitrogen and $-0.443930 \rightarrow -0.422483 \rightarrow -0.420202 \rightarrow -0.418037$ for the oxygen. Replacement of the CH_3 group in the $(CH_3)_2NNO_2$ molecule by the aromatic ring changes the sign of the charge on the carbon atom directly connected to N(1). For example, according to the MP2/3-21g* data, the charge changes from –0.344572 to +0.284417. At the same time, the charge on this C(1) atom remains practically unchanged when substituents are added to the aromatic ring. For the MP2/3-21g* data the change is $0.289108 \approx 0.292498 \approx 0.293020$.

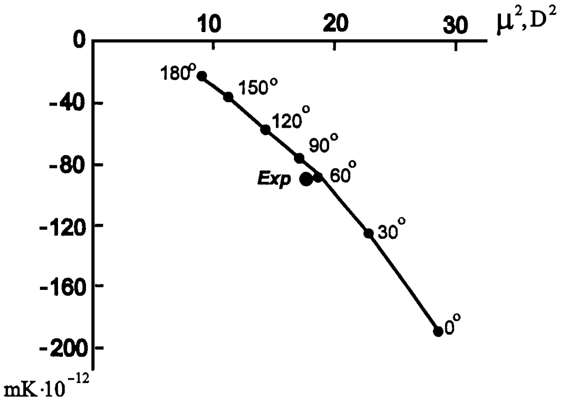


Figure 3. Molar Kerr constant ($mK \cdot 10^{-12}$) and dipole moment squared (μ^2, D^2) as a function of the rotation angle of aromatic ring around N1–C1 bond for compound I.

Table 3. Bond lengths [Å], bond angles [°] and torsion angles [°] for compound I.

Cl	C(3)	1.732(2)	N(2)	N(1)	C(1)	119.4(2)	C(1)	N(1)	N(2)	O(1)	–4.0(4)
O(1)	N(2)	1.228(3)	N(2)	N(1)	C(7)	117.6(2)	C(7)	N(1)	N(2)	O(1)	–172.1(3)
O(2)	N(2)	1.233(3)	C(1)	N(1)	C(7)	121.9(2)	C(1)	N(1)	N(2)	O(2)	175.5(3)
N(1)	N(2)	1.338(3)	O(1)	N(2)	O(2)	123.7(2)	C(7)	N(1)	N(2)	O(2)	7.4(4)
N(1)	C(2)	1.433(3)	O(1)	N(2)	N(1)	119.6(2)	N(2)	N(1)	C(1)	C(6)	–122.0(3)
N(1)	C(7)	1.454(3)	O(2)	N(2)	N(1)	116.7(2)	C(7)	N(1)	C(1)	C(6)	45.5(4)
C(1)	C(6)	1.372(3)	C(6)	C(1)	C(2)	121.6(2)	N(2)	N(1)	C(1)	C(2)	61.4(3)
C(1)	C(2)	1.381(3)	C(6)	C(1)	N(1)	118.7(2)	C(7)	N(1)	C(1)	C(2)	–131.1(3)
C(2)	C(3)	1.384(3)	C(2)	C(1)	N(1)	119.6(2)	C(6)	C(1)	C(2)	C(3)	2.2(4)
C(3)	C(4)	1.377(4)	C(1)	C(2)	C(3)	117.8(2)	N(1)	C(1)	C(2)	C(3)	178.7(2)
C(4)	C(5)	1.363(4)	C(4)	C(3)	C(2)	121.6(2)	C(1)	C(2)	C(3)	C(4)	–0.9(4)
C(5)	C(6)	1.382(4)	C(2)	C(3)	Cl	118.7(2)	C(1)	C(2)	C(3)	Cl	179.6(2)
			C(5)	C(4)	C(3)	119.0(2)	C(2)	C(3)	C(4)	C(5)	–0.6(4)
			C(4)	C(5)	C(6)	121.1(2)	Cl	C(3)	C(4)	C(5)	178.9(2)
			C(1)	C(6)	C(5)	118.9(2)	C(3)	C(4)	C(5)	C(6)	1.0(5)
							C(2)	C(1)	C(6)	C(5)	–1.9(4)
							N(1)	C(1)	C(6)	C(5)	–178.4(3)
							C(4)	C(5)	C(6)	C(1)	0.3(5)

Table 4. Experimental (μ_{exp}, D) and calculated by the vector addition scheme (μ_{calc}, D) dipole moments and experimental (mK_{exp}) and calculated by tensor addition scheme (mK_{calc}) molar Kerr constant for 3-chloro-N-methyl-N-nitroaniline (I), 4-chloro-N-methyl-N-nitroaniline (II) and N-methyl-N-nitroaniline (III).

Compound	α_H α_L	β_H β_L	γ_L	δ_L	$P_{2\infty}$, cm^2	P_D, cm^2	μ_{exp}, D	μ_{calc}, D	$sK \cdot 10^{14}$	$mK_{exp} \cdot 10^{12}$	$mK_{calc} \cdot 10^{12}$
I	$\frac{10.80}{4.532}$	$\frac{1.046}{0.441}$	0.0394	–11.59	387.5	49.80	4.06	4.34	47.04	–87.7	–95.3
II	$\frac{8.170}{3.420}$	$\frac{0.513}{0.612}$	0.0333	–19.67	312.1	49.80	3.58	3.80	–173.6	–324	–375
III	$\frac{11.89}{6.165}$	$\frac{0.354}{0.304}$	0.0964	28.9	429.1	44.51	4.34	4.45	161.1	244.8	258

Table 5. Quantum-chemically calculated values of dipole moments (μ, D) and molar Kerr constants ($mK \cdot 10^{12}$) of the compounds investigated.

Compound[*)]	Calculating method	μ_x, D	μ_y, D	μ_z, D	b_{xx}, Å^3	b_{xy}, Å^3	b_{yy}, Å^3	b_{xz}, Å^3	b_{yz}, Å^3	b_{zz}, Å^3	μ, D	$mK \cdot 10^{12}$
I	MP2/3-21g*	–0.114	4.284	1.266	19.533	0.612	14.561	0.767	–0.981	6.836	4.468	–26.21
	HF/6-31g*	–1.647	2.515	3.612	18.940	0.446	13.826	1.047	–0.558	8.901	4.700	–1253
	B3LYP/6-31g*	–0.620	4.530	1.501	21.690	0.535	16.120	0.729	–0.944	8.286	4.813	–181.9
II	MP2/3-21g*	–0.349	2.864	1.339	21.529	0.704	12.692	0.368	–1.640	7.066	3.180	–481.5
	HF/6-31g*	–1.338	3.639	1.416	20.646	1.112	9.558	0.222	–1.449	11.867	4.128	–1239
	B3LYP/6-31g*	–0.973	3.095	1.545	19.188	0.625	14.043	0.352	–1.546	8.481	3.594	–609.8
III	MP2/3-21g*	–2.613	2.615	1.208	17.278	0.730	12.233	0.580	–1.698	6.563	3.889	130.9
	HF/6-31g*	–3.643	3.398	1.193	16.597	1.190	8.928	0.254	–1.467	11.372	5.123	–414.6
	B3LYP/6-31g*	–3.108	2.832	1.409	19.188	0.652	13.510	0.558	–1.599	7.925	4.434	285.6

[*)] Compound numbers are the same as in Table 4.

Table 6. Total atomic Mulliken charges for compounds I, II and III calculated by MP2/3-21g*, HF/6-31g* and B3LYP/6-31g* methods.

Atom	MP2/3-21g*			HF/6-31g*			B3LYP/6-31g*		
	I	II	III	I	II	III	I	II	III
Cl	0.027168	0.025003	–	0.013758	0.013156	–	–0.008616	–0.010752	–
C(1)	0.297023	0.282977	0.284417	0.259919	0.253826	0.256884	0.293020	0.292498	0.289108
C(2)	–0.146423	–0.147986	–0.160629	–0.161111	–0.170735	–0.180152	–0.109792	–0.106368	–0.111113
C(3)	–0.195217	–0.181677	–0.193758	–0.171958	–0.190085	–0.208768	–0.083493	–0.145856	–0.148135
C(4)	–0.184665	–0.147295	–0.195494	–0.204202	–0.127507	–0.188168	–0.119481	–0.057473	–0.118655
C(5)	–0.148826	–0.185687	–0.197622	–0.145388	–0.189714	–0.208422	–0.139381	–0.142374	–0.140834
C(6)	–0.183252	–0.180592	–0.192426	–0.171286	–0.167694	–0.176361	–0.144888	–0.143636	–0.144955
N(1)	–0.538888	–0.540906	–0.537581	–0.541151	–0.544073	–0.542177	–0.377768	–0.379531	–0.375753
C(7)	–0.341829	–0.342532	–0.339228	–0.274521	–0.274436	–0.272326	–0.312001	–0.312533	–0.310071
N(2)	0.471253	0.470642	0.469212	0.848528	0.848456	0.847480	0.641591	0.640346	0.638883
O(1)	–0.312270	–0.314207	–0.317162	–0.500979	–0.502392	–0.504681	–0.418037	–0.420202	–0.422483
O(2)	–0.308948	–0.309655	–0.315079	–0.507000	–0.508112	–0.512592	–0.416067	–0.416591	–0.421893
H(2)	0.247044	0.231610	0.207947	–0.257044	0.237270	0.221432	0.177735	0.165118	0.154725
H(3)	–	0.233373	0.208406	–	0.240960	0.213781	–	0.151070	0.139678
H(4)	0.231526	–	0.221255	0.239222	–	–0.226632	0.161767	–	0.138122
H(5)	0.217095	0.235435	0.204867	0.225087	0.241007	0.212676	0.150143	0.163653	0.141883
H(6)	0.215173	0.218058	0.206407	0.229572	0.231950	0.213780	0.147817	0.165840	0.141433
H(7a)	0.213707	0.213215	0.211586	0.197941	0.197678	0.196137	0.177783	0.177282	0.175649
H(7b)	0.203993	0.203886	0.202106	0.190379	0.190361	0.188510	0.177910	0.177758	0.175944
H(7c)	0.236337	0.236319	0.232765	0.221000	0.220083	0.217013	0.210760	0.201752	0.198467

Table 7. Total atomic Mulliken charges and dipole moments (μ, D) for N,N-dimethylnitramine calculated by MP2/3-21g*, MP2/6-31g*, HF/6-31g* and B3LYP/6-31g* methods.

Atom	MP2/3-21g*	MP2/6-31g*	HF/6-31g*	B3LYP/6-31g*
N(1)	–0.423673	–0.312661	–0.454501	–0.238007
N(2)	0.466647	0.606958	0.843622	0.635426
C(1)	–0.344572	–0.350133	–0.300931	–0.328299
C(2)	–0.322091	–0.324563	–0.269780	–0.300758
O(1)	–0.337010	–0.416927	–0.528678	–0.443930
O(2)	–0.327535	–0.406001	–0.517349	–0.432900
H(1)	0.197613	0.182861	0.184117	0.164812
H(2)	0.218619	0.203657	0.207608	0.189040
H(3)	0.218619	0.203657	0.207608	0.189040
H(4)	0.249116	0.240746	0.253861	0.223124
H(5)	0.202133	0.186202	0.187212	0.171226
H(6)	0.202133	0.186202	0.187212	0.171226
μ_{X}, D	–0.0170	–0.0327	–0.0135	–0.0435
μ_{Y}, D	4.2503	4.6518	5.0678	4.6794
μ_{Z}, D	0.0000	0.0000	0.0000	0.0000
μ, D	4.2504	4.6519	5.0678	4.6796

The above results testify that *n*-electrons of the N atom of the imide are more strongly conjugated with the π-electrons of the NO_2 group than of the aromatic ring. NNO_2 is formed as a *distinct functional group*. The NNO_2 group is insensitive to various influences, including the replacement of the CH_3 group by the C_6H_5 group and the introduction of various substituents to the aromatic ring.

Acknowledgment

We would like to thank Professor A. Koll, University of Wroclaw, Poland, for participation in discussion of this paper.

REFERENCES

1. Williams D.H.L, in: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives, Vol. 1, S. Patai (Ed), J. Wiley & Sons, Chichester 1982.
2. Mialocq J.C. and Stephenson J.C., *Chem. Phys.,* **106**, 281 (1986).
3. Stolevik R. and Rodemacher P*., Acta Chem. Scand.*, **23,** 672 (1969).
4. Filhol A., *Acta Cryst*., **B36**, 575 (1980).
5. Cady H.H*., Acta Cryst*., **23**, 601 (1967).
6. Anulewicz R., Krygowski T.M., Gawinecki R. and Rasala D., *J. Phys. Org. Chem*., **6**, 257 (1993).
7. Ejsmont K., Kyziol J., Daszkiewicz Z. and Bujak M*., Acta Cryst*., **C54**, 672 (1998).
8. Vedasankari K., Murthy G.S. and Udupa M.R., *Acta Cryst*., **C46**, 1709 (1990).
9. Holden J.R. and Dickinson C., *J. Phys. Chem*., **73,** 1199 (1969).

10. Heuer L., Schmutzler R. and Schomburg D*, Z. Naturforsch*., **B44**, 911 (1989).
11. Meiyappan M., Bagieu-Beucher M. and Le Fur Y., *Z. Krystallogr. - New Crystal Structures*, **214**, 201 (1999).
12. Zaleski J., Daszkiewicz Z. and Kyziol J*., Acta Cryst*., **C55**, 691 (1999).
13. Zaleski J., Daszkiewicz Z. and Kyziol J*., Acta Cryst*., **C55**, 1292 (1999).
14. Butcher R.J., Gilardi R.D. and George C*., J. Chem. Cryst.,* **26**, 381 (1996).
15. Growenlock B.G., Pfab J. and Young V.M*., J. Chem. Soc. Perkin Trans. 2*., 915 (1997).
16. White W.N., Wolfarth E.F, Klink J.R., Kindig J., Hathway Ch. and Lazdins D., *J. Org. Chem*., **26**, 4124 (1961).
17. Cober-Hermandes P. and Habraken C.L., *J. Org. Chem*., **36**, 3084 (1971).
18. Deady L.M. and Korytsky O.L., *Austr. J. Chem*., **36**, 1159 (1983).
19. Baushin M.A., Golod E.I. and Gidaspov B.V., *Zh. Org. Khim*., **13**, 11 (1977).
20. Daszkiewicz Z., Nowakowska E., Prezhdo V.V. and Kyziol J.B., *Polish J. Chem*., **26**, 1437 (1995).
21. Daszkiewicz Z., Nowakowska M. and Kyziol J.B., *Tetrahedron*, **54**, 5991 (1998).
22. Vereschagin A.N., Nasyrov D.M., Vulfson S.G., Ivshin V.P. and Komelin M.C., *Izv. AN SSSR, Khimia*, No 11, 2261 (1982).
23. Prezhdo V.V., Bykova A.S., Daszkiewicz Z., Halas M., Iwaszkiewicz-Kostka M., Prezhdo O.V., Kyziol J. and Blaszczak Z., *Zh. Obsch. Khim.*, (in press).
24. Vereschagin A.N., Polarizability of Molecules, Nauka, Moscow 1980 (in Rus.).
25. Daszkiewicz Z., Domanski A. and Kyziol J.B., *Org. Prep. Proced*., **26**, 337 (1994).
26. Khashchina M.V., Tyurin S.A. and Prezhdo V.V., Electro-optical Effects in Technics, Vyscha Shkola, Kharkov 1989 (in Rus.).
27. Minkin V.I., Osipov O.A. and Zhdanov Yu.A., Dipole Moments in Organic Chemistry, Chemistry, Leningrad 1968 (in Rus.).
28. Frisch M.J., Trucks G.W., et al., Gaussian, Inc., Pittsburgh PA, 1998.
29. Kuma KM-4 User Guide. Version KM-4b8. Kuma Diffraction. Wrocław, Poland 1997.
30. Sheldrick G.M., SHELXS-86. Program for Solution of Crystal Structures, University of Goettingen, Germany (1990).
31. Sheldrick G.M., SHELXL-93. Program for the Refinement of Crystal Structure, University of Goettingen, Germany (1993).
32. Ogle C.A., Van der Kooi K.A., Mendenhall G.D. and Lorprayoon V., *J. Am. Chem. Soc*., **105**, 5114 (1982).
33. Cameron A.F., Hair N.J. and Morris D.G., *J. Chem. Soc. Perkin Trans. 2*, 1071 (1972).