# CRYSTAL AND MOLECULAR STRUCTURE OF N-METHYL-N-NITROANILINE

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Nitroamines and related N-nitro compounds attract the attention of researchers in view of their applications in rocket fuel and as explosives [1]. The crystal and molecular structure of N,N-dimethylnitroamine and some cyclic and aliphatic nitroamines was studied in [2, 3]. In the series of aromatic N-nitroamines, the compounds which were studied are tetryl (compound I) [4], 4-nitro-N-methyl-N-nitroaniline (II) [5], 4-chloro-N-methyl-N-nitroaniline (III) [6], 2,4-N-trinitro-anilinoacetic acid (IV) [7], N-(β,β,β-trifluoroethyl)-N,2,4,6-tetranitroaniline (V) [8], bis(2,6-dimethoxyphenyl)nitroamine (VI) solvated by dichloromethane [9], and a number of compounds in which the nitroamino group is bonded to the pyridine nucleus: 4-(nitroamino)pyridinium nitrate (VII) [10], 1-methyl-4-(N-methylnitroamino)pyridinium bromide (VIII) [11], 4-(N-methylnitroamino)pyridinium 1-oxide (IX) [12], and N,N′-dinitro-N,N′-bis(2-pyridyl)-1,4-diaminocubane (X) [13].

Interest in N-methyl-N-nitroaniline arises from the ability of these compounds to undergo nitroamine rearrangement at elevated temperatures or in acid media [14], or in conditions of photolysis [15]. Molecular structure investigation of secondary arylnitroamines permits one to elucidate the mechanism of the nitroamine rearrangement. Compound (XI) containing no substituents in the aromatic ring is the first to be studied in this series:

$$CH_3-N-NO_2$$

XI
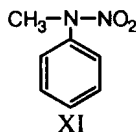
Experimental. Compound (XI) was prepared by the reaction of *n*-butylnitrate with the Grignard reagent obtained *in situ* from N-methylaniline and ethylmagnesium bromide, as described in [16]. The product was recrystallized from *n*-hexane. Single crystals for X-ray diffraction analysis were obtained by slowly cooling a methylene chloride solution of XI; the single crystal is a parallelepiped sized 0.15×0.15×0.25 mm. The parameters of the orthorhombic unit cell were determined on a Kuma KM-4 diffractometer (MoK_α radiation, λ = 1.5418 Å): $a = 8.822(2)$, $b = 10.939(3)$, $c = 15.946(2)$ Å, space group *Pbca*, $M = 151.15$, $V = 1538.9(6)$ Å^3, $Z = 8$. The independent part of the cell contains one molecule XI, i.e., 11 nonhydrogen atoms and 8 hydrogen atoms.

The three-dimensional set of 762 unique observed reflections with $I \geq 2\sigma(I)$ were obtained on a Kuma KM-4 diffractometer at 293(2) K (θ/2θ scan mode, 2θ ≤ 160°). The programs of the Kuma KM-4 User Guide were used for primary processing of the intensities and to obtain a set of structural factors [17]. To prepare the data for crystal structure determination we employed the SHELXS-86 program [18]. All nonhydrogen atoms were localized in *E*-synthesis. Their positional and thermal parameters were refined (SHELXL-93 [19]) isotropically and then anisotropically to $R = 0.0620$. The coordinates and the isotropic thermal parameters of the H atoms were calculated by the least-squares procedure using the riding model [19]. Then the positions of the nonhydrogen atoms were refined anisotropically. The wR_2 and S values were 0.1012 and 1.075, respectively. The final R index was 0.0368. The atomic coordinates of molecule XI and the equivalent isotropic displacement parameters are presented in Table 1. The *ab initio* quantum-chemical calculations were performed with GAUSSIAN-94 software [20]. The potential energy (*E*, kcal/mole) from the rotation angle of the N-methyl-N-nitroamino

TABLE 1. Atomic Coordinates (x, y, z) and Equivalent Isotropic Displacement Parameters (U_{eq})

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
O(1)	0.1835(2)	0.58991(15)	0.11037(10)	0.0769(6)	H(2)	0.093	0.922	0.077	0.078
O(2)	0.1727(2)	0.5455(2)	−0.02208(11)	0.0818(7)	H(3)	−0.013	1.026	0.189	0.096
N(1)	0.0436(3)	0.7028(2)	0.02585(10)	0.0581(6)	H(4)	−0.182	0.930	0.275	0.096
N(2)	0.1369(3)	0.6075(2)	0.03890(12)	0.05879(6)	H(5)	−0.249	0.730	0.252	0.096
C(1)	−0.0180(3)	0.7642(2)	0.09774(12)	0.0515(6)	H(6)	−0.147	0.625	0.139	0.078
C(2)	0.0234(2)	0.8837(2)	0.11166(15)	0.0648(7)	H(7A)	−0.054	0.804	−0.062	0.121
C(3)	−0.0393(4)	0.9453(3)	0.1785(2)	0.0799(8)	H(7B)	−0.098	0.665	−0.067	0.121
C(4)	−0.1401(4)	0.8880(3)	0.23015(15)	0.0803(9)	H(7C)	0.062	0.709	−0.098	0.121
C(5)	−0.1805(4)	0.7684(3)	0.21592(14)	0.0769(9)					
C(6)	−0.1197(3)	0.7060(2)	0.14915(13)	0.0653(7)					
C(7)	−0.0168(4)	0.7216(3)	−0.05741(13)	0.0805(9)					

group around the N(1)–C(1) bond was calculated by the AM1 method, and optimal structure calculations were carried out by the *ab initio* method using the GAUSSIAN-94 program with the B3LYP/6-31G** basis.

   Results and discussion. Figure 1 presents the crystal structure of molecule XI. The carbon framework of the aromatic ring is planar with deviations of up to 0.002(2) Å from planarity (Table 2). For the N(1) atom, the deviation is 0.050(3) Å, whereas in N,N-dimethylaniline this atom lies in the plane of the aromatic ring [21]. This supports the assumption about weaker interaction between the N(1) atom and the aromatic ring of molecule XI [22]. Participation of the N(1) atom in a stronger interaction with the nitro group is supported by the fact that the nitroamino group in XI is planar. The bond lengths and angles in XI agree with the corresponding values for N,N-dimethylnitroamine $(CH_3)_2NNO_2$ (XII) [1]; the differences do not exceed 0.025 Å and 0.6°, respectively. In N-nitroamines, the N–N bond is considerably longer (from 1.346 in II to 1.408 Å in V) than in hyponitrous acid esters and azo compounds (1.25 Å [23]) but shorter than the N–N single bond (1.48 Å [24]). This indicates that a pair of π-electrons from the sextet occupying the set of four-center π-orbitals migrates to the antibonding orbital.

   In arylnitroamines with two nitro groups in the *ortho*-positions, the NNO_2 group is almost perpendicular to the plane of the aromatic ring [4]. Although there are no bulky substituents in the *ortho*-positions of XI or its 4-substituted derivatives [22], e.g., in tetryl, the value of the N(2)–N(1)–C(1)–C(2) dihedral angle (114.9(2)°) indicates that there are steric interactions between the $(CH_3)NNO_2$ group and the aromatic ring and that there is no conjugation between the two π-electronic systems. This may be inferred by comparing the interatomic distances in crystal (R_{cr}) and the sum of van der Waals radii (ΣR) [25]. For example, R_{cr} = 2.873(2) Å, ΣR = 1.52 + 1.80 = 3.32 Å for O(1)···C(6); R_{cr} = 3.005(3) Å, ΣR = 2·1.80 = 3.60 Å for C(7)···C(2); R_{cr} = 2.683(2) Å, ΣR = 1.80 + 1.52 = 3.32 Å for C(1)···O(1). This repulsion between the heavy atoms of the $(CH_3)NNO_2$ group and the aromatic ring results in nonplanarity of molecule XI as well as of other
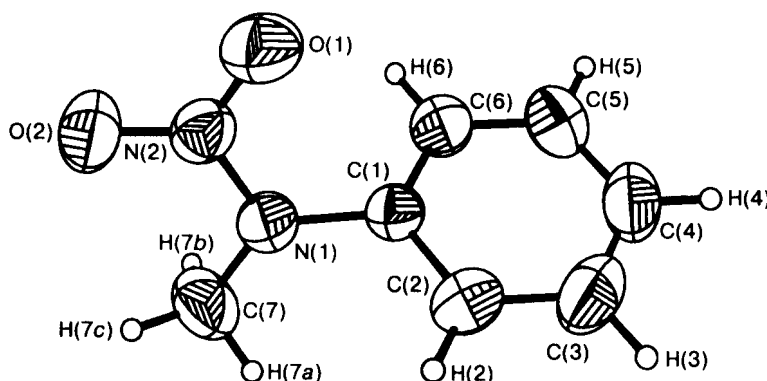
Fig. 1. Molecular structure of compound XI (thermal ellipsoids drawn at 50% probability).

TABLE 2. Deviations of Atoms from the Mean Square Plane, Å

| Atom	Deviation	Atom	Deviation
C(1)*	0.000(2)	N(1)	0.050(3)
C(2)*	–0.002(2)	C(7)	1.287(5)
C(3)*	0.002(2)	N(2)	–1.012(4)
C(4)*	0.000(2)	O(1)	–2.044(4)
C(5)*	–0.002(2)	O(2)	–0.893(5)
C(6)*	0.002(2)		

*Atoms of the plane.

molecules with the N-methylnitroamino group I-VI, VIII-X). The 4-nitroamine-1H-pyridine cation in molecule VIII with the $HNNO_2$ group is planar [10], since there is less steric interaction in the absence of a nitrogen-bonded CH_3 group.

The value of the dihedral angle N(2)–N(1)–C(1)–C(6) (−67.5(3)°) in XI is close to the value (−65.6(4)°) in II [6]. This agrees with the minimum on the curve of the dependence of the potential energy on the rotation angle of the NNO_2 group around the N(1)–C(1) bond relative to the plane of the benzene ring (70°) (Fig. 2), for which the calculated dipole moment of XI (4.416 D) is close to the experimental value (4.34 D) [22]. This mutual arrangement of molecular fragments in XI and its 4-substituted analogs explains the fact that substituents in the aromatic ring do not affect the spectral and optoelectronic characteristics of these compounds [22].

The nitroamino group is polar. According to quantum-chemical calculations, the N(2) atom bears a large positive charge and there are negative charges on all neighboring atoms (B3LYP/6-31G** method with full geometry optimization, Table 3). Dipole interaction of N–O groups also affects the crystal structure, but the shortest intermolecular distance N···O (3.08 Å) is close to the sum of the van der Waals radii of the reactant atoms.

The good agreement between the experimental and calculated values of the bond and dihedral angles (Table 4) and bond lengths (Table 5) merely points to a slight deformation of the molecule in the crystal field. The values of the dihedral angles C(7)–N(1)–N(2)–O(1) and C(1)–N(1)–N(2)–O(2) are close to 180°, and the angles C(1)–N(1)–N(2)–O(1) and C(7)–N(1)–N(2)–O(2) are close to zero, showing that the molecular fragments involving these atoms are almost coplanar.

It is interesting to compare the parameters of XI with those of XII obtained in [3, 26]. Note that the N(1)–N(2) bond length is constant (1.341 Å ≈ 1.345 Å), and the C(1)–N(1) bond length is only slightly greater than the C–N bond length in XII (1.435 Å < 1.460 Å); the CNC and CNN angles slightly decrease from XII to XI: 125° >121.8° and 120° >118.1 and 118.8°, respectively. Analysis of charge distribution on the N(1), N(2), O(1), C(1), and C(7) atoms shows that
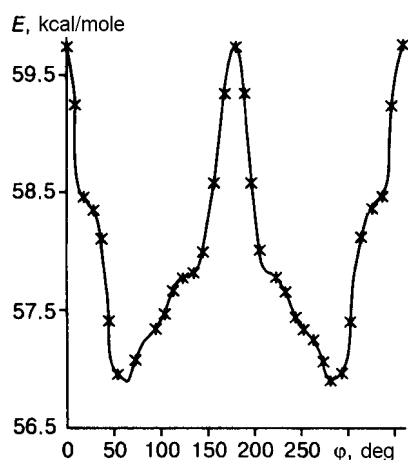
Fig. 2. Dependence of the potential energy (*E*, kcal/mole) on the rotation angle of the NO_2 group around the N(1)–N(2) bond relative to the plane of the benzene ring (φ, deg) in XI.

TABLE 3. Mulliken Charges on Atoms in Molecule XI

Atom	Charge	Atom	Charge
C(3)	–0.101	O(1)	–0.423
C(2)	–0.051	O(2)	–0.423
C(1)	0.261	H(1)	0.095
C(6)	0.089	H(2)	0.096
C(5)	–0.098	H(5)	0.098
C(4)	–0.075	H(6)	0.110
N(1)	–0.392	H(7A)	0.136
C(7)	–0.166	H(7B)	0.132
H(4)	0.093	H(7C)	0.156
N(2)	0.640		

TABLE 4. Selected Bond and Torsion Angles (α, deg) in XI

Angle	α_{exp}	α_{calc}	Angle	α_{exp}	α_{calc}
N(2)–N(1)–C(1)	118.1(2)	119.0	C(3)–C(4)–C(5)	120.4(3)	119.7
N(2)–N(1)–C(7)	118.6(2)	115.4	C(6)–C(5)–C(4)	120.0(3)	120.2
C(1)–N(1)–C(7)	121.8(2)	122.0	C(1)–C(6)–C(5)	119.2(2)	119.9
O(1)–N(2)–O(2)	124.3(2)	126.1	C(1)–N(1)–N(2)–O(1)	–11.3(3)	–14.1
O(1)–N(2)–N(1)	118.1(2)	117.9	C(7)–N(1)–N(2)–O(1)	–177.6(2)	–173.4
O(2)–N(2)–N(1)	117.6(2)	115.9	C(1)–N(1)–N(2)–O(2)	170.4(2)	167.4
C(6)–C(1)–C(2)	121.2(2)	120.1	C(7)–N(1)–N(2)–O(2)	4.1(3)	8.1
C(6)–C(1)–N(1)	120.5(2)	120.3	N(2)–N(1)–C(1)–C(6)	–67.5(3)	–63.6
C(2)–C(1)–N(1)	118.2(2)	119.6	C(7)–N(1)–C(1)–C(6)	98.3(3)	102.6
C(1)–C(2)–C(3)	118.9(3)	119.6	N(2)–N(1)–C(1)–C(2)	114.9(2)	119.4
C(4)–C(3)–C(2)	120.3(3)	120.5	C(7)–N(1)–C(1)–C(2)	–79.3(3)	–74.4

TABLE 5. Selected Bond Lengths (L, Å) in Molecule XI

Bond	L_{exp}	L_{calc}	Bond	L_{exp}	L_{calc}
O(1)–N(2)	1.227(2)	1.23	C(1)–C(6)	1.372(3)	1.40
O(2)–N(2)	1.227(2)	1.23	C(1)–C(2)	1.375(3)	1.39
N(1)–N(2)	1.345(3)	1.39	C(2)–C(3)	1.376(4)	1.39
N(1)–C(1)	1.435(3)	1.43	C(3)–C(4)	1.364(4)	1.40
N(1)–C(7)	1.445(3)	1.46	C(4)–C(5)	1.374(4)	1.39
			C(5)–C(6)	1.374(3)	1.39

the aromatic ring has a certain effect on the NNO_2 group, leading to increased values of charges on passing from XI to XII on the atoms N(1) (–0.182 vs –0.362), N(2) (0.452 → 0.640), and O (–0.226 → –0.426) and to a decreased charge on C(7) (–0.426 → –0.1663). The dipole moment also slightly decreases (from 4.61 D to 4.41 D). Analysis of these data confirms the above conclusion that the bonding between the *n*-electrons of the imide nitrogen and the π-electrons of the nitro group is greater compared to the same bonding with the aromatic ring, forming NNO_2 as a functional group, which is not very sensitive to various kinds of treatment including the substitution of the CH_3 group by C_6H_5.

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