

CRYSTAL AND MOLECULAR STRUCTURE OF 1-PHENYL-2-NITROGUANIDINE

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The molecular structure of 1-phenyl-2-nitroguanidine is nonplanar, but contains two almost planar fragments: nitroguanyl and phenyl groups. Unlike previously studied nitroguanidines, in 1-phenyl-2-nitroguanidine, the nitro group is turned to the secondary amino group. However, the structural parameters of the nitroguanyl group are little different from those of nitroguanidine and its alkyl derivatives. In the benzene ring, the symmetry in the geometric parameters is not observed, which is explained by the intermolecular interaction with the neighboring molecule.

Keywords: nitrimines, nitroguanidine, single crystal X-ray diffraction study, molecular structure.

To date, structural data for nitroguanidine and more than a dozen of its derivatives have been published in the literature [1]. Nitroguanidine and its monosubstituted derivatives have a generally similar structure. The common features are the near-planar geometry of the nitroguanyl moiety stabilized by the intramolecular hydrogen bond and the delocalization of π electron density over the nitroguanyl moiety and, in some cases, also over the substituent [2]. Due to the redistribution of electron density, C–N, N–N, and N–O bond lengths are intermediate between the values typical of the respective single and double bonds, and the formally double C=NNO₂ bond is actually not only a double one, but, to the contrary, appears to be the longest C–N bond [1, 3-5]. Accordingly, the traditional structural formulas of nitroguanidine and its derivatives do not reflect their composition, at least in the crystalline state [6]. In all nitroguanidines with the known structural data, the nitro group is oriented towards the primary amino group, to the opposite side from the substituent of the secondary amino group.

This work considers the crystal and molecular structure of 1-phenyl-2-nitroguanidine (**I**) determined by X-ray methods.

Experimental. Compound **I** was synthesized using the technique described in [7]. Transparent needles suitable for the single crystal X-ray diffraction study were produced by recrystallization of the compound from ethanol.

The intensities of 1313 reflections (including 1238 independent ones) were measured on an automated KM-4 diffractometer (KUMA-diffraction) at 300(1) K (CuK α radiation, graphite monochromator, $\theta/2\theta$ variable rate scanning). The structure model was found by direct methods and refined by full-matrix LSM in the anisotropic approximation (isotropic for hydrogen atoms) using the SHELX-97 software [8]. Hydrogen atoms were located from the difference electron density synthesis, and their positions were further refined under conditions of rigid link with the main atom.

Crystals of compound **I** are monoclinic, space group $P2_1/n$, $a = 7.1079(8)$ Å, $b = 10.225(2)$ Å, $c = 11.945(2)$ Å, $\beta = 103.29(1)^\circ$, $V = 844.89(5)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.416$ g/cm³, $\mu_{\text{Cu}} = 0.92$ mm⁻¹, $M = 180.17$. Resulting values: $wR2 = 10.33$; $S = 1.55$ over all reflections and $R1 = 0.037$ over 1033 reflections with $|F| > 4\sigma_F$. Interatomic distances and bond angles for non-hydrogen atoms are listed in Table 1.

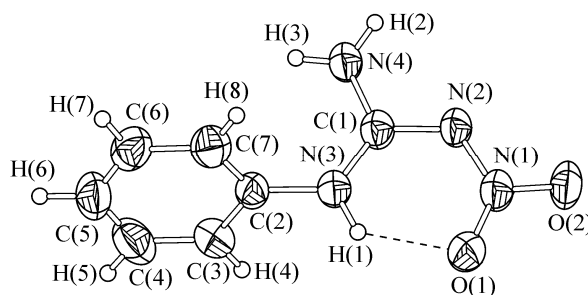
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TABLE 1. Bond Lengths d (Å) and Bond Angles ω (deg) in the Structure of Compound **I**

Bond	d	Bond	d	Bond	d
N(1)–N(2)	1.336(2)	C(2)–C(3)	1.372(2)	C(6)–C(7)	1.380(3)
N(2)–C(1)	1.360(2)	C(3)–C(4)	1.392(3)	C(7)–C(2)	1.380(2)
C(1)–N(3)	1.323(2)	C(4)–C(5)	1.361(3)	N(1)–O(1)	1.250(2)
C(1)–N(4)	1.321(2)	C(5)–C(6)	1.364(3)	N(1)–O(2)	1.231(2)
N(3)–C(2)	1.430(2)				
Angle	ω	Angle	ω	Angle	ω
N(1)–N(2)–C(1)	119.9(1)	N(3)–C(2)–C(7)	120.8(2)	C(6)–C(7)–C(2)	119.4(2)
N(2)–C(1)–N(3)	126.4(1)	C(2)–C(3)–C(4)	118.9(2)	C(7)–C(2)–C(3)	120.4(2)
N(2)–C(1)–N(4)	112.9(1)	C(3)–C(4)–C(5)	120.8(2)	N(2)–N(1)–O(1)	123.8(1)
N(3)–C(1)–N(4)	120.7(1)	C(4)–C(5)–C(6)	120.0(2)	N(2)–N(1)–O(2)	115.6(1)
C(1)–N(3)–C(2)	125.3(1)	C(5)–C(6)–C(7)	120.5(2)	O(1)–N(1)–O(2)	120.6(1)
N(3)–C(2)–C(3)	118.7(2)				

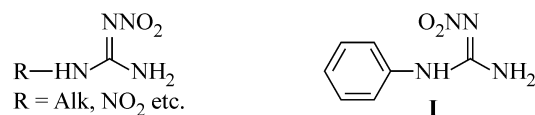
TABLE 2. Geometric Characteristics of Intermolecular NH...A Hydrogen Bonds in the Crystal Structure of Compound **I** (bond lengths in Å, angles in deg)

N–H	A	$d(\text{N–H})$	$d(\text{H...A})$	$\angle\text{NHA}$	$d(\text{N...A})$
N(3)–H(1)	O(1)	0.86	1.94	129	2.570(2)
N(4)–H(2)	N(2)*	0.86	2.13	174	2.989(2)

*N2: $(-x, -y+1, -z)$.**Fig. 1.** Molecular structure of compound **I**.

The CIF-file containing full information on the studied structure was deposited with CCDC under No. 626122, from where it can be obtained free on request at the following web-site: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. A general view of the molecular geometry of compound **I** is shown in Fig. 1. Attention is immediately directed to the fact that, as opposed to previously studied nitroguanidines, the nitro group in compound **I** is turned to the secondary amino group containing the substituent.



In general, the molecule of compound **I** is nonplanar, but contains two almost planar fragments: nitroguanidyl and phenyl groups. A deviation from the plane passing through C(1), N(1)–N(4), O(1), and O(2) atoms is 0.043(1) Å (mean square) and 0.064(1) Å (maximum).

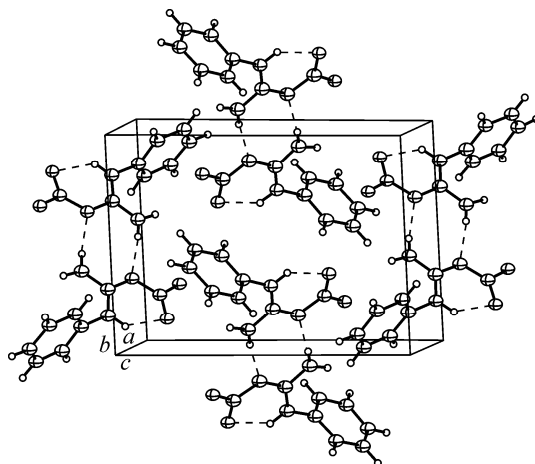


Fig. 2. Packing of molecules in the crystal of compound **I**. Intra- and intermolecular hydrogen bonds are denoted by dashed lines.

As in other nitrimines [1], the C–N, N–N, and N–O bonds in the nitroguanyl moiety of compound **I** have the lengths intermediate between the values typical of the respective single and double bonds (Table 1), which is indicative of the delocalization of *p* electron density. Formally, the double C(1)–N(2) bond is also the longest C–N bond in the nitroguanyl group.

The angle between the planes of nitroguanyl and phenyl groups is $64.30(5)^\circ$. This mutual orientation of two groups prevents their conjugation through the overlapping of π orbitals, which could occur with the general planar geometry of the molecule. The length of the N(3)–C(2) bond linking nitroguanyl and phenyl groups is $1.430(2)$ Å, which confirms the absence of through conjugation in the molecule. In turn, this explains why the mutual orientation of the nitro group and the substituent at the amino group does not affect the geometric parameters of the nitroguanyl moiety in the molecule of compound **I**. The value of the *ipso* C(7)–C(2)–C(3) angle, being a function of substituent electronegativity, is $120.4(2)^\circ$ and is in the middle of a range 113 – 125° observable for the molecules of other aromatic compounds [9], which is consistent with the electron-acceptor properties of the nitroguanyl moiety.

The average C–C bond length is $1.375(3)$ Å in the phenyl group, which is somewhat less than that in other aromatic compounds [1]; in nitrobenzene, e.g., this value is 1.390 Å [10]. The C–C bond lengths themselves vary in a rather wide range from $1.361(3)$ Å for the C(4)–C(5) bond to $1.392(3)$ Å for the C(3)–C(4) bond. Our attention was engaged by the absence of symmetry in the geometric parameters of the phenyl group. The absence of the pairwise equivalence of C(2)–C(3)/C(2)–C(7), C(3)–C(4)/C(6)–C(7), and C(4)–C(5)/C(5)–C(6) bonds and the respective bond angles in the presence of only one substituent in the benzene ring cannot be explained by intramolecular reasons. This can be caused only by intermolecular interaction. The analysis of the crystal structure of compound **I** (Fig. 2) revealed the presence of intermolecular contacts: O(2)...C(3) $3.116(3)$ Å and N(1)...C(3) $3.265(2)$ Å. These interatomic distances are near the limits of the acceptable ranges (3.11 and 3.27 Å for the O...C and N...C contacts respectively), recommended in [11] as the upper limit of van der Waals interactions. The involvement of the electron density of the *p* orbital of the C(3) atom in the intermolecular contact weakens its involvement in the delocalization of the electron density in the benzene ring, leading to an elongation of the C(3)–C(4) bond. In turn, this results in the redistribution of the electron density over the whole benzene ring. Therefore, the intermolecular interaction between the nitro and phenyl groups of the neighboring molecules in the crystal of compound **I** allows us to explain the observed non-equivalence of the geometric parameters of the phenyl group of compound **I**. This is additionally supported by the ^1H and ^{13}C NMR spectroscopy data [12]. In the spectra of compound **I** in the DMSO-*d*₆ solution, the described intermolecular interaction is absent, and the pairwise equivalence of chemical shifts of the signals from C(3)/C(7), C(4)/C(6), and H(4)/H(8), H(5)/H(7) atoms, which is typical of monosubstituted benzene derivatives, is observed.

The parameters of the intramolecular N(3)–H(1)...O(1) hydrogen bond in compound **I** (Table 2) are at the levels observed for nitroguanidine and its alkyl derivatives [3-5]. In the crystal, the molecules of compound **I** are linked in pairs by two intermolecular N(4)–H(2)...N(2) hydrogen bonds. This type of the intermolecular bonding is also typical of nitroguanidines [3-5].

Therefore, in general, the structure of compound **I** largely coincides with the structure of nitroguanidine and its alkyl derivatives, and the aryl substituent almost does not affect the structural parameters of the nitroguanidyl moiety.

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