Chemistry of Heterocyclic Compounds, Vol. 34, No. 10, 1998

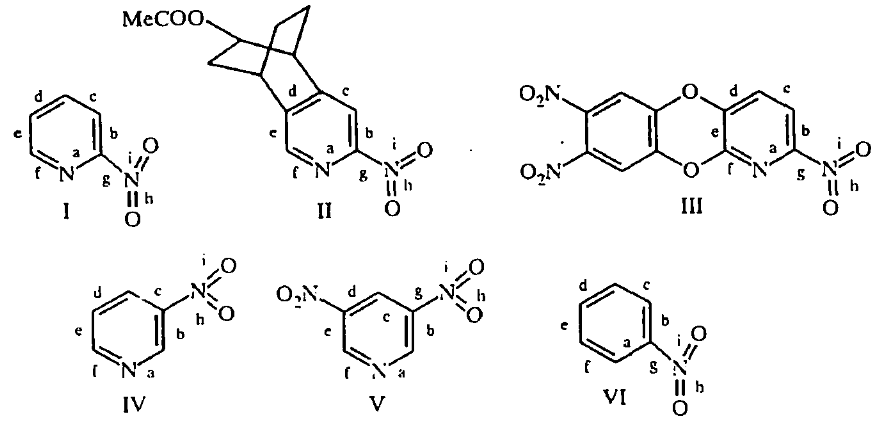
CRYSTAL STRUCTURE OF 2-NITROPYRIDINE

T. V. Rybalova, V. F. Sedova, Yu. V. Gatilov,
and O. P. Shkurko

The crystal structure of 2-nitropyridine has been determined by x-ray diffraction analysis. The influence of the nitro group on the geometric parameters of the molecule was evaluated, as well as its influence on the molecular parameters of other nitropyridines, depending on the position of this group in the pyridine ring.

Substituents in aromatic compounds have a significant influence on the geometric parameters of the ring [1]. Thus, when a nitro group, which has strong electron-acceptor properties, is introduced into a benzene ring, the endocyclic angles undergo the greatest deformation, particularly the angle at the ipso-carbon atom connected to the nitro group, whereas the bond lengths in the benzene ring are very little changed [2]. It has been shown that the nitrobenzene molecule is planar and that many of its meta- and para-substituted derivatives have a nearly coplanar configuration; the angle of rotation of the nitro group is usually no greater than 20° [3, 4]. For the ortho-substituted nitrobenzenes, steric interactions of the neighboring substituents tend to drive the nitro group out of the plane of the ring; this alters the physical characteristics and reactivity of such compounds [3].

In comparison with nitrobenzenes, the geometry of nitropyridines has received much less attention. The published data pertain mainly to substituted 3- or 5-nitropyridines, where the structural parameters of the nitro group are comparable to those of the nitro group in benzene derivatives. Very little information is available on the structure of 2- and 4-nitropyridines. According to data from the Cambridge Bank of Structural Data [5], the geometry of 4-nitropyridines has been studied only in the example of derivatives of 4-nitropyridine-N-oxides. For 2-nitropyridine (I), no data whatever have been reported; for compounds containing the 2-nitropyridine fragment, the crystal structure has been determined for 6-exo-acetoxy-3-nitro-5,6,7,8-tetrahydro-5,8-methanoisoquinoline (II) [6] and 2,7,8-trinitro-1,4-benzodioxino[2,3-b]pyridine (III) [7]. For the latter compounds, however, we must consider the possibility of structural distortion of the molecules under the influence of the other structural fragments.



Here we are reporting on an experimental determination of the crystal structure of 2-nitropyridine (I). The coordinates of the atoms in this molecule are presented in Table 1, the bond lengths in Table 2.

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090. E-mail: gatilov@nioch.nsc.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1367-1371, October, 1998. Original article submitted December 9, 1997.

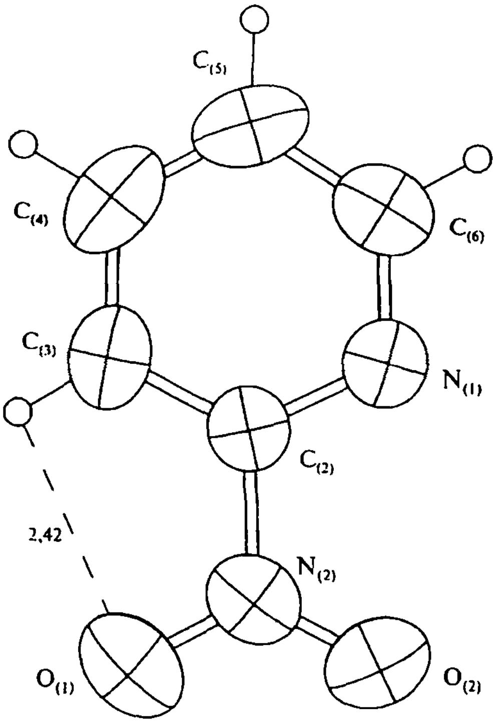


Fig. 1. Structure of molecule of 2-nitropyridine I according to x-ray diffraction data (25% thermal ellipsoids are shown).

The molecule of compound I in the crystal is planar. In the stacking of the molecules there are weak intermolecular hydrogen bonds (O...H contact shorter than 2.6 Å [9]) with the following parameters: length $O_{(1)}...H_{(6)}$ 2.57 Å; angle $O_{(1)}...H_{(6)}-C_{(6)}$ 175°; length $O_{(2)}...H_{(3)}$ 2.51 Å; angle $O_{(2)}...H_{(3)}-C_{(3)}$ 147°; length $O_{(2)}...H_{(5)}$ 2.58 Å, angle $O_{(2)}...H_{(5)}-C_{(5)}$ 169°.

In earlier calculations [10] of the geometric parameters of isomeric nitropyridines, performed by the *ab initio* method in the 3-21G basis, it was shown that when the nitro group is in position 2 of the pyridine ring, it has the greatest influence on the length of the $N_{(1)}-C_{(2)}$ bond (a). This bond is shortened to 1.305 Å, in comparison with the calculated value of 1.331 Å for pyridine itself. Further support is provided by the x-ray diffraction data for compounds I and II, in which the length of this bond is 1.306(4) and 1.313(6) Å (for two independent molecules of II in the crystal cell), and 1.308(6) Å, respectively; these lengths are significantly shorter than the value determined experimentally for pyridine, i.e., 1.337(1) Å [11]; also, these lengths are shorter than the statistical mean value of 1.339(19) Å for substituted pyridines [12]. The influence of the nitro group on the other bonds is less significant (Table 2). Let us note that the experimentally determined lengths of the C-C bonds in compound I proved to be 0.010-0.036 Å shorter than indicated by the calculations. The deviations of the calculated C-C bond lengths in 3-nitropyridine (IV) [10] and the values found for the same bonds in 3,5-dinitropyridine (V) [15] range from 0.006 to 0.017 Å.

According to the diffraction data, the length of the $C_{(2)}-NO_2$ bond in the molecule of 2-nitropyridine (I) is 1.492(5) Å, considerably greater than the calculated value of 1.460 Å and greater than the values found for the $C-NO_2$ bond in nitrobenzene (VI), for which a value of 1.449 Å was obtained by calculation [10] and a value of 1.465(2) Å was obtained experimentally [13]. At the same time, this value [for the bond in 2-nitropyridine] is comparable to the measured length of the $C_{(2)}-NO_2$ bond in compound II, 1.499(6) and 1.502(6) Å. Let us note that the length of the $C-NO_2$ bond in 3,5-dinitropyridine, 1.468(3) Å according to [15], is close to the length of the $C-NO_2$ bond in nitrobenzene, and it corresponds to the average length of this bond for nitroarenes, 1.468(14) Å according to [12]; and the length of this bond in 4-nitropyridine-N-oxide is even shorter, 1.455(3) Å [16].

According to calculations for ortho-, meta, and para-nitropyridines, the lengths of the two N-O bonds (h,i) differ among each other only in the case of the ortho-isomer IV [10]. However, the experimentally determined values of these bonds are little different for compounds I, II, and V (Table 2).

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Factors ($Å^2 \times 10^3$) of Nonhydrogen Atoms of 2-Nitropyridine (I)

Atom	x/a	y/b	z/c	U_{eq}
$O_{(1)}$	9573(3)	2500	8049(4)	103(1)
$O_{(2)}$	10961(2)	2500	6216(3)	79(1)
$N_{(1)}$	9502(2)	2500	3643(4)	61(1)
$N_{(2)}$	9940(3)	2500	6590(4)	63(1)
$C_{(2)}$	9054(3)	2500	5186(4)	49(1)
$C_{(3)}$	7906(3)	2500	5614(5)	68(1)
$C_{(4)}$	7140(3)	2500	4258(7)	83(1)
$C_{(5)}$	7543(4)	2500	2631(6)	76(1)
$C_{(6)}$	8718(4)	2500	2370(5)	75(1)

TABLE 2. Bond Lengths (Å) in Molecules of Nitrobenzene and Nitropyridines

Bond	Pyridine		2-Nitropyridines			IV,* calc. [10]	V,† x-ray [15]	Nitrobenzene VI	
			I		II				
	calc. [10]	x-ray [11]	calc. [10]	x-ray	x-ray [6]‡			calc. [10]	x-ray [13]
a	1,331	1,337(1)	1,305	1,306(4)	1,311(6)	1,326	1,327(4)	1,378	1,387(2)
b	1,383	1,382(2)	1,374	1,358(5)	1,388(6)	1,379	1,373(4)	1,378	1,384(2)
c	1,384	1,376(7)	1,383	1,373(6)	1,374(6)	1,378	1,361(3)	1,381	1,385(2)
d	1,384	1,379(3)	1,384	1,348(7)	1,395(6)	1,380	1,370(3)	1,386	1,388(2)
e	1,383	1,379(7)	1,385	1,362(6)	1,385(6)	1,383	1,374(4)	1,386	1,387(2)
f	1,331	1,334(3)	1,329	1,337(5)	1,334(6)	1,333	1,330(3)	1,381	1,384(2)
g	—	—	1,460	1,492(5)	1,501(6)	1,440	1,468(3)	1,449	1,465(2)
h	—	—	1,228	1,210(4)	1,222(7)	1,243	1,212(4) 1,208(4)	1,244	1,228(2)
i	—	—	1,253	1,206(4)	1,198(9)	1,244	1,220(3) 1,215(4)	1,244	1,223(2)

---

*3-Nitropyridine.

†3,5-Dinitropyridine.

‡Average for two independent molecules in crystal lattice.

According to the x-ray diffraction data presented in Table 3, the O-N-O angle (angle hi) in compounds I (124.3(3)°), II (125.6(4) and 125.1(5)° [6]), III (124.9(2) [7]), V (124.7(2)° and 124.9(3)° [15]) is greater than in nitrobenzene VI (1.23.2(1)° [13]). However, while we see in the series of substituted nitrobenzenes an elongation of the $C-NO_2$ bond with an increase of the $O-N-O$ angle [3], there is no such relationship observed in the series of nitropyridines that we have examined (I-III, V).

We have followed the change of the endocyclic angle (ab) in the pyridine ring at the ipso-carbon atom as the most sensitive parameter characterizing the effect of an electron-acceptor substituent in the molecules of nitroarenes [14]. In 2-nitropyridine (I) the $N_{(1)}-C_{(2)}-C_{(3)}$ angle is increased to 127.4(3)° in comparison with the same angle in pyridine, which is 123.8(5)° [11], and also in comparison with the value of 124(1)° that we obtained by averaging the corresponding angles for a series of 2-amino-substituted pyridines according to data reported in [5]. An analogous increase of the $N_{(1)}-C_{(2)}-C_{(3)}$ angle was noted previously for compounds II (128.3(4) and 127.6(4)° [6]) and III (125.6(2)° [7]). In Table 4 we have listed values characterizing the increase of the endocyclic angle at the ipso-carbon atom in the molecules of the 2-nitropyridines I and II and 3,5-dinitropyridine (V) in comparison with pyridine, and also the angle in molecules of nitrobenzene (VI) in comparison with benzene. We can note a difference in the influence of the nitro group on the endocyclic angle depending on the position of the group in the pyridine ring, with the greatest effect manifested when the nitro group is introduced into position 2.

TABLE 3. Bond Angles (deg) in Molecules of Nitrobenzene and Nitropyridines

Bond	Pyridine		2-Nitropyridines			IV,* calculated [10]	V,† x-ray [15]	Nitrobenzene VI	
			I		II				
	calc. [10]	x-ray [11]	calc. [10]	x-ray	x-ray[6]‡			calc. [10]	x-ray [13]
ab	123	123,8(5)	124	127,4(3)	128,0(4)	121	122,2(2)	122	122,9(1)
bc	119	118,6(1)	118	115,6(4)	114,0(4)	120	121,4(2)	119	118,0(1)
cd	119	118,8(2)	119	120,1(3)	120,6(4)	118	115,8(2)	120	120,3(1)
de	119	118,5(2)	118	118,6(3)	119,1(4)	118	121,1(2)	120	120,5(1)
ef	119	123,5(2)	119	123,7(3)	121,5(4)	123	122,2(2)	120	120,2(1)
af	119	116,6(2)	119	114,6(3)	116,9(4)	119	117,4(2)	122	118,1(1)
hi	—	—	126	124,3(3)	125,4(5)	125	124,7(2) 124,9(3)	125	123,2(1)

---

[*] 3-Nitropyridine.

[†] 3,5-Dinitropyridine.

[‡] Average for two independent molecules in crystal lattice.

TABLE 4. Change of Endocyclic Angle upon Introduction of Nitro Group into Ring

Compound	Angle	Increase of angle, deg	Angle of rotation of NO_2, deg	Reference
I	*ab*	3,6*	0,0	
II	*ab*	4,2*	2,4(3) & 9,3(2) †	[6]
IV	*bc*(*de*)	2,6(2,8)*	1,5(7,0)	[15]
V	*ab*	2,9 ‡	2,18(5)	[13]

---

[*] Relative to corresponding angle of pyridine ring [11].

[†] For two independent molecules in crystal lattice.

[‡] Relative to internal angle of benzene ring.

These data indicate a redistribution of electron population for the sp^2-hybrid orbitals of the $C_{(2)}$ atom of the pyridine ring, participating in the formation of the bonds $N_{(1)}-C_{(2)}$ and $C_{(2)}-NO_2$ in the molecule of 2-nitropyridine, with the redistribution taking place in such a manner that the fraction of s-electrons in the endocyclic bond $N_{(1)}-C_{(2)}$ increases, while the fraction of p-electrons increases in the exocyclic bond $C_{(2)}-NO_2$.

EXPERIMENTAL

X-ray Diffraction Studies of 2-Nitropyridine I. Crystals of compound I were obtained by crystallization of the reagent preparation from ethanol, mp 71-72°C [8]. The x-ray diffraction experiment was performed in a Syntex $P2_1$ diffractometer (CuK_α radiation with a graphite monochromator, $2\theta/\theta$ scanning in the region $2\theta < 110°$). The crystals of I are transparent, light-yellow, volatile, dimensions 0.5×0.4×0.3 mm. These crystals were placed in a polyethylene capillary for the measurements. The cell is rhombic, space group Pnma, a = 11.465(2), b = 6.388(1), c = 7.782(1) Å, V = 569.9(2) $Å^3$, Z = 4. $C_5H_4N_2O_2$. $d_{calc} = 1.446$ g/cm^3, $\mu = 0.99$ mm^{-1}. The intensities of 404 independent reflections were measured; for these values, corrections were introduced for the drop of intensity of control reflections down to 80.4%, and also for absorption, in accordance with the DIFABS program (correction 0.13-1.30). The structures were deciphered by the direct method, using the SHELXL-86 program, and were refined by the full-matrix least squares method by means of the SHELXL-93 program in the anisotropic approximation with respect to all F^2 down to $wR_2 = 0.1314$, S = 1.067 (R = 0.0443 for 334 $F > 4\sigma$). The positions of the hydrogen atoms were found from a difference synthesis; however, in refining the coordinates, they were calculated geometrically with fixed U_{iso}.

The authors wish to thank the International Scientific Fund for financial support (Grant NQN300), and the Russian Fund of Fundamental Research for assistance in payment of the licensing fee for use of the Cambridge Bank of Structural Data (Project 96-07-89187).

REFERENCES

1. A. Domenicano, A. Vaciago, and C. A. Coulson, Acta Crystallogr., Ser. B, **31**, 1630 (1975).
2. R. Norrestam and L. Schepper, Acta Chem. Scand., Ser. A, **35**, 91 (1981).
3. N. I. Sadova and L. V. Vilkov, Usp. Khim., **51**, 153 (1982).
4. Z. V. Zvonkova, Usp. Khim., **46**, 907 (1977).
5. F. H. Allen and O. Kennard, Chem. Des. Automat. News, **8**, 31 (1993).
6. H. Tanida, T. Irie, and Y. Wakisaka, J. Heterocycl. Chem., **23**, 177 (1986).
7. A. Piorko, S. Christie, M. Crook, and P. Sampson, J. Heterocycl. Chem., **31**, 717 (1994).
8. A. Kirpal and W. Bohm, Ber., **64**, 767 (1931).
9. A. I. Kitaigorodskii, Molecular Crystals [in Russian], Nauka, Moscow (1971).
10. J. S. Murray, J. M. Seminario, and P. Politzer, J. Mol. Struct., **187**, 95 (1989).
11. D. Mootz and Y. G. Wussow, J. Chem. Phys., **75**, 1517 (1981).
12. F. H. Allen, O. Kennard, D. J. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc., Perkin Trans. 1, No. 12, S31 (1987).
13. R. Boese, D. B. Becuser, M. Nussbaumev, and T. M. Krygowski, Struct. Chem., **3**, 363 (1992).
14. A. Domenicano and P. Murray-Rust, Tetrahedron Lett., No. 24, 2283 (1979).
15. R. Destro, T. Pilate, and M. Simonetta, Acta Crystallogr., Ser. B, **30**, 2071 (1974).
16. P. Coppens and M. S. Lehmann, Acta Crystallogr., Ser. B, **32**, 1777 (1976).