

Resonance Interactions in the *N*-Nitramino Group. X-Ray Study of α -, β - and γ -Nitraminopyridines

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The crystal and molecular structure of three isomers (α , β and γ) of nitraminopyridine have been solved by X-ray diffraction at room temperature with Cu K α radiation. All isomers exist as the imino tautomeric form with strong resonance interactions in the nitramino group. NN and NO bond lengths and ONO bond angles are interrelated as found from consideration of 61 structures taken from the Cambridge Structural Database (release April 1995). Changes in geometry of the nitramino group are explained by differences in the *s/p*-character of the bond. Stabilization of the imino form seems to be due to the H-bonding net in the crystal, a phenomenon not taken into account in the *ab initio* calculation of α -isomers, which favors the amino form.

Nitramine derivatives are interesting and important organic systems for many reasons.^{1,2} In particular they may undergo tautomerisation³ and the nitramino group participates in complex inductive/resonance interactions within the group and exerts an almost entirely polar substituent effect in interactions with other groups.^{4,5}

The parent nitramine, H₂N–NO₂, is non-planar^{6–8} with the N–H bonds arranged similarly to those in the ammonia molecule. However, it is also known that substitution at the amine nitrogen induces a strong tendency toward planarity, thus, dimethylnitramine is planar both in the crystal^{9,10} and in the gas phase.¹¹ It should also be mentioned that in these compounds the dihedral angle R–N–N–O diminishes with shortening of the N–N distance. X-Ray measurements² have shown that the N–N bond in nitrodimethylamine has remarkable double-bond character. Similarly, in 1,2-di(nitramino)ethane this bond² is 1.33 Å. The N–N bond length in *N*-methyl-*N*-nitro-*p*-nitroaniline is equal⁴ to 1.346 Å. In this compound the benzene ring and the *p*-nitro group were found to be almost coplanar. However, the N(Me)NO₂ group is twisted out of the plane of the benzene ring by –72.3°, indicating the almost entirely field/inductive effect of the substituent.⁴

From a structural point of view the strongly electro-negative NO₂ group attached to the electron-donating nitrogen atom of the amino group creates an opportunity to form a strongly flexible π -electron system. Owing to this property the nitramino group exhibits considerable variations in its structural parameters, such as NO and NN bond lengths, as well as ONO bond angle.

In this paper we discuss how these structural parameters are inter-related, based upon structural data obtained from the Cambridge Structural Database. In addition, the results of a detailed study of the crystal and molecular structures of α -, β - and γ -nitraminopyridines together with a detailed *ab initio* study of α -nitraminopyridine are presented.

Experimental

The X-ray measurements were made on a KM-4 KUMA diffractometer with graphite monochromated Cu K α radiation. The data were collected at room temperature using ω – 2θ scan techniques. The intensity of the control reflections for both compounds varied by less than 5%, and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was

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applied. All structures were solved by direct methods¹² and refined using SHELXL.¹³ Non-hydrogen atoms were refined anisotropically and four H-atoms were placed in calculated positions and refined with isotropic thermal parameters. The H-atom connected with the N1-atom was obtained from a difference map and refined with an isotropic thermal temperature factor. Atomic scattering factors were taken from Ref. 14. The details of X-ray measurements, structural computation and crystal data for α -, β - and γ -*N*-nitraminopyridines are given in Table 1. Table 2 together with the atomic numbering Scheme 1 present the observed bond lengths and bond angles for the compounds α , β and γ . All *N*-nitramino-

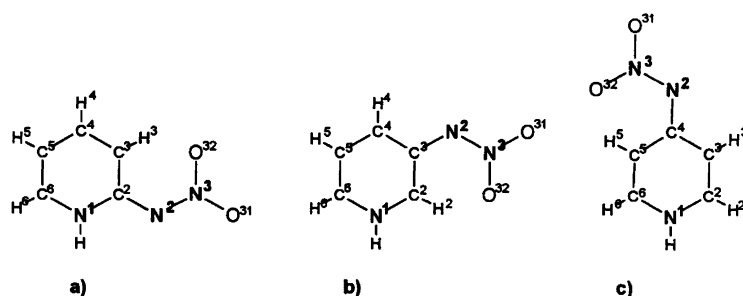
pyridines were obtained according to the references given in Ref. 15.

Computational details

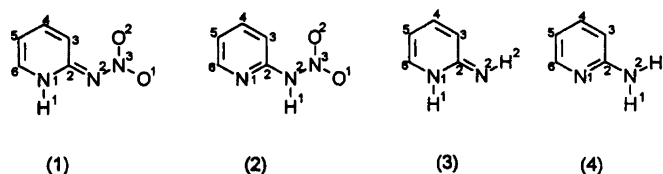
Full *ab initio* optimizations¹⁶ of molecular structures were performed by use of the GAUSSIAN 94 program system, developed by Pople,¹⁷ on a Convex C 3860 computer¹⁸ using the 6-31G split-valence basis set¹⁹ with coplanarity of all constituent atoms assumed. The numbering of atoms of the two isomeric α -nitraminopyridine molecules 1 and 2 and of α -aminopyridine 3 and 4

Table 1. Crystal data and structure refinement for α -, β - and γ -*N*-nitraminopyridines.

Compound	α	β	γ
Empirical formula	C ₅ H ₅ N ₃ O ₂	C ₅ H ₅ N ₃ O ₂	C ₅ H ₅ N ₃ O ₂
Formula weight	139.12	139.12	139.12
Temperature		293(2) K	
Wavelength		1.54178 Å	
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>C2/c</i>	<i>Fdd2</i>	<i>P2₁/c</i>
Unit cell dimensions	<i>a</i> = 23.190(5) Å <i>b</i> = 3.680(10) Å <i>c</i> = 17.087(3) Å β = 128.39(3) Å	<i>a</i> = 18.370(4) Å <i>b</i> = 32.800(7) Å <i>c</i> = 3.780(10) Å	<i>a</i> = 3.679(10) Å <i>b</i> = 12.616(3) Å <i>c</i> = 12.338(2) Å β = 90.4(3) Å
Volume	1142.9(4) Å ³	2277.6(9) Å ³	572.6(2) Å ³
Z	8	16	4
Density (calculated)	1.617 Mg m ³	1.623 Mg m ³	1.614 Mg m ³
Absorption coefficient	1.106 mm ⁻¹	1.110 mm ⁻¹	1.103 mm ⁻¹
<i>F</i> (000)	576	1152	288
Crystal size	0.1 × 0.1 × 1 mm	0.1 × 0.7 × 1 mm	0.1 × 0.5 × 1 mm
Theta range for data collections	4.87–70.04°	5.39–70.17°	5.01–70.11°
Index ranges	–26 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 4 0 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 19 0 ≤ <i>k</i> ≤ 34 0 ≤ <i>l</i> ≤ 3	–4 ≤ <i>h</i> ≤ 4 0 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 12
Reflections collected	1961	557	1031
Independent reflections	1064	557	991
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data/restraints/parameters	1063/0/99	553/0/99	986/0/99
Goodness-of-fit on <i>F</i> ²	1.082	1.105	1.130
Final <i>R</i> indices	<i>R</i> = 0.0524	<i>R</i> = 0.0651	<i>R</i> = 0.0562
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR2</i> = 0.1391	<i>wR2</i> = 0.1528	<i>wR2</i> = 0.1479
<i>R</i> indices (all data)	<i>R</i> = 0.0551	<i>R</i> = 0.0674	<i>R</i> = 0.0618
	<i>wR2</i> = 0.1532	<i>wR2</i> = 0.1735	<i>wR2</i> = 0.1657
Largest diff. peak and hole	0.302 and –0.358 e Å ⁻³	0.351 to –0.0337	0.256 to –0.320



Scheme 1.



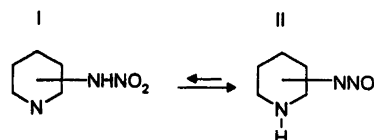
Scheme 2.

(optimized by use of GAUSSIAN 82²⁰) are shown in Scheme 2.

Results and discussion

Analysis of X-ray structural data of α -, β - and γ -nitraminopyridines. Selected data on molecular geometry for the three title nitramino derivatives of pyridine are given in Table 2. From these data a number of interesting findings emerge, which are presented and discussed below.

(1) *Position of the proton.* The title compounds may exhibit tautomerisation, as shown in Scheme 3. The α -derivative, as studied by NMR spectroscopy in solution¹⁵ exists mostly as tautomer II. In the crystalline state all three derivatives exist as tautomer II. This may be readily interpreted as being the result of the electron-accepting action of the NO₂ group which increases the



Scheme 3.

acidity of the N2-H bond in I, leading to formation of II. The role of the nitro group in the nitramino group can be readily seen if we compare the ΔE values (Table 3, Scheme 2), which testify to the stability of amino form over the imino form of α -nitraminopyridine and α -aminopyridine; the values are -9.17 and -18.59 kcal mol⁻¹, respectively, indicating strong destabilization of the N-H bond in the nitramino derivative. However, the 6-31G optimization energy values for α -nitraminopyridine are at variance with the observed localization of the proton in the crystalline state. The fact that compound I occurs in the crystalline state is most probably due to favourable H-bonding in the crystalline network [cf. section (4)].

Comparison of the calculated geometries of 1 and 2 with the geometry determined experimentally (Tables 4 and 5) shows that the structure of α -nitraminopyridine is somewhere between that of 1 and 2. Comparison of changes in bond lengths (defined as $\Sigma |\Delta R_{tu}|$, where the differences are taken for imino- and amino-forms) estimated for α -aminopyridine and α -nitraminopyridine shows that tautomerisation of α -aminopyridine is associated with considerably greater changes in bond length than is observed for α -nitraminopyridine. A decrease in the energy of tautomerisation is also observed (Table 3), as well as a surprisingly good agreement between experimentally determined bond angles and those calculated for the imino-form (Table 5).

(2) *Deformation of bond angles at substituted carbon atoms.* The endocyclic bond angles at α , β and γ carbon atoms of the substituted pyridine ring are almost of the same value, ranging from 116.3° to 116.8°. This follows the Bent-Walsh rule,²¹ which states that if a group X attached to carbon atom is replaced by more electronegative group X', then the carbon atom valency toward X' yields more p character than toward X. The low values of these bond angles and the increase in the *ortho-ipso* bond lengths (~ 1.4 Å) point to low electronegativity of the nitrogen atom N2 in the NNO₂ group.

Attention is drawn to the considerable deformation of two exocyclic bond angles at the substituted C atom.

Table 2. Bond lengths (Å) bond angles (deg) and dihedral bond angles (deg) for α -, β - and γ -N-nitraminopyridines.

	α	β	γ
N(1)-C(2)	1.363(2)	1.337(4)	1.336(3)
N(1)-C(6)	1.339(2)	1.338(4)	1.336(3)
C(2)-C(3)	1.408(2)	1.397(5)	1.364(3)
C(3)-C(4)	1.373(2)	1.404(4)	1.407(3)
C(4)-C(5)	1.391(3)	1.376(4)	1.410(3)
C(5)-C(6)	1.366(3)	1.369(5)	1.366(3)
C(2)-N(2)	1.363(2)	—	—
C(3)-N(2)	—	1.392(3)	—
C(4)-N(2)	—	—	1.379(3)
N(2)-N(3)	1.339(2)	1.304(3)	1.341(2)
N(3)-O(31)	1.240(2)	1.281(3)	1.243(2)
N(3)-O(32)	1.238(2)	1.245(4)	1.240(2)
N(1)-C(2)-C(3)	116.4(2)	119.7(3)	120.3(2)
C(2)-C(3)-C(4)	119.6(2)	116.8(2)	121.1(2)
C(3)-C(4)-C(5)	121.8(2)	121.2(3)	116.3(2)
C(4)-C(5)-C(6)	117.5(2)	119.3(2)	119.5(2)
C(5)-C(6)-N(1)	120.5(2)	119.1(3)	122.2(2)
C(6)-N(1)-C(2)	124.3(2)	123.7(3)	120.5(2)
N(1)-C(2)-N(2)	110.3(2)	—	—
C(3)-C(2)-N(2)	133.4(2)	—	—
C(2)-C(3)-N(2)	—	129.6(2)	—
C(4)-C(3)-N(2)	—	113.6(3)	—
C(3)-C(4)-N(2)	—	—	113.5(2)
C(5)-C(4)-N(2)	—	—	130.2(2)
C(2)-N(2)-N(3)	119.5(2)	—	—
C(3)-N(2)-N(3)	—	119.0(2)	—
C(4)-N(2)-N(3)	—	—	119.9(2)
N(2)-N(3)-O(31)	114.8(2)	115.6(2)	114.3(2)
N(2)-N(3)-O(32)	123.8(2)	125.4(2)	124.5(2)
O(31)-N(3)-O(32)	121.4(2)	118.9(2)	121.2(2)

Table 3. Energies and dipole moments of 6-31G optimizations of α -nitraminopyridine isomers and related molecules as labelled in Scheme 2 (ΔE =difference between amino- and imino-forms).

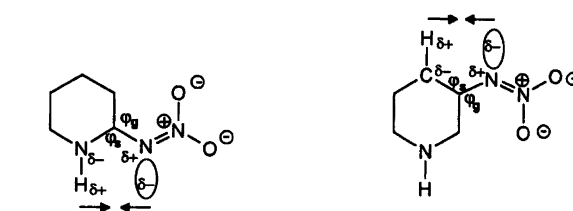
Parameter	Imino-forms		Amino-forms	
	3	1	2	4
$E^{\text{tot}}/\text{Hartree}$	-301.585333	-504.919960	-504.934574	-301.614958
$\Delta E/\text{Hartree}$	—	—	-0.014614	-0.029625
$\Delta E/\text{kcal mol}^{-1}$	—	—	-9.170	-18.590
μ/Debye	3.238	10.659	5.726	2.095

Table 4. 6-31G optimized bond lengths (Å).

Atoms	Imino-forms			Amino-forms	
	3	1	1 X-Ray	2	4
N1-C2	1.3891	1.3630	1.363	1.3265	1.3329
N1-C6	1.3647	1.3571	1.339	1.3285	1.3337
N2-C2	1.2780	1.3284	1.363	1.4055	1.3636
N2-N3	—	1.3432	1.339	1.3259	—
N3-O1	—	1.2211	1.240	1.2341	—
N3-O2	—	1.2511	1.238	1.2314	—
C2-C3	1.4573	1.4278	1.408	1.3877	1.4026
C3-C4	1.3451	1.3619	1.373	1.3877	1.3780
C4-C5	1.4393	1.4186	1.391	1.3865	1.3940
C5-C6	1.3438	1.3510	1.366	1.3844	1.3803
N1-H1	0.9938	0.9971	—	—	—
N2-H2	—	—	—	0.9953	0.9900
N2-H3	1.0023	—	—	—	0.9883
C3-H3	1.0719	1.0629	—	1.0645	1.0722
C4-H4	1.0733	1.0723	—	1.0720	1.0732
C5-H5	1.0691	1.0688	—	1.0705	1.0707
C6-H6	1.0704	1.0691	—	1.0700	1.0715

The differences between the greater (ϕ_g) and the smaller (ϕ_s) exocyclic bond angles are as large as 22.1° for α , 16.3° for β and 16.7° for the γ -derivatives, respectively. Apart from that, there is observed a large deformation of HNC bonds at the protonated N-atom in the ring: the angle on the side of the NNO_2 substituent is 6.3° smaller than that on the other side, and in spite of the low precision of the X-ray determination of the proton location, the difference is statistically significant. It may be interpreted as follows: the lone pair at N2 atom of the NNO_2 group interacts attractively with the N1-H dipolar bond leading to a decrease in both angles H1N1C2 and N1C2N2. A similar mechanism is suggested for interactions between the lone pair with C2H2 and C3H3 bonds in the β - and γ -derivatives of pyridine. The greater deformation in the case of the α -derivative in comparison with the β - and γ -derivatives is in line with the above interpretation, the N-H bond being more acidic than C-H. The suggested interaction is presented in Scheme 4. The above observations are not exceptional: for systems in which similar interactions exist, similar effects are observed.^{22,23}

(3) *Relationships between NN, NO bond lengths and ONO bond angles.* Our experimental data for the geo-


Scheme 4.
Table 5. 6-31G calculated valence angles (deg).

Angles	Imino-forms			Amino-forms	
	3	1	1 X-Ray	2	4
N1-C2-C3	113.75	115.58	116.4	122.08	121.50
C2-C3-C4	121.34	119.46	119.6	116.94	118.46
C3-C4-C5	121.34	122.18	121.8	120.45	119.98
C4-C5-C6	117.67	117.51	117.5	117.94	117.50
C5-C6-N1	121.09	120.02	120.5	122.07	123.18
C6-N1-C2	124.81	125.24	124.3	119.63	119.38
N1-C2-N2	117.47	110.72	110.3	110.36	116.52
C3-C2-N2	128.78	133.70	133.4	126.67	121.98
C2-N2-N3	—	121.55	119.5	129.14	—
N2-N3-O1	—	115.93	114.8	115.92	—
N2-N3-O2	—	121.62	123.8	119.54	—
O1-N3-O2	—	122.45	121.4	124.54	—
H1-N1-C2	114.57	114.33	—	—	—
H1-N2-C2	—	—	—	116.85	118.28
H1-N1-C6	120.62	110.43	—	—	—
H1-N2-N3	—	—	—	114.02	—
H3-C3-C2	117.34	118.83	—	121.60	120.34
H3-C3-C4	121.32	121.71	—	121.47	121.2
H4-C4-C3	119.80	118.74	—	119.19	119.76
H4-C4-C5	118.86	119.07	—	120.36	120.26
H5-C5-C4	121.13	121.45	—	121.43	121.53
H5-C5-C6	121.20	121.04	—	120.63	120.97
H6-C6-C5	123.06	123.86	—	121.79	121.15
H6-C6-N1	115.85	116.13	—	116.15	115.67
H2-N2-C2	115.02	—	—	—	122.28
H1-N1-C2	114.57	—	—	—	—
H1-N2-C2	—	—	—	—	118.28
H1-N2-H1	—	—	—	—	119.44

metry of the NNO_2 group added to those for 61 NNO_2 -derivatives deposited in the CSD.^{24,25} Of this number of crystal structures 112 NNO_2 fragments were subject to further analysis. The scatter plot of ONO angles vs. NO bond lengths is given in Fig. 1, of NN bond lengths vs. ONO angles in Fig. 2, and NN bond length vs. NO bond lengths in Fig. 3. All of these relationships are significant

Table 6. Hydrogen bond lengths (Å) and bond angles (deg) for α -, β - and γ -*N*-nitraminopyridines.

H-bond	H...A length	D...A length	H-bond angle	Code symmetry
<i>α</i> - <i>N</i> -nitraminopyridine				
N1-H1...N2	2.058(22)	2.904(2)	171.87(2.06)	1-x, -y, 1-z
C4-H4...O31	2.578(3)	3.302(3)	146.47(2)	0.5-x, -0.5+y, 0.5-z
C4-H4...O32	2.565(2)	3.166(3)	152.28(2)	1-x, -y, 1-z
C6-H6...O32	2.557(2)	3.304(2)	169.46(3)	x, -y, -0.5+z
<i>β</i> - <i>N</i> -nitraminopyridine				
N1-H1...O31	1.847(61)	2.712(4)	179.96(4.8)	0.25+x, 0.75-y, 0.75+z
N1-H1...N3	2.641(60)	3.429(4)	161.19(0.3)	-0.25+x, 0.75-y, -0.75+z
N1-H1...N2	2.652(52)	3.214(4)	123.64(3.5)	0.25+x, 0.75-y, 0.75+z
C4-H4...O32	2.578(4)	3.494(4)	158.33(3)	0.25+x, 0.75-y, 0.75+z
C6-H6...O31	2.402(4)	3.218(4)	165.27(3)	0.25-x, 0.25+y, -0.75+z
C6-H6...O31	2.719(4)	3.256(4)	161.48(3)	0.25-x, 0.25+y, 0.25+z
<i>γ</i> - <i>N</i> -nitraminopyridine				
N1-H1...N2	1.999(29)	2.870(2)	174.38(2.24)	1-x, -0.5+y, 1.5-z
N1-H1...O31	2.490(29)	3.066(2)	124.06(2.20)	1-x, -0.5+y, 1.5-z
C2-H2...O32	2.426(3)	3.225(3)	141.21(4)	-x, 1-y, 2-z
C6-H6...O31	2.621(3)	3.164(3)	153.30(3)	1-x, 0.5+y, 1.5-z
C6-H6...O31	2.466(3)	3.272(3)	173.68(2)	-1+x, 1.5-y, 0.5+z

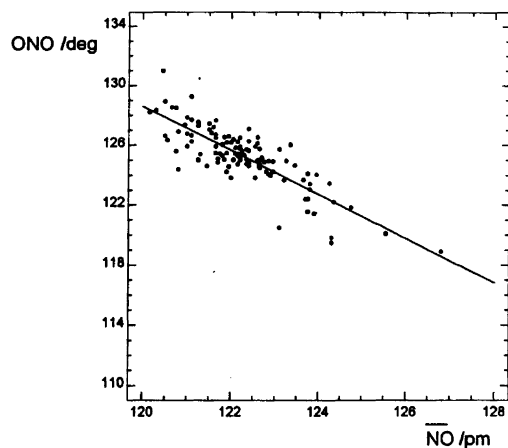


Fig. 1. Scatter plot of ONO bond angles vs. averaged NO bond lengths.

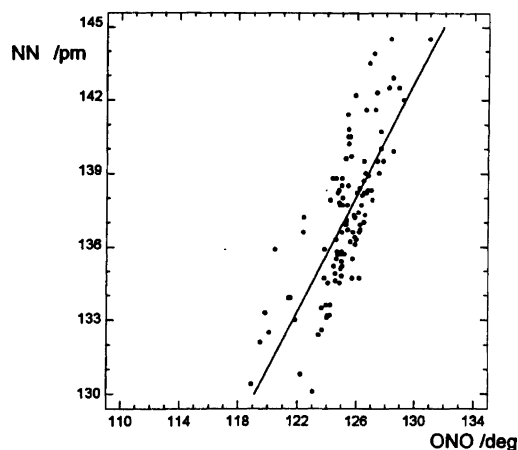
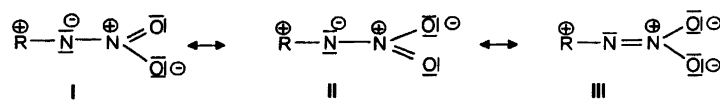


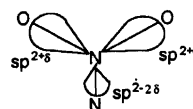
Fig. 2. Scatter plot of NN bond lengths vs. ONO bond angles.



Scheme 5.

(significance level $\alpha < 0.0001$) and hence must be interpreted as not found by chance. The significance level was determined by use of the standard t-test.²⁶

The *N*-nitramino group is a strongly mesomeric system and may be represented by the canonical structures (given in Scheme 5). The values of the N-N bond lengths in the α , β and γ isomers are 1.334, 1.304 and 1.341 Å, respectively, and may be compared to typical single (1.420 Å),²⁷ double (1.254 Å)¹⁶ and optimal²⁸ (1.309 Å) N-N bond lengths. Undoubtedly, the contribution of **III**



Scheme 6.

to the NNO_2 group must be large, if the N-N bond length is significantly shorter than the single N-N bond that would support **I** and **II**. Thus, as a result of interactions between the electronegative NO_2 group and

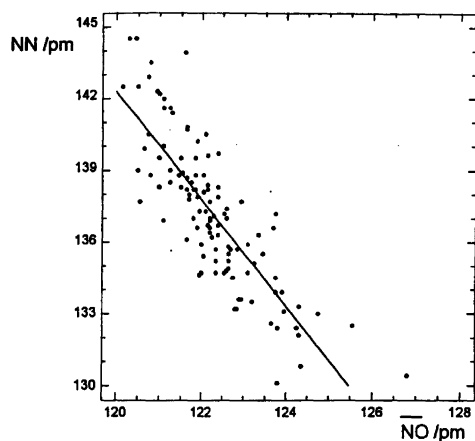


Fig. 3. Scatter plot of NN bond lengths vs. averaged NO bond lengths.

the electron-donating amine nitrogen atom a strong mesomeric effect is observed. The consequences of this shortening of the N–N bond length may also be explained by the Bent–Walsh rule.²¹ The nitrogen atom in the NO₂

group has formally sp² hybridization. The oxygen atoms in the NO₂ group are more electronegative than the nitrogen atom and polarize 2p more than 2s contributions to sp², leading to the hybridization sp^{2+δ} (δ > 0). In consequence, the other hybrid orbital, along the NN bond, becomes sp^{2-2δ} (Scheme 6). As a consequence, the bond angle ONO becomes tighter (since in the case of sp³ hybridization it should be equal to 109.5°) and the NO bonds become longer, while the NN bond gets shorter. These trends are well represented in Figs. 1–3.

(4) *Hydrogen bonding interaction in α-, β- and γ-N-nitraminopyridines.* In the crystal lattice, molecules of α-, β- and γ-N-nitraminopyridines are involved in a network of H-bonds, as shown in Figs. 4–6 and Table 6. In the α and γ isomers a relatively strong H-bond is found between N1H1 and N2 (of the N-nitro group, Figs. 4 and 6). Application of the approximate formula enabling estimation of the H···N energy^{27,29} gives 6.0 and 7.6 kJ mol⁻¹, respectively. All other H-bonds are very weak; 1 kJ mol⁻¹ or even less. In the β isomer a stronger

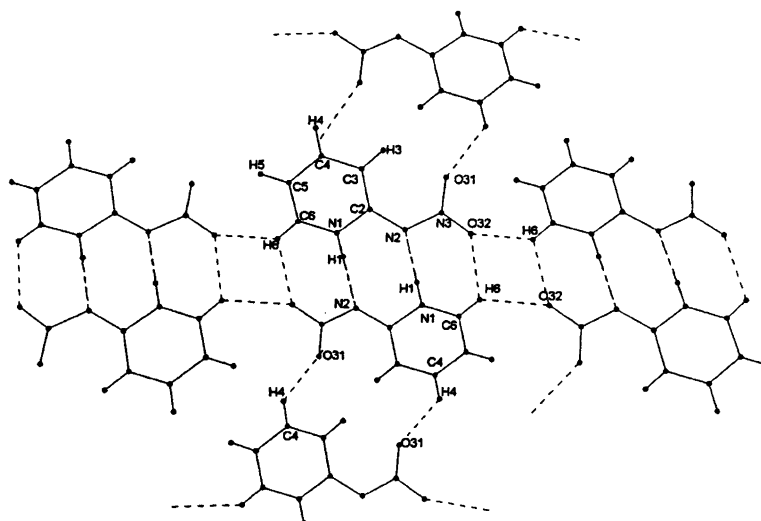


Fig. 4. H-bond net in α-nitraminopyridine.

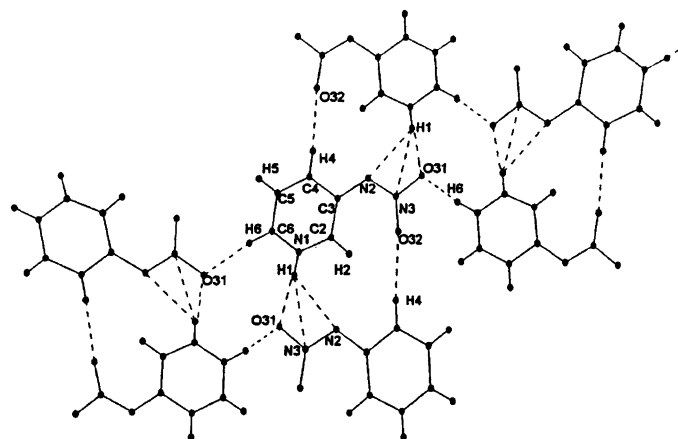


Fig. 5. H-bond net in β-nitraminopyridine.

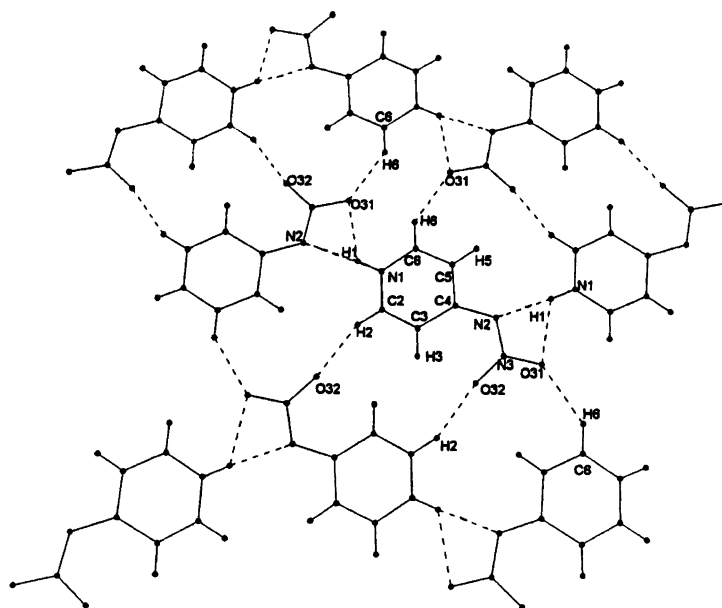


Fig. 6. H-bond net in γ -nitraminopyridine.

bond is found between N1H1...O31, having an energy of 9.8 kJ mol^{-1} . This is associated with the increase in N3O31 bond length to 1.281 \AA . All other NO bonds in the α , β and γ isomers are involved in much weaker H-bonds. In the α isomer we observed dimerization through two linear H-bridges (N1-H1...N2, N1...H1-N2) as in carboxylic acids, which is not observed in the β and γ isomers; there are triple bridges in the β -isomer (H1...O31, N3 and N2) and double bridges in the γ -isomer (H1...N2, O31). Such networks of intermolecular H-bonding (e.g., that shown in Figs. 4-6) for α -, β - and γ -nitraminopyridine may be responsible for the reversed tautomerisation in the crystalline state, compared with that in the isolated molecule [*ab initio* study, section (1)].

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References

1. Urbański, T. *Chemistry and Technology of Explosives*, Laverton, S., Ed., Pergamon Press – PWN, Warsaw 1967.
2. Wright, G. F. In: Feuer, H., Ed., *The Chemistry of Functional Groups; the Chemistry of the Nitroso Group, Part I*, Interscience, New York 1969, p. 613.
3. Gawinecki, R., Kolehmainen, E., Rasała, D. and Suontamo, R. *J. Phys. Org. Chem.*, **8** (1995) 689.
4. Anulewicz, R., Krygowski, T. M., Gawinecki, R. and Rasała, D. *J. Phys. Org. Chem.* **6** (1993) 257.
5. Charton, M. *Progr. Phys. Org. Chem.* **13** (1981) 119.
6. Beevers, C. A. and Trotman-Dickenson, A. F. *Acta Crystallogr.* **10** (1954) 34.
7. Tyler, J. K. *J. Mol. Spectrosc.* **11** (1963) 39.
8. Sadova, N. I., Slepnev, G. E., Tarasenko, N. A., Zeukin, A. A., Vilkov, L. V., Shiskov, I. F. and Pankraushev, Y. A. *Zh. Strukt. Khim.* **18** (1977) 865.
9. Allen, P. W. and Sutton, L. E. *Acta Crystallogr.* **3** (1950) 679.
10. Krebs, B., Mandt, J., Cobbleddick, R. E. and Small, R. W. H. *Acta Crystallogr., Sect. B* **35** (1979) 402.
11. Stolevick, R. and Rademacher, P. *Acta Chem. Scand.* **23** (1969) 672.
12. Sheldrick, G. M., *Acta Crystallogr., Sect. A* **46** (1990) 467.
13. Sheldrick, G. M. SHELXL 93. *Program for the Refinement of Crystal Structures*, Univ. of Göttingen, Germany.
14. *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham 1974.
15. Kolehmainen, E., Laihia, K., Kauppinen, R., Gawinecki, R., Rasała, D. *Magn. Reson. Chem.* **31** (1993) 659.
16. Hehre, W. J., Radom, L., Schleyer, P. von R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, London 1986.
17. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T. A., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanow, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. J., Head-Gordon, M., Gonzalez, C. and Pople, J. A. GAUSSIAN 94 (Revision B.1), Gaussian Inc., Pittsburg PA, USA 1995.
18. Calculations at the Zentrum für Datenverarbeitung der Universität Tübingen.
19. Hehre, W. J., Ditchfield, R. and Pople, J. A. *J. Chem. Phys.* **56** (1972) 2257.
20. Binkley, J. S., Frisch, M. J., DeFrees, D. J., Raghavachari, K., Whiteside, R. A., Schlegel, H. B., Fluder, M. and Pople, J. A. GAUSSIAN 82, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburg PA, 1984.
21. Bent, H. A. *Chem. Rev.* **61** (1961) 275.
22. Zhuji, F., Zhiwei, C., Kezhen, P., Renxiao, G. and Zhuyue, D. *J. Struct. Chem.* **4** (1985) 206.
23. Nordenson, S. *Acta Crystallogr., Sect. B* **37** (1981) 1774.
24. Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., McRae Mitchell, E. M. Mitchell, G. F., Smith, J. M. and Watson, D. G. *J. Chem. Inf. Comput. Sci.* **31** (1991) 187.

25. Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink-Peters, B. G. M. C., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. and Watson, D. G. *Acta Crystallogr. Sect. B* 35 (1979) 2331.
26. Czermiński, J., Iwasiewicz, A., Paszek, Z. and Sikorski A. *Statistical Methods in Applied Chemistry*, PWN, Warsaw and Elsevier, Amsterdam 1990.
27. Dziembowska, T., Szczodrowska, B., Krygowski, T. M. and Grabowski, S. J., *J. Phys. Org. Chem.* 7 (1994) 142.
28. Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* 33 (1993) 70.
29. Krygowski, T. M., Kalinowski, M. K., Turowska-Tyrk, I., Hiberty, P. C., Milart, P., Silvestro, A., Topsom, R. D. and Daehne, S. *Struct. Chem.* 3 (1991) 71.

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