N-Nitroso and *C*-Nitro Derivatives from Di-(2-pyridyl)amine and Butyl Nitrite

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The reaction between di-(2-pyridyl)amine and butyl nitrite produced *N*-nitrosodi-(2-pyridyl)amine, (5-nitro-2-pyridyl)-2-pyridylamine and (3-nitro-2-pyridyl)-2-pyridylamine of which the likely conformations are evinced from spectral data. Structural elucidation of *N*-nitrosodi-(2-pyridyl)amine in the solid state by X-ray diffraction excluded any substantial contribution of the rings to resonance structures.

Recent experiments from our laboratory have shown the versatile reactivity of alkyl nitrites with aromatic amines, which underwent *N*-nitrosation and ring nitration.[1] *N*-Nitrosamines may be obtained also by the action of alkyl nitrites on secondary amines[2] without the use of solvent, being this an advantage whenever the substrate to be nitrosated is somehow water or acid sensitive. Since the *N*-nitrosation of di-(2-pyridyl)amine (**1**) by the classical $NaNO_2$–HCl procedure does not occur at all, probably because of complete inactivation of the reactive site due to protonation, we have carried out the reaction between **1** and butyl nitrite (**2**) in the dark at 75 °C over 14 h under nitrogen, a treatment which gave *N*-nitrosodi-(2-pyridyl)amine (**3**) in fair yield as the main product. Beside unreacted starting amine, the material balance was made up by two other colored products **4** and **5**, as detected by TLC. The reaction was found to be of low reproducibility as to the relative concentrations of the four components present at the end. The factors affecting the course of the process are not clear; by and large, it was not possible to push the reaction to higher conversions by further additions of **2**, perhaps because of developed acidity. The identification of product **3** was based on the elemental analysis, supported by its mass spectral pattern: a molecular ion of modest intensity at 200 u, a base peak at 170 u for the reaction $M^{\oplus}$–NO, two consecutive losses of H and HCN from the peak at 170 u, and a charged fragment $C_5H_4N^{\oplus}$. The IR spectrum of **3** exhibited a single sharp absorption in the H–X bond stretching region at 3032 cm^{-1} for the aromatic H–C's. The ^1H NMR spectrum of **3** confirmed the disappearance of the N–H resonance, but also showed a more complicated pattern than for **1** in the aromatic region. In the same way, the ^{13}C NMR spectrum of **1** showed only five lines in the range 100—160 ppm, as expected for two equally located pyridine rings with respect to the NH group, as is the case for an (almost) completely flat and symmetrical arrangement A (Fig. 1) or for very rapidly averaging different positions, but **3** exhibited doubling of the number of lines for carbon resonances in the same range, an indication of non-identical rings.

The *N*-nitroso compounds of secondary amines are known to possess a rigid skeleton, where rotation about the N–N axis is hindered.[3] *N*-Nitrosation of **1** caused a downfield shift of ca. 0.40 ppm of the three clusters of peaks for the aromatic protons which, moreover, appeared regrouped according to the ratio 3:3:2 (2:4:2 in **1**) in proceeding from higher to lower fields. The presence of a clean doublet of doublets at the lowest field location (at $\delta=8.40$ and 8.70), though, indicated that two protons are identical and close to only one other proton, a situation which is compatible solely with configuration B. The fixed configuration of the nitroso group could be the cause of the differentiation of the pyridyl rings.

A detailed picture of *N*-nitrosodi-(2-pyridyl)amine (**3**) in the solid state was secured by an X-ray diffraction structure determination: Figure 2 shows an arbitrary view of **3**. The final fractional coordinates of non-hydrogen atoms are listed in Table 1, whereas Table 2 reports the most significant geometrical data.

One ring appeared in the plane of the N–NO function in an *anti–anti* arrangement which locates all the het-

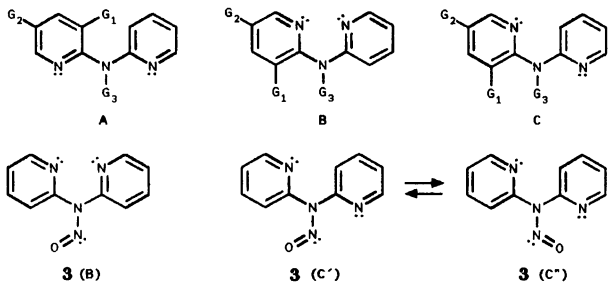

Fig. 1. Configurations of planar di-(2-pyridyl)amines.

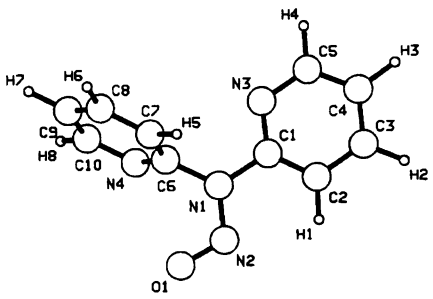

Fig. 2. Arbitrary view of *N*-nitrosodi-(2-pyridyl)amine (**3**).

Table 1. Fractional Atomic Coordinates (10^4) and Equivalent Isotropic Thermal Parameters (Å) for Non-hydrogen Atoms[a)]

Atom	x/a	y/b	z/c	B
O	1546(5)	4091(3)	1483(3)	5.1(4)
N1	731(5)	3517(3)	2772(3)	3.2(4)
N2	911(6)	3444(4)	1847(3)	4.2(5)
N3	58(6)	2789(3)	4138(3)	4.1(4)
N4	2723(5)	4349(3)	3401(4)	4.4(4)
C1	−96(7)	2821(3)	3219(4)	3.1(4)
C2	−984(7)	2244(4)	2706(4)	4.3(5)
C3	−1749(8)	1578(4)	3177(5)	5.0(6)
C4	−1623(8)	1530(4)	4136(5)	4.9(6)
C5	−736(8)	2141(4)	4585(4)	4.9(6)
C6	1240(6)	4294(4)	3279(4)	3.3(5)
C7	216(7)	4906(4)	3604(4)	3.7(5)
C8	741(7)	5635(4)	4113(4)	4.2(5)
C9	2268(8)	5718(4)	4250(4)	4.5(6)
C10	3200(7)	5073(4)	3877(4)	4.7(6)

a) The complete list of structure factors, fractional atomic coordinates, and thermal parameters are deposited as Document No. 67029 at the Office of the Editor of Bull. Chem. Soc. Jpn.

eroatoms as far as possible apart in order to minimize lone pair reciprocal repulsions. The other ring presented only C(6) and C(9) in this plane, but the whole ring was at an angle of ca. 68° with the ring nitrogen, directed away from the nitroso function. The parameters for the *N*-nitroso function are coincidental with those for *N,N*-dimethylnitrosamine obtained by electron diffraction.[4)] This is a strong indication that, contrary to what it was inferred from the value of the rotational barrier about the N–N bond[5)] and the reduced dipole moment[6)] of *N*-nitrosodiphenylamine, the resonance interaction between the ring in the same plane and the N–NO function is of no significance. Confirmation comes from the values of the C(1)–N(1) (1.42 Å) and C(6)–N(1) (1.43 Å) distances for the two almost perpendicular rings: they are practically identical and well within expectation for an sp^2N–sp^2C single bond.[7)] Also, the two rings showed quite similar geometric characteristics. The lack of substantial rings-NNO conjugation and the perfect planarity of one ring with the NNO function appear as a rather contradictory and surprising feature. Our present values may be compared with the *ipso*-C–N distance of 1.44 Å found for *N*-methyl-*N*-nitrosoaniline,[3b)] which exhibited a torsional angle of ca. 30° about this bond; the N–N distance in that case was found to be 1.33 Å. The NO distance was determined as 1.24 Å, a value clearly indicating that the significant resonance in all these compounds is the same and that the aryl group is excluded from any effective conjugation with the nitrogen.[3b)] Exclusion of the ring conjugation with the amino nitrogen is reinforced by the observation of one of the rare X-ray structural determinations of aromatic nitrosamine ever reported,[8)] where the phenyl ring was perpendicular to the NNO function.

Repeated extraction with hot hexane of the whole mixture from the reaction between **1** and **2** left behind a bright yellow solid **4**, corresponding to the slowest eluted component in the TLC analysis, which was purified by crystallization from toluene. Its properties (mp 197 °C) were found to be identical with those of the compound obtained from the classical nitration in H_2SO_4 of **1**:[9)] Its mass spectrum showed a conspicuously intense parent ion corresponding to a mononitration product and a base peak at 78 u (C_5H_4N). Compound **4** is known[9)] to be (5-nitro-2-pyridyl)-2-pyridylamine: Its ^1H NMR spectrum offered a number of unexpected features, such as the location of the rather broad singlet for the nonaromatic proton at δ=8.08 and the spread of the other resonances over δ=ca. 2.20, one of the protons appearing as a closely spaced doublet of doublets at δ=9.16. The IR spectrum showed the typical absorptions expected for ammonium ions between 3240 and 2400 cm^{-1}, although a small single band was found at 3360 cm^{-1}. It seems reasonable to conclude that the crystals of **4** are made up of tautomer **4′**, which is also the prevailing form present in $CHCl_3$ solution (Chart 1).

The quickest way of isolating the third product **5** was to chromatograph the reaction mixture on alumina using hexane as eluent; it was the first eluted product, a bright orange compound, mp 119 °C, whose mass spectrum and elemental analysis indicated to be a mononitroderivative of **1**. The base peak of **5** corresponded to the loss of a nitro group from the parent ion which was of modest intensity. The very minor, but still appreciable features of nitroaromatics under electron impact cleavages, characteristic of the fragmentations ($M^{\oplus}$–O, $M^{\oplus}$–NO) present in **4**, were replaced in the mass spectrum of **5** by a weak ion for the loss of a hydrogen atom, a behavior typical of nitroaromatics with the nitro group *ortho* to substituents bearing protons. The proton on the nitrogen resonated in the ^1H NMR spectrum at a very low field (δ=10.55), the aromatic protons are gathered in three regions in the ratio 4:1:2 (from lower to higher field). The IR spectrum of **5** showed a sharp singlet for the isolated N–H group and a broadened weak singlet for the aromatic C–H bonds in the stretching region. All this evidence points to the identification of **5** as (3-nitro-2-pyridyl)-2-pyridylamine in the configuration A both in the solid state and in $CHCl_3$ solution, but capable of rotation once it has been transformed into its gaseous radical positive ion upon electron impact. Product **5** has been synthesized before by an unambiguous, but unpractical route: the reported properties appear completely consistent with **5**.[10)]

Formation of nitrogen oxides, the observation of a definite induction period in the reaction, the unforeseen production of nitro derivatives all pointed to the need to build up a sufficient concentration of some reactant for the reaction to proceed, perhaps H_2O, which, however, might be detrimental if in too great a concentration.

Table 2. Molecular Dimensions

Bond lengths (Å)		Bond angles (°)		Selected torsion angles (°)	
O–N(2)	1.229(7)	C(1)–N(1)–C(6)	121.4(4)	C(1)–N(1)–N(2)–O	175.4(0.5)
N(1)–N(2)	1.342(6)	N(2)–N(1)–C(6)	122.0(4)	C(6)–N(1)–N(2)–O	0.2(0.7)
N(1)–C(1)	1.421(7)	N(2)–N(1)–C(1)	116.8(4)	C(1)–N(1)–C(6)–N(4)	111.0(0.6)
N(1)–C(6)	1.435(7)	O–N(2)–N(1)	114.4(5)	N(2)–N(1)–C(6)–N(4)	−74.1(0.7)
N(3)–C(1)	1.326(7)	C(1)–N(3)–C(5)	116.3(5)	C(1)–N(1)–C(6)–C(7)	−68.5(0.7)
N(3)–C(5)	1.354(8)	C(6)–N(4)–C(10)	115.4(5)	N(2)–N(1)–C(6)–C(7)	106.4(0.6)
N(4)–C(6)	1.334(7)	N(1)–C(1)–N(3)	114.9(5)	N(2)–N(1)–C(1)–C(2)	−16.4(0.8)
N(4)–C(10)	1.340(8)	N(3)–C(1)–C(2)	124.6(5)	C(6)–N(1)–C(1)–N(3)	−20.8(0.7)
C(1)–C(2)	1.378(8)	N(1)–C(1)–C(2)	120.4(5)	N(2)–C(1)–C(1)–N(3)	164.0(0.5)
C(7)–C(8)	1.384(8)	C(8)–C(7)–C(6)	118.2(5)	C(6)–N(1)–C(1)–C(2)	158.8(0.5)
C(7)–C(6)	1.368(8)	C(8)–C(9)–C(10)	118.5(6)	C(5)–N(3)–C(1)–N(1)	179.0(0.5)
C(9)–C(8)	1.379(9)	C(1)–C(2)–C(3)	117.8(6)	C(10)–N(4)–C(6)–N(1)	−179.8(0.5)
C(9)–C(10)	1.374(9)	C(7)–C(8)–C(9)	118.5(6)	N(1)–C(1)–C(2)–C(3)	179.5(0.5)
C(2)–C(3)	1.376(9)	C(2)–C(3)–C(4)	119.0(6)	C(8)–C(7)–C(6)–N(1)	178.2(0.5)
C(3)–C(4)	1.382(10)	C(3)–C(4)–C(5)	118.9(6)		
C(4)–C(5)	1.364(9)	N(4)–C(6)–C(7)	125.0(5)		
		N(1)–C(6)–C(7)	119.7(5)		
		N(1)–C(6)–N(4)	115.4(5)		
		N(4)–C(10)–C(9)	124.3(6)		
		N(3)–C(5)–C(4)	123.3(6)		

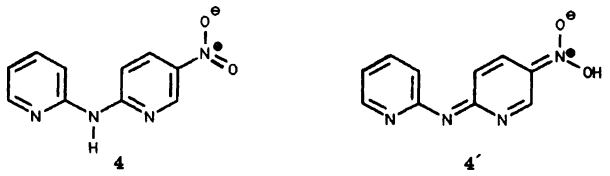

Chart 1.

As a final comment, the reaction here presented may be considered as a convenient, economic and rapid way of making not only the elusive nitrosamine **3**, but also the nitro derivatives **4** and **5**; it opens also a new route to similar derivatives from other aminopyridines.

Experimental

Materials. Di-(2-pyridyl)amine (**1**) was purchased from Aldrich and used as received. "Aged" preparations of butyl nitrite[1] (**2**) were redried over anhydrous calcium chloride as taken out of cold storage and the center cut of a distillation was used. Otherwise, freshly prepared and freshly distilled product was used.

Equipment. All ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer, using TMS as internal standard. MS spectra (direct inlet, 70 eV, vaporization temperature is reported) in the electron impact positive ion mode were obtained with a Finnigan 1020 apparatus. IR spectra (KBr) were recorded with a JASCO spectrometer mod. DS-702G. Melting points were determined with an automatic Mettler (mod. FP61) apparatus and are not corrected. X-Ray diffraction analysis was obtained from a crystal of **3** ($C_{10}H_8N_4O$, M.W. 200.20) ca. 0.4×0.2×0.1 mm that was mounted on a CAD-4 single crystal diffractometer with graphite monochromatized Mo $K\alpha$ radiation: orthorhombic, *Pbca*, $a=8.899(2)$, $b=14.816(3)$, $c=14.349(3)$ Å, $V=1892(1)$ Å^3, $Z=8$, $D_x=1.41$ Mg m^{-3}, λ (Mo $K\alpha$)=0.71069 Å, $\mu=0.91$ cm^{-1}, $F(000)=832$, room temperature, 1666 reflections measured with the ω scan in the range $6<2\theta<50°$. The structure was solved with SHELXS86[11] adopting direct methods. Refinement was carried out with SHELX76[12] with all non-hydrogen atoms allowed to vibrate anisotropically. Hydrogen atoms were located at calculated positions and the refinement cycles were computed by allowing the hydrogens to ride with the corresponding bonded atoms and refining an overall isotropic thermal parameter common to all hydrogen atoms. Unit weights were adopted throughout the refinement procedure. The final disagreement factor is $R=0.056$ with 137 refinable parameters and 730 reflections with $I>2.5\sigma(I)$.

Reaction between Di-(2-pyridyl)amine (1) and Butyl Nitrite (2): Standard Procedure. A solution of **1** (4.09 g, 23.9 mmol) in **2** (33 mL, 280 mmol) was refluxed during 14 h under inert atmosphere. Some red vapors were formed after some 15 min and the product formed rapidly after this stage. Volatile material was removed by reduced pressure distillation (4 kPa), max bath temperature: 120 °C for a short period). If the residue were taken up with more **2** and refluxed, no further development of the reaction could be achieved. The mixture was found to contain beside starting material **1** (50±10%), 40—20% *N*-nitrosodi-(2-pyridyl)amine (**3**), 5—30% (5-nitro-2-pyridyl)-2-pyridylamine (**4**) and 15—30% (3-nitro-2-pyridyl)-2-pyridylamine (**5**), according to a still unclear dependence on the quality of **2**: "aged" samples of **2** seemed to yield larger conversions to nitro-derivatives. The material balance of the reaction was accounted for quite well by the above four components. TLC (Merck aluminium oxide 60 F_{254}, neutral, elution with CH_2Cl_2) R_F were: 0.48 (yellow, bright spot in 254 nm light) for **5**, 0.39 for **3**, 0.18 (yellow, dark spot at 254 nm) for **4** and 0.12 for **1**. All the components of the mixture could be detected both in the 366 and 254 nm light.

In order to obtain **3** the reaction mixture was allowed to cool to room temperature for some time: some unreacted **1** separated and was filtered off. The solution was freed from all volatile material and an orange solid residue was left, from which pure **3** was obtained by recrystallization

from cyclohexane or *t*-butyl methyl ether/hexane mixtures as pale yellow fine needles, mp 80.3 °C; IR (KBr) 3032, 1584, 1562, 1494, 1447, 1430, 1302, 1195, 1108, 1063, 1035, 761, 732, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.45—7.18 (m, 3H), 8.05—7.80 (m, 3H), 8.38 (d, 1H, J=4.18 Hz), 8.65, (d, 1H, J=4.18 Hz); ^{13}C NMR ($CDCl_3$) δ=113.71, 121.80, 123.78, 124.32, 138.17, 138.45, 148.29, 149.20, 150.20, 154.56; MS m/z (56 °C) 200 ($M^{\oplus}$, 4), 171 (22), 170 (100), 169 (15), 143 (3), 142 (4), 117 (2), 116 (8), 79 (11), 78 (70), 52 (18), 51 (49), 50 (8), 39 (18).

It did not withstand prolonged contact with the different types of alumina used for preparative column adsorption chromatography, yielding colored, strongly retained, unidentified products along the column.

If, after the precipitation of part of unreacted **1** and its separation by filtration, the volatile free residue was submitted to adsorption column chromatography (aluminium oxide, neutral, Brockman grade I, BDH, UK) using hexane as the mobile phase, a quick, perfect separation of (3-nitro-2-pyridyl)-2-pyridylamine (**5**) could be achieved as a bright orange solid, easily sublimed in vacuo, which could be recrystallized from hot cyclohexane, mp 119 °C, lit,[10] 114—116 °C; IR (KBr) 3280 (sharp), 1604, 1588, 1570, 1502, 1340, 1378, 1245, 1220, 1187, 1040, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.91—7.11 (m, 2H), 7.69—7.82 (m, 1H), 8.34—8.64 (m, 4H), 10.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=99.82, 114.92, 114.97, 119.30, 135.56, 137.90, 148.30, 148.68, 151.83; MS m/z (100 °C) 216 ($M^{\oplus}$, 17), 170 (100), 169 (20), 142 (5), 116 (5), 85 (9), 78 (67), 52 (20), 51 (39), 50 (9), 39 (18).

Further elution with CH_2Cl_2–EtOH (99 : 1 vol/vol) gave a homogeneous yellow solid **4**, mp 197 °C, lit,[9] 196—197 °C, after recrystallization from hot toluene; IR (KBr) 3400—2400 (broad), 1615, 1590, 1568, 1545, 1488, 1457, 1437, 1327, 1300, 1285, 1118, 1105, 1055, 830, 770, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.98—7.07 (m, 1H), 7.48—7.56 (m, 1H), 7.66—7.78 (m, 1H), 7.83—7.91 (m, 1H), 8.09 (broad s, 1H), 8.33—8.44 (m, 2H), 9.12—9.19 (m, 1H); ^1H NMR (DMSO-d_6) δ=6.92—7.08 (m, 1H), 7.71—7.79 (m, 2H), 7.91 (d, 1H, J=9.39 Hz), 8.27—8.46 (m, 2H), 9.05—9.09 (m, 1H), 10.68 (s, 1H); ^{13}C NMR (DMSO-d_6) δ=110.57, 113.32, 118.06, 133.11, 137.09, 138.09, 145.30, 147.59, 152.85, 157.91; MS m/z (120 °C) 216 ($M^{\oplus}$, 76), 215 (83), 170 (28), 169 (49), 144 (4), 143 (7), 142 (6), 116 (5), 85 (15), 79 (30), 78 (100), 52 (28), 51 (48), 50 (14), 39 (27).

Nitrosamine **3**, originally present in the reaction mixture (TLC, MS), did not withstand the contact with alumina, as was evidenced separately by allowing a solution of **3** in CH_2Cl_2 to stand for two days in the presence of chromatographic grade aluminium oxide in the dark and under nitrogen. Thorough extraction of alumina with CH_2Cl_2 gave a solution where **3** was totally absent (TLC, MS) and replaced by other unidentified products.

Preparation of *N*-Nitrosodi-(2-pyridyl)amine (3). Di-(2-pyridyl)amine (**1**, 2.02 g, 11.8 mmol) and freshly prepared butyl nitrite (**2**, 25 mL, 213 mmol) were kept at 75 °C for 14 h: Upon cooling to room temperature some unreacted **1** crystallized out and was separated by filtration. The remaining solution was freed from volatile material by careful distillation under reduced pressure to obtain an orange solid. Recrystallization from *t*-butyl methyl ether and hexane or cyclohexane yielded a pale yellow, TLC homogeneous solid, **3**, (0.76 g, yield 32%, mp 80.3 °C).

Nitration of Di-(2-pyridyl)amine (1) with HNO_3–H_2SO_4. A solution of **1** (5.00 g, 29.2 mmol) in concentrated H_2SO_4 (96%, 10 mL) kept at 0 °C was treated with a solution of fuming HNO_3 (100%, 0.30 mL, 6.7 mmol) in H_2SO_4 (96%, 10 mL). After 4 d at room temperature the reaction mixture was poured onto ice and made alkaline with NaOH. Extraction with CH_2Cl_2 gave an orange solution from which a yellow solid **4**, mp 197 °C, was obtained by solvent evaporation and simple recrystallization from toluene (1.26 g, 20%). From the mother liquor the nitro derivative **5**, mp 119 °C, was obtained by fractional crystallization (0.93 g, 14.8%). These products exhibited no mp depression upon admixture with the corresponding solids obtained by treatment of **1** with butyl nitrite and showed identical TLC and spectral properties.

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