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PYRIDINE 1-NITROIMIDE : CRYSTAL STRUCTURE, CONFORMATION, ELECTRONIC STRUCTURE, SITE OF PROTONATION, AND REACTIVITY

Jean Arriau and J. Deschamps*
Laboratoire de Chimie Structurale, Faculté des Sciences, Université de Pau,
Avenue Philippon, 64 - Pau, France

J. Reginald C. Duke*
Explosives Research and Development Establishment, Powdermill Lane, Waltham Abbey,
Essex, England

Jan Epsztajn[1a], Alan R. Katritzky*, Edward Lunt[1b], James W. Mitchell[1c],
S. Q. Abbas Rizvi, and Gilberto Roch[1d]
School of Chemical Sciences, University of East Anglia, Norwich, England

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Heterocyclic N-nitroimides, a new class of N-oxide analogues,[2] possess interesting conjugated systems, capable of push-pull electronic interaction. We now report on the physico-chemical properties and reactivity of these compounds.

The X-ray determined bond lengths and angles are shown for the parent (Fig 1) and 3-bromo derivative (Fig 2). The $\overset{+}{N}\text{-}\bar{N}\text{-}NO_2$ systems are almost planar, but at dihedral angles of 71.7° or 77.9° respectively to the ring planes; in the solid state this angle is probably limited by the approach of O2 to C1, the observed distances being close to the expected van der Waals separation of *ca* 2.90 Å. The bond lengths and angles found in the two structures are closely similar with the exception of the alternating angles found in the ring of the 3-bromo-compound; the ring dimensions are in agreement with those found in pyridine N-oxide[3] but compared[4] with $Me_3\overset{+}{N}\text{-}\bar{N}\text{-}NO_2$ there is a significant shortening of the N1-N2 bond, a lengthening of N2-N3 and a decrease in angle N1-N2-N3.

A CNDO/2 molecular orbital calculation for pyridine 1-nitroimide, using the bond lengths and bond angles of Fig 1, has been performed, with the dihedral angle between the ring plane and the $N\text{-}N\text{-}NO_2$ group as a variable parameter. The minimum energy was found for a dihedral angle of 43°, in reasonable agreement with experiment; the rotational barrier was determined as 5 kcal $mole^{-1}$. The total charge distribution so found (Fig 3) is compared with that for pyridine 1-oxide (Fig 4) : for both molecules the cyclic nitrogen carries a considerable nett positive charge, but this is greater in the N-oxide. Variations in the charge on the ring carbon atoms in both compounds should reflect different reactivities at the 2-, 3-, and 4-positions. The oxygen atoms of the nitro-group are negatively charged as expected.

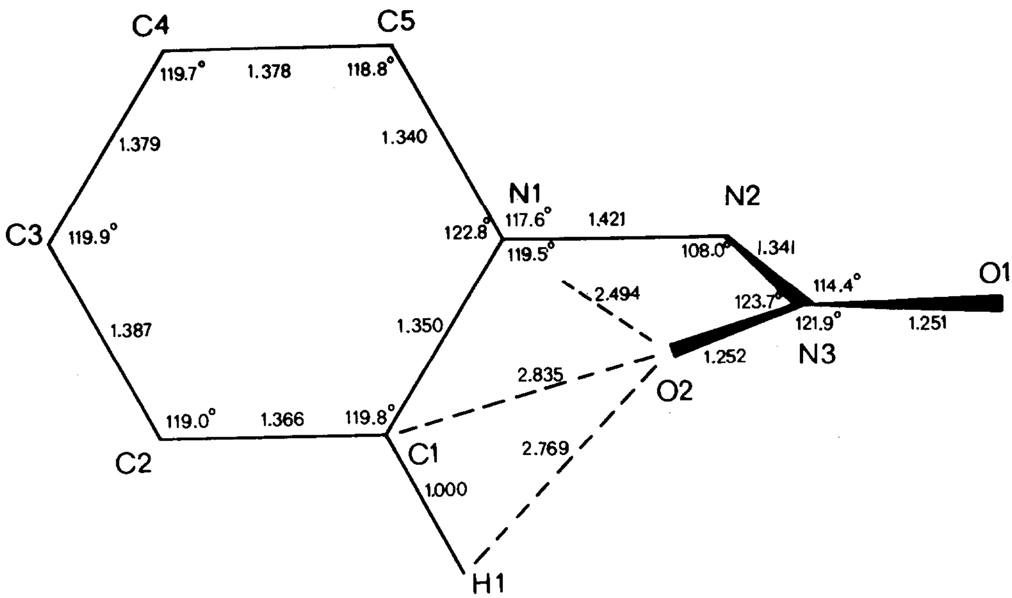


Fig 1: Bond lengths (Å) and angles (°) in pyridine 1-nitroimide; only one hydrogen atom is included in the Figure.

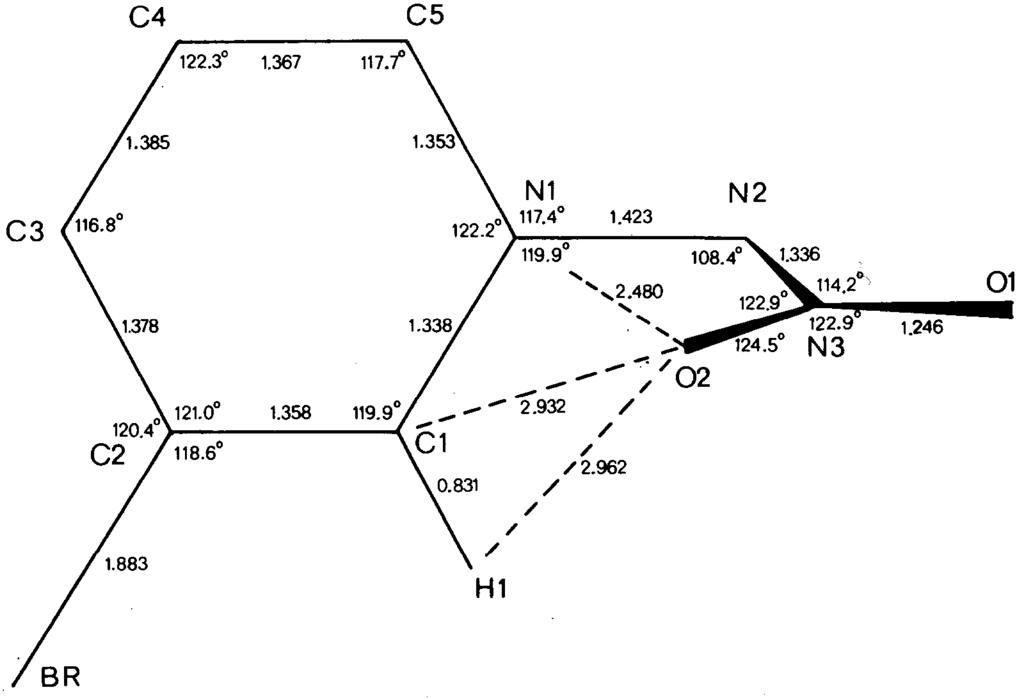


Fig 2: Bond lengths (Å) and angles (°) in 3-bromopyridine 1-nitroimide; only one hydrogen atom is included in the Figure.

Pyridine 1-nitroimide is a weak base with pK$_a$ -4.6^5. Protonation could occur at nitrogen to give cation (I) or at oxygen to give cation (II). CNDO/2 calculations for the alternative cations give lower total energies for the O-protonated cation II (E$_T$ -111.741 to -111.568 u.a. depending on the O-H bond length) than for the N-protonated cation I (E$_T$ = -111.712 to -111.558). In support of this, the experimental spectra show a weak band at 258 nm (log ε 3.81) which is predicted by the M.O. calculations only for the O-protonated cation II.

Pyridine 1-nitroimide does not undergo electrophilic substitution at carbon: attempted nitration and sulphonation left starting material unchanged. Other electrophiles attack the exocyclic nitrogen and effect loss of the N-nitroimide group: e.g., acetic anhydride yielded pyridine. Attempted nucleophilic substitution failed: organometallic reagents give complex mixtures, cyanide ion forms pyridine, amines do not react, and OH$^-$ or OR$^-$ ions cause ring opening to derivatives of glutaconic dialdehyde. However, base catalysed

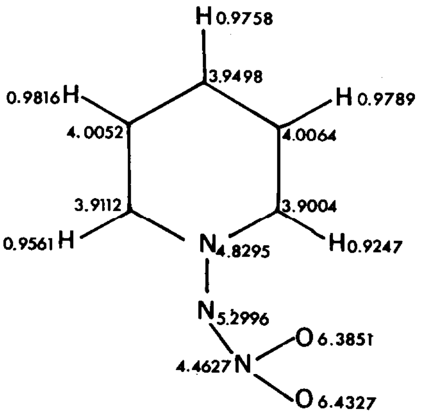


Figure 3

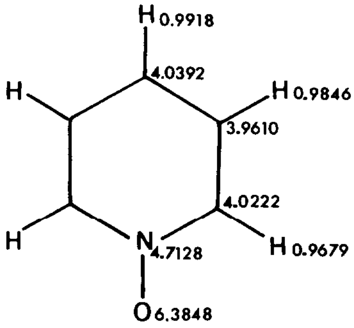
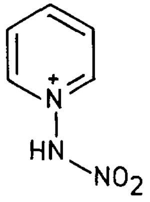
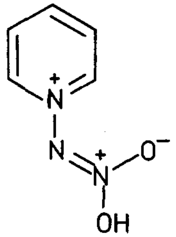


Figure 4

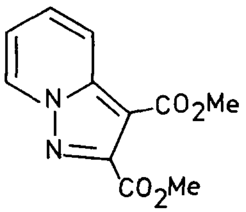
Figs 3 and 4: Total charge distribution calculated for pyridine 1-nitroimide (Fig 1) and pyridine 1-oxide (Fig 2) by the CNDO/2 method.



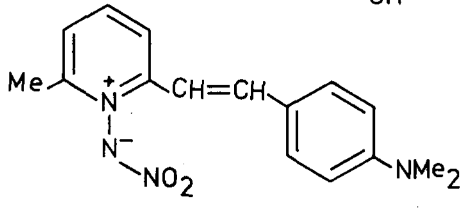
I



II



III



IV

hydrogen - deuterium exchange occurs readily (at 20° in 0.1N - NaOH) at the 2- and 6-positions of pyridine 1-nitroimide and a variety of its substituted derivatives. Pyridine 1-nitroimide also undergoes 1,3-dipolar cycloadditions; thus, dimethyl acetylenedicarboxylate yields III. α-Methyl groups in the pyridine 1-nitroimide ring are reactive, and dyestuffs such as IV have been obtained by reaction with *p*-dimethylaminobenzaldehyde.

The markedly acid character (see Fig 3) of the 2-position hydrogen *syn* to the NO_2 group in pyridine 1-nitroimide (positive charge 0.075) compared with the other ring hydrogen atoms is in line with the observed easy base-catalysed hydrogen exchange at 2,6-positions.

FOOTNOTES AND REFERENCES

(1) Present addresses:
- (a) Department of Organic Chemistry, University of Lodz, Lodz 90136, Narutowicza 68, Poland
- (b) May and Baker Ltd., Dagenham, Essex
- (c) Chemistry Division, Department of Scientific and Industrial Research, Box 2224, Auckland, New Zealand
- (d) Radioisotopi, Sorin, 13040 Saluggia, Italy

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