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STRUCTURES OF PYRIDINE AND QUINOLINE-N-OXIDES

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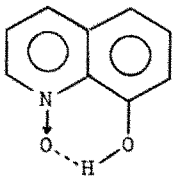
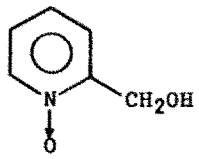
There have been few reports in the literature concerning the structural properties of aromatic ring compounds containing the N-O dative bond. Three dimensional x-ray structural analyses have been completed on two such compounds, 8-hydroxyquinoline-N-oxide (I), and 2-hydroxymethylpyridine-N-oxide (II) in an attempt to provide such information.



(I)



(II)

The preliminary x-ray data are:

	crystal symmetry	space group	molecules per cell	a	b	c	cosβ
(I)	monoclinic	$P2_1/c$	4	12.136	4.921	13.138	-0.3376
(II)	monoclinic	$P2_1/c$	4	7.079	8.046	10.599	-0.2254

Both structures were solved by a direct phasing procedure due to Long (1) and were refined by full matrix least squares techniques. The final residual factors (R) for (I) and (II) are 0.053 and 0.111, respectively. There are two features of interest in the structures. The N-O bond distances are 1.333(2) Å and 1.332 Å for (I) and (II), respectively. These are in good agreement with N-O distances reported for similar compounds such as 1.33 Å in pyridine-N-oxide (2), and 1.335 Å in tetra(pyridine oxide)copper(II)perchlorate(3). Also, both structures exhibit hydrogen bonding: intramolecular in (I) and intermolecular in (II). In (I), the hydrogen bond is between the hydroxyl hydrogen and the dative oxygen; its length is 1.42 Å. In (II), the hydroxyl hydrogen atom is bonded to an N-oxide oxygen atom

of a neighboring, symmetry related molecule. Its length is 1.99 Å. These data appear to support a correlation between the strength of the hydrogen bonding and the length of the N-O bond as proposed by Hanson (4) and Hanson and Huml (5) in their studies of the compounds, myxin and iodinin; that is, as the hydrogen bond to the N-oxide is strengthened, the N-O distance is lengthened. This effect is attributed to the delocalization of the nonbonding electrons on the oxygen atom affected by hydrogen bonding which results in a decrease in the ionic character of the N-O bond. The N-O distances in myxin and iodinin are 1.32 and 1.31 Å, respectively, when the N-oxide oxygen atoms are affected by intramolecular hydrogen bonding. However, the additional N-O bond in myxin is unaffected by hydrogen bonding and its distance is given as 1.28 Å. Other features of these two structures appear to be normal: the pyridine and quinoline moieties are planar within experimental error and bond distances and angles are as expected for these two types of aromatic systems.

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