

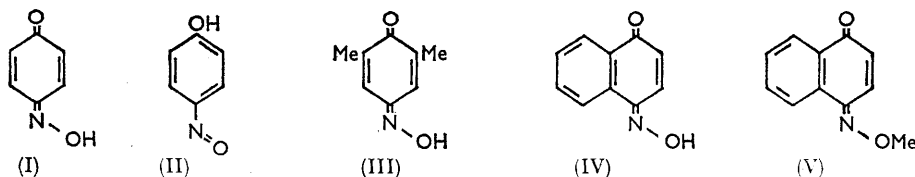
1127. Nuclear Magnetic Resonance Studies of Some Aromatic Nitroso-compounds

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2,6-Dimethyl-4-nitrosophenol and 4-nitroso-1-naphthol exist in the quinone monoxime forms in dilute dimethyl sulphoxide solution whereas 4-nitrosophenol exists in the phenolic form. No temperature-dependent equilibria were observed.

4-NITROSOPHENOLS are tautomeric. In solution both phenolic and quinonoid forms will exist in equilibrium although one form may be present at too low a concentration to be detected. Infrared studies of the hydroxyl stretching frequency suggest that 4-nitrosophenol is in the quinonoid form in dilute carbon tetrachloride solution.¹ The low p*K* values found for 4-nitrosophenol in aqueous² and aqueous-ethanolic solution have been taken to indicate that the phenolic tautomer predominates in these solutions.³ Recent ultraviolet measurements suggest⁴ that both forms are present in methanol solution, whilst earlier measurements⁵ were interpreted as indicating that the quinonoid form predominates in ether, chloroform, dioxan, ethanol, and aqueous acid solutions. Infrared studies⁶ show that, in the solid state, the compound exists in the quinone monoxime form and that this form predominates in chloroform solution. Simple Hückel M.O. calculations⁷ predict that the quinonoid form is the more stable. Infrared⁶ studies of 4-nitroso-1-naphthol show that this compound exists in the quinonoid form in chloroform.

In this Paper we examine the compounds 4-nitrosophenol, 2,6-dimethyl-4-nitrosophenol, and 4-nitroso-1-naphthol in detail, using nuclear magnetic resonance and infrared studies. We show that in dilute dimethyl sulphoxide solutions the last two compounds



exist in the quinonoid forms (III) and (IV), respectively, whereas the first exists in the phenolic form (II). However, in dilute chloroform solution 4-nitrosophenol also exists in the quinonoid form (I).

EXPERIMENTAL

Compounds.—4-Nitrosophenol, m. p. 139° (decomp.), and 2,6-dimethyl-4-nitrosophenol, m. p. 171°, were obtained by nitrosation of phenol and 2,6-dimethylphenol, respectively. 4-Nitroso-1-naphthol, m. p. 197° (decomp.), was a commercial product. 1,4-Naphthaquinone monoxime methyl ether, m. p. 78°, was prepared⁸ by reacting 1,4-naphthaquinone with *O*-methylhydroxylamine.

¹ A. W. Baker, *J. Phys. Chem.*, 1958, **62**, 744.

² M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *J. Amer. Chem. Soc.*, 1959, **81**, 4226.

³ L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, 1963, **85**, 3397.

⁴ E. Havinga and A. Schors, *Rec. Trav. chim.*, 1950, **69**, 457; 1951, **70**, 59; A. Schors, E. Kraaijeveld, and E. Havinga, *ibid.*, 1955, **74**, 1243.

⁵ L. C. Anderson and M. B. Geiger, *J. Amer. Chem. Soc.*, 1932, **54**, 3064; L. C. Anderson and R. L. Yanke, *ibid.*, 1934, **56**, 732.

⁶ D. Hadži, *J.*, 1956, 2725.

⁷ H. H. Jaffé, *J. Amer. Chem. Soc.*, 1955, **77**, 4448.

⁸ H. Goldschmidt and H. Schmid, *Ber.*, 1885, **18**, 2229.

Nuclear Magnetic Resonance Spectra.—The proton magnetic resonance (p.m.r.) spectra of the compounds were measured with a Varian DP 60 Spectrometer. About 2% hexadeuterio-dimethyl sulphoxide [(D₃C)₂SO] solutions were used for all compounds. 2,6-Dimethyl-4-nitrosophenol and 1,4-naphthaquinone monoxime methyl ether were sufficiently soluble in chloroform to allow their p.m.r. spectra to be obtained but the spectra were essentially the same in both solvents. Double- and triple-resonance techniques were used to confirm the proton chemical shifts and coupling constants. The p.m.r. results are summarised in Table 1.

TABLE 1

P.m.r. data results for the nitroso-compounds studied: (chemical shifts are given in p.p.m. from TMS)

Compound	Structure	Chemical shift of aromatic protons				Chemical shift of methyl protons		Chemical shift of hydroxyl proton	Coupling constants (c./sec.)
		(2)	(3)	(5)	(6)				
4-Nitrosophenol	(II)	6.63	7.68	7.68	6.63	—	—	*	$J_{2,3} = J_{5,6} = 10$
2,6-Dimethyl-4-nitrosophenol	(III)	—	7.12	7.58	—	1.82	—	1.84	$J_{3,5} = 3, J_{H-CH_3} = 1$
4-Nitroso-1-naphthol	(IV)	6.65	8.02	—	—	—	—	13.45	$J_{2,3} = 10$
1,4-Naphthaquinone monoxime methyl ether	(V)	6.58	7.85	—	—	4.18	—	—	$J_{2,3} = 10$

* Not observed.

Infrared Spectra.—A Perkin-Elmer model 21 infrared recording spectrophotometer with sodium chloride optics was used. The spectra of all compounds were recorded in dilute dimethyl sulphoxide solutions [(H₃C)₂SO]. The spectrum of 4-nitrosophenol was also recorded in chloroform solution. Infrared results are summarised in Table 2.

TABLE 2

Characteristic infrared bands (cm.⁻¹) of the nitroso-compounds studied

Compound	Structure	Solvent	Concentration	N—OH	Aromatic C=C	C=O
4-Nitrosophenol	(I)	DMS	0.1M	—	1505, 1585, 1595	1635
	(I)	CHCl ₃	0.1M	3550, 1020	Absent	1640
2,6-Dimethyl-4-nitrosophenol (III)	(I)	CHCl ₃	0.02M	3550, 995	Absent	1640
	(III)	DMS	0.1M	—	Absent	1620, 1640 *
4-Nitroso-1-naphthol ...	(IV)	DMS	0.1M	—	1485, 1600, 1605	1650
1,4-Naphthaquinone monoxime methyl ether	(V)	DMS	0.1M	—	1530, 1600	1650

* One of these bands may be due to a vinyl C=C vibration.

RESULTS AND DISCUSSION

Nuclear Magnetic Resonance Studies.—We shall consider first the expected p.m.r. spectra for species (I) and (II). In species (I) the C=N—O fragment is rigid and non-linear (comparing other =N— systems⁹ and several oximes¹⁰): hence protons (2), (6) and (3), (5) will not be equivalent. The expected p.m.r. spectrum will thus be rather complex, an ABCD or an ABKM pattern with four slightly different screening constants for the four protons and different coupling constants $J_{2,3}$, $J_{5,6}$, $J_{3,5}$, and $J_{2,6}$. In species (II) the protons (2), (6) and (3), (5) will be equivalent since the nitroso-group should be freely rotating and we would observe a simple AB (or AX) pattern.

If detectable amounts of the two forms (I) and (II) are both present the spectral pattern

⁹ L. C. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 3rd edn., 1960.

¹⁰ *Chem. Soc. Special Publ.*, No. 11.

would be a superposition of both spectra, or an averaged spectrum, depending upon the rate of exchange between the two forms. In either case the spectrum should be temperature-dependent.

Thus, we may expect one of the following three types of spectra from a dilute liquid solution of 4-nitrosophenol:

- (i) a complex spectrum arising from species (I).
- (ii) a simple AB spectrum arising from species (II).
- (iii) a complex temperature-dependent spectrum arising from an equilibrium between species (I) and (II).

A similar argument applies to 2,6-dimethyl-4-nitrosophenol.

4-Nitrosophenol. The p.m.r. spectrum of 4-nitrosophenol in $(D_3C)_2SO$ yields a simple AB pattern (Figure 1). The peaks are broader than usually observed in p.m.r. spectra

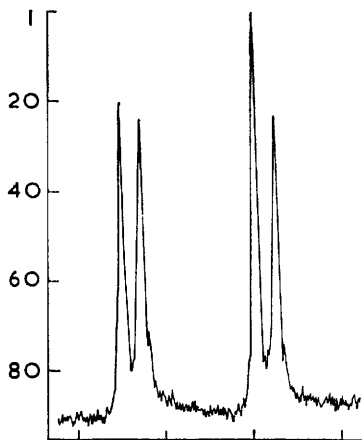


FIGURE 1. The 60 Mc./sec. proton magnetic resonance spectrum of 4-nitrosophenol in hexadeuteriodimethyl sulphoxide

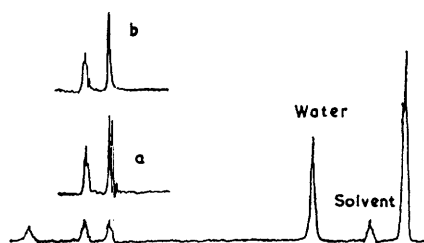


FIGURE 2. The 60 Mc./sec. (W) proton magnetic resonance spectrum of 2,6-dimethyl-4-nitrosophenol in hexadeuteriodimethyl sulphoxide

(a) Double resonance experiment, $W \pm 317$ c./sec. (b) Triple resonance, $W \pm 317$ c./sec. and $W \mp 28$ c./sec.

and the widths of the spectral lines are temperature-independent from 20 to 65° although slightly concentration-dependent. Adding deuteriochloroform to a dimethyl sulphoxide solution of 4-nitrosophenol broadens the peaks, especially the lower-field doublet (7.6 p.p.m.) which becomes a single broad peak. The shape of the lower peak is very dependent on the ratio of chloroform to $(D_3C)_2SO$, but is not temperature-dependent. Unfortunately the compound is not sufficiently soluble in chloroform to allow its p.m.r. spectrum to be recorded. These results suggest that 4-nitrosophenol is in the aromatic form, species (II). The broadening of the peaks in chloroform may be due to hydrogen bonding or some other exchange process occurring in solution.

2,6-Dimethyl-4-nitrosophenol. The p.m.r. spectra of this compound in $(D_3C)_2SO$ (Figure 2) and in chloroform show peaks due to two non-equivalent methyl groups separated by about 0.03 p.p.m. each peak being a doublet arising from a proton-methyl interaction of about 1 c./sec. The two ring protons are also non-equivalent, giving broad peaks separated by 0.46 p.p.m. Double- and triple-resonance experiments (Figure 2) show that $J_{3,5} = 3$ c./sec. and $J_{H-OH} = 1$ c./sec. This spectral pattern was temperature-independent.

It follows that in $(D_3C)_2SO$ solutions 2,6-dimethyl-4-nitrosophenol is present in the quinonoid form, species (III).

4-Nitroso-1-naphthol. For this compound we are unable to apply the above arguments to identify the species present in solution. However, the spectrum of 4-nitroso-1-naphthol is very similar to that of 1,4-naphthaquinone monoxime methyl ether (V), and we infer that the nitrosophenol exists in $(D_3C)_2SO$ solution as the quinonoid tautomer (IV). The spectrum is temperature-independent and hence it is unlikely that significant amounts of the phenolic form are present.

Infrared Studies.—The infrared spectra of the compounds in dilute chloroform and in $(D_3C)_2SO$ liquid solutions were studied to correlate n.m.r. and infrared data. No investigation was made of the temperature dependence of the infrared spectra.

4-Nitrosophenol. In dilute chloroform solutions the band at 3550 cm^{-1} has been assigned¹ to an N—OH stretching frequency and the 1025-cm^{-1} band, which is deuterium sensitive,⁶ also to an N—OH vibration. A strong band at 1648 cm^{-1} has been assigned to the carbonyl stretching frequency.⁶ Our results (Table 2) are in agreement with these and, together the significant absence of C=O aromatic frequencies, leave little doubt that in dilute chloroform solution 4-nitrosophenol exists in form (I). In dilute chloroform solutions the position of one peak was concentration-dependent (Table 2), namely, the peak near 1000 cm^{-1} . This must be due to changes in hydrogen bonding in the solution through the N—OH group.

In dimethyl sulphoxide $[(H_3C)_2SO]$ solution the situation is not so clear-cut. We observe the aromatic C=C frequencies which suggests that species (II) is present, in confirmation of the n.m.r. results. However, if the band at 1635 cm^{-1} is assigned to carbonyl absorption then, tentatively, both tautomers may be present, the quinonoid form not at a sufficiently high concentration to give a detectable signal with a 60 Mc./sec. n.m.r. spectrometer.

2,6-Dimethyl-4-nitrosophenol. The absence of aromatic C=C stretching frequencies in the infrared spectra supports the n.m.r. evidence that this compound is in the quinonoid form (III). The strong bands at 1620 and 1640 cm^{-1} must therefore arise from the C=O stretching frequency and perhaps a C=C vinyl stretching frequency. 2,6-Di-*t*-butyl-4-nitrosophenol gives similar p.m.r. and infrared results. It has been suggested from pK_a measurements in ethanol solution that this compound is in the quinonoid form.³

4-Nitroso-1-naphthol. The spectrum of this compound and of 1,4-naphthaquinone monoxime methyl ether are very similar, supporting our p.m.r. evidence that both compounds exist in the same form in dilute dimethyl sulphoxide $[(H_3C)_2SO]$ solutions. Previous infrared studies⁶ with 4-nitroso-1-naphthol have shown that this compound is in the quinonoid form in chloroform solutions.

Molecular Orbital Treatment.—From a simple Hückel M.O. theory it has been shown⁷ that the quinonoid form of 4-nitrosophenol is the more stable with respect to the π -electron system. However, this result appears to be most insensitive to a choice of integral values and varying the coulomb and resonance integrals over a wide range of values made no difference to the result. Since our p.m.r. and infrared results have shown that 4-nitrosophenol exists in different forms in two different solvents it would appear that forms (I) and (II) differ only slightly in energy. An accurate prediction of this small energy difference would appear to require a refined Hückel M.O. model.

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[Received, April 20th, 1965.]