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Nuclear Magnetic Resonance Studies of Nitrosonaphthols

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In solution, nitrosophenols are in tautomeric equilibrium[1–5] with quinone monoximes. Fischer *et al.*,[6] using nuclear magnetic resonance and infrared spectra, found that 4-nitrosophenol exists in the phenolic form in a dilute dimethyl sulfoxide solution. On the basis of nuclear magnetic resonance spectra, supported by UV and IR data, Norris and Sternhell[7] suggested that 4-nitrosophenol exists predominantly in the quinone monoxime form in an organic solvent. Jaffé[8] has calculated, by the molecular orbital method, that the oxime form of 4-nitrosophenol should be the more stable. As for nitrosonaphthols, Buraway[1] and his associates, on the basis of electronic spectra, have shown that 1-nitroso-2-naphthol exists in the oxime form only.

Hadži[9] investigated the monoximes of *p*-benzoquinone and 1,2-naphthoquinone (1-oxime and 2-oxime) by means of their infrared spectra. It has been found that the oxime formulation correctly represents the structure of these compounds in the solid state, and that this structure predominates also in their chloroform solutions. However, 2-nitroso-1-naphthol (1,2-naphthoquinone 2-oxime) seems to exist in the chelated nitroso form in solution in carbon tetrachloride. With the exception of a brief mention of the nuclear magnetic resonance spectrum of 4-nitroso-1-naphthol, the literature contains no reference to nuclear magnetic resonance investigation of the tautomeric nitrosonaphthols; this has prompted us to examine 1- and 2-nitrosonaphthols and their derivatives.

Experimental

Compounds. The 1-nitroso-2-naphthol which has been taken as the sample was a commercial product, mp 109—110°C, recrystallized from ligroin. The 2-nitroso-1-naphthol, mp 153—154°C, was synthesized by the method of Henriques.[10] 1-Methyloximino-2-naphthoquinone,[11] mp of 74—75°C. Found: C, 70.57; H, 4.79; N, 7.45%. Calcd for $C_{11}H_9O_2N$: C, 70.58; H, 4.81; N, 7.48%. 2-Methyloximino-1-naphthoquinone;[12] mp 89—90°C. Found: C, 70.60; H, 4.85; N, 7.51%. Calcd for $C_{11}H_9O_2N$: C, 70.58; H, 4.81; N, 7.48%. Both were prepared by the reaction of nitrosonaphthol with methyl iodide and were recrystallized from ligroin.

Nuclear Magnetic Resonance Spectra. The proton magnetic resonance spectra (PMR) of the compounds were measured by means of a JNM-3H-60 spectrometer; the results are summarized in Table 1.

Infrared Spectra. A Hitachi model EPI-S2 infrared recording spectrophotometer was used.

Results and Discussion

If detectable amounts of both isomeric forms, I and

Table 1. PMR results for the nitrosonaphthols
(Chemical shift are given in τ value)

Compound	Solvent	Concentration (%)	Chemical shift of aromatic protons			Chemical shift of hydroxyl proton	Isomer ratio (%)	
			(3)	(4)	(8)		oxime,	phenol
1-Nitroso-2-naphthol	Dimethylsulfoxide (DMSO)	5	3.52	2.21	1.18	—	100	—
	Hexamethylphosphoramide (HMPA)	5	3.72	2.27	1.12	−7.00	100	—
	$CDCl_3$	5	3.53	2.36	1.80	−7.73	100	—
	Dioxane	5	3.48	2.35	1.70	—	100	—
	DMSO-acetic acid (5%)	10	3.57	2.33	1.28	—	100	—
1-Methyloximino-2-naphthoquinone	DMSO	5	3.66	2.34	1.45	—	100	—
2-Nitroso-1-naphthol	DMSO	10	3.01	2.80	1.95	−3.7	100	—
	DMSO-dioxane (5%)	5	3.11 3.41	2.80 —	1.95	—	80	20
	DMSO-acetic acid (5%)	10	3.09 3.39	2.82 —	1.95	—	80	20
2-Methyloximino-1-naphthoquinone	DMSO	5	3.03	2.84	2.00	—	100	—

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[1] A. Buraway, M. Cais, J. T. Chamberlain, F. Liversedge, and A. R. Thompson, *J. Chem. Soc.*, **1955** 3727.

[2] W. R. Vaughan and G. K. Finch, *J. Org. Chem.*, **21** 1201 (1956).

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[9] D. Hadži, *J. Chem. Soc.*, **1956** 2725.

[10] R. Henriques and J. Ilinsky, *Ber.*, **18**, 706 (1885).

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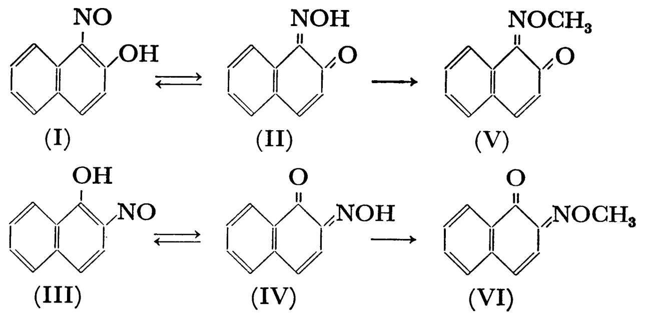

II or III and IV, were present, the spectral pattern would be either a superposition of both forms, or be composed of an independent pattern for each one, depending upon the rate of exchange between the two isomers. If there was any difference between the chemical shifts of the two hydroxyl protons (phenol and oxime) of each tautomer, it should be possible to establish the equilibrium isomer ratio from the signal area. Unfortunately, as is shown in Table 1, the hydroxyl proton gave only one broad peak. The PMR spectrum of both the methyl ethers of nitrosonaphthol, V and VI, are shown in Fig. 1. The difference in the spectra of V and VI is remarkable, particularly at the chemical shifts of the (3) and (4) protons. This difference may be attributed to the existence of the conjugation between the double bond and the carbonyl group. Both compounds, V and VI, seem to exist in the same quinoid form, for the wave numbers of the C=O bands (1670, 1660 cm^{-1} respectively) of V and VI in solution are not much different from those for quinones[13] (benzoquinone 1667, 1,2-naphthoquinone 1678 and 1,4-naphthoquinone 1675 cm^{-1}), and no nitroso group was detected by the Liebermann reaction.

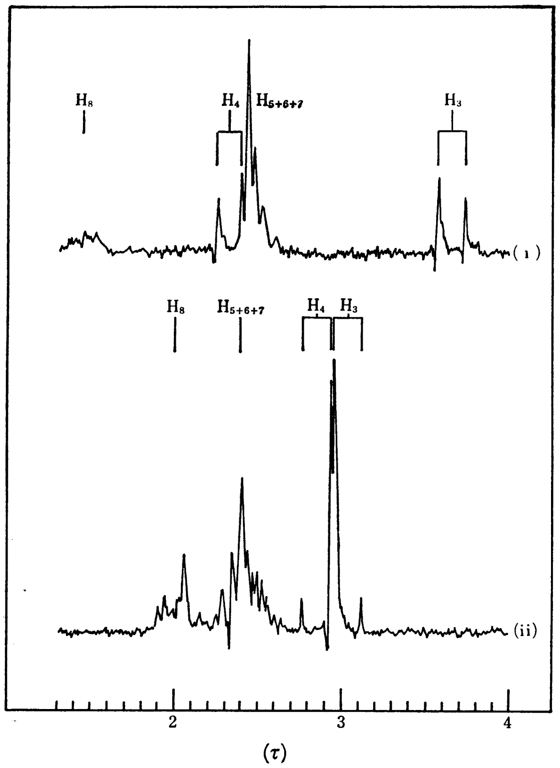

Fig. 1. NMR spectra of methyloximino-naphthoquinone in DMSO (5%), (18°C).
(i) 1-nitroso-2-naphthol (ii) 2-nitroso-1-naphthol

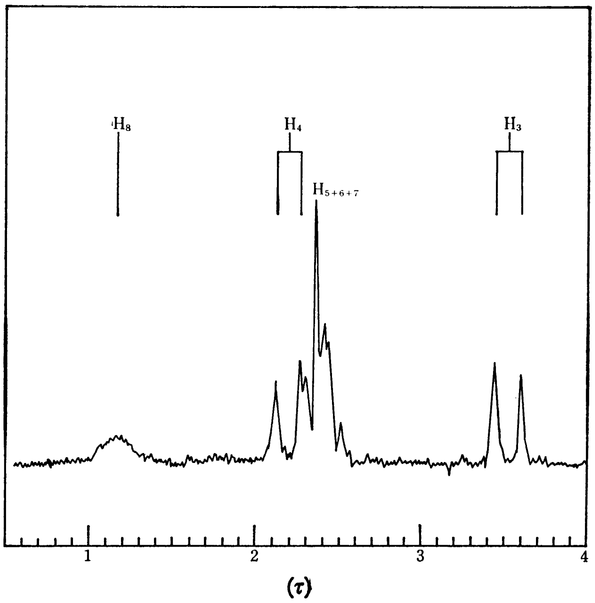

Fig. 2. NMR spectrum of 1-nitroso-2-naphthol in DMSO (5%), (20°C).

In 1-nitroso-2-naphthol, the aromatic protons at (3) and (4) show the AX pattern ($J_{3,4}=10$ Hz) and are very similar to the methyl ether protons, as is shown

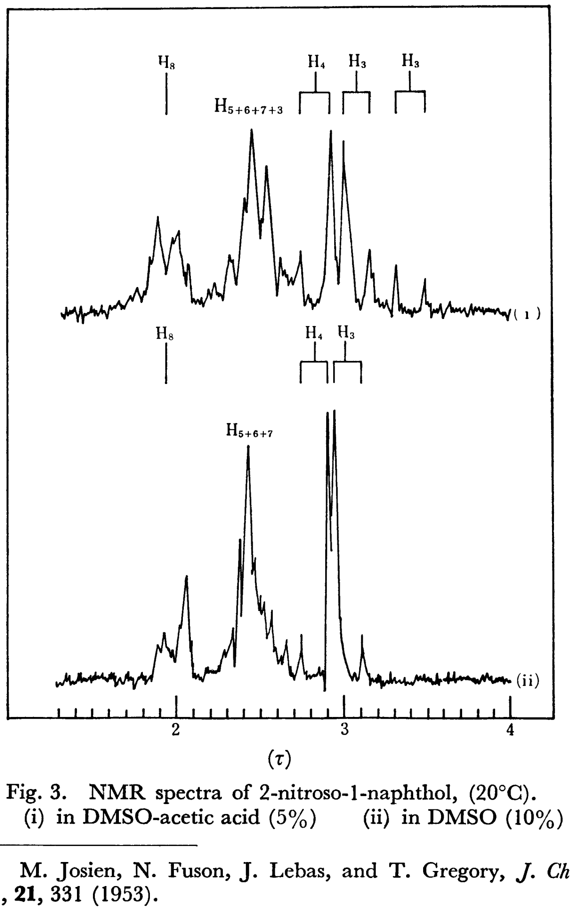

Fig. 3. NMR spectra of 2-nitroso-1-naphthol, (20°C).
(i) in DMSO-acetic acid (5%) (ii) in DMSO (10%)

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[13] M. Josien, N. Fuson, J. Lebas, and T. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

in Fig. 2. As has been mentioned above, Buraway[1] and Hadži[9] have shown that 1-nitroso-2-naphthol exists in the oxime form on the basis of only the electronic and infrared spectra. The chemical shift of the aromatic proton at (3) appeared in a very high field, (τ=3.48−3.72). These facts show that the oxime formulation (II) correctly represents the structure of 1-nitroso-2-naphthol. On the contrary, in 2-nitroso-1-naphthol the aromatic protons at (3) and (4) show a mixture of the AB ($J_{3,4}$=9.8 Hz) and AX ($J_{3,4}$=10 Hz) patterns depending upon the solvent, as is shown in Fig. 3.

This fact shows that detectable amounts of the two forms, III and IV, are both present. From the singal area, the equilibrium isomer ratio is determined to be as is shown in Table 1. In assigning the aromatic protons at (3) and (4) of nitrosonaphthols and their methyl ethers, we have decided that the downfield signal is a (4) proton by analogy with the results obtained with α,β-unsaturated cyclic carbonyl compounds. In a planar cycloalk-2-en-1-one with efficient conjugation between the double bond and carbonyl group, the C-3 proton is strongly deshielded relative to the C-2 proton by mesomeric electron withdrawal.[14]

It is worth noting that the chemical shift of the aromatic proton at (8) appeared in a very low field as a broad line. This seems to be a deshielding effect of the carbonyl and oxime groups of the α-position.

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[14] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Edition, Pergamon Press, Oxford (1969), pp. 188—189.