A Carbon-13 Relaxation and Chemical Shift Studies in 2- Methyl-8-Hydroxyquinoline

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Summary: Carbon-13 chemical shift and relaxation time studies have been carried out on 2-methyl-8-hydroxyquinolien(2- methyloxine). The chemical shifts studies are for a 90% solution in $CDCl_3$ at room temperature and are comparable to earlier work done in DMSO-d_6 solution. Spin-lattice relaxation time T_1 studies are for a neat compound in liquid state at 80°C. The T_1 range from 2.9 to 3.9 s for non-quaternary carbon atoms. Methyl carbon has T_1 of 6.6 s, while for quaternary carbon atom T_1's range is from 40 to 72 s. Various relaxation mechanism are suggested.

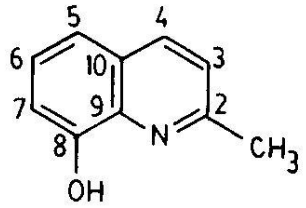
Introduction

Carbon-13 NMR on 8-hydroxyquinoline or oxine and its metal complexes has been reported by various workers [1-3]. There has been some C-13 chemical shift study in DMSO-d_6 solution of 2-methyl-oxine, but no relaxation data are available [3].

The present study is a continuation of work done in these laboratories [4] on quinoline, oxine, its derivatives and metal complexes. 2-Methyl-oxine solution is studied in $CHCl_3$ for carbon-13 chemical shifts while for relexation time T_1 a neat compound is used at elevated temperature (80°C). 2- Methyl-oxine differs from oxine in many ways as far as NMR study is concerned. It has four quaternary carbon atoms and a methyl group. Relaxation studies and chemical shifts behaviour is therefore different.

Experimental

2-Methyl-8-hydroxyquinoline or 2-methyl-8-quinolinol or 2-methyl- Oxine (I) was obtained from Merck. It was 99% pure. It was purified by filtering it in liquid form above 80°C as it had some carbon particles in it. For chemical shift studies a 90% solution in $CDCl_3$ (99% D from Merck) was used. TMS was used as internal standard for carbon-13 studies. Chemical shifts studies were done at room temperature.



(I)

For T_1 studies neat compound was used. It was sealed in a 10 mm od NMR tube by removing dissolved oxygen by freeze-pump-thaw method. (The compound was melted and freezed). It was sealed under vacuum. T_1 measurements were carried out using saturation recovery $(90^\circ\text{-HSP-t-}90^\circ)_n$ (SR) method. An autostacking programme was used for T_1 calculations which plots ln [(Io-It/Io]

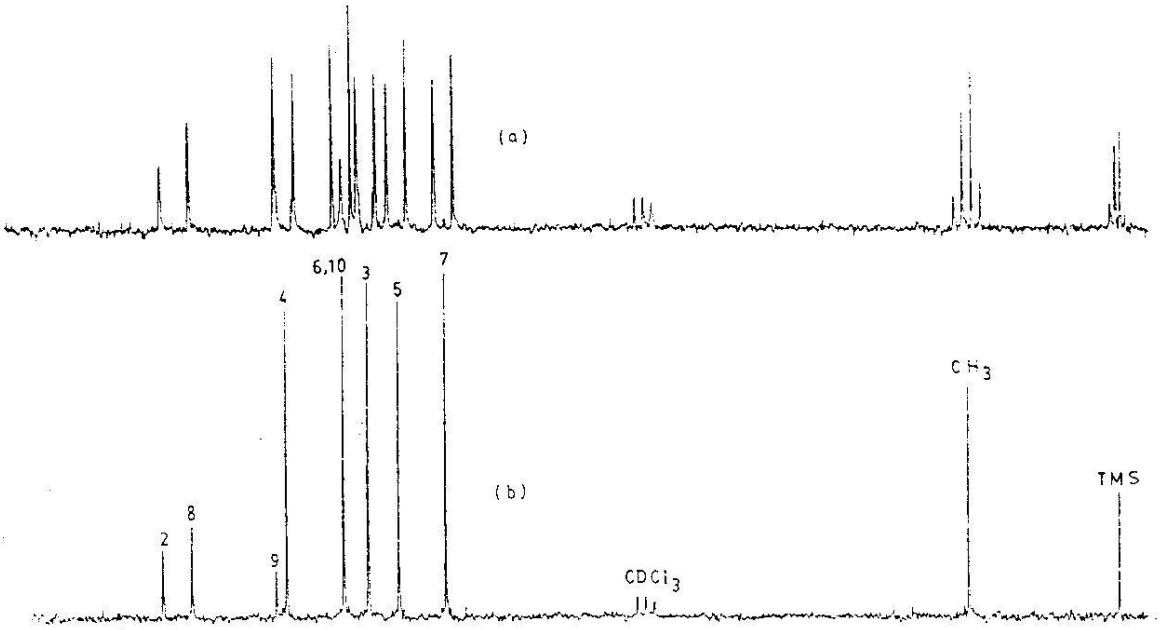


Fig. 1: Carbon-13 spectrum of a 90% solution in $CDCl_3$ of 2-Methyl-8-Hydroxyquinoline at room temperature. (a) Top: Off-Resonance C-13 spectrum showing methyl quartet and methine (CH) doublet. (b) Bottom: Complete proton noise decoupled C-13 spectrum.

Table-1: Carbon-13 chemical shifts in 2-methyl-8-hydroxyqyinoline (2-methyl-8-quinolinol or 2-methyl-oxine) at room tempe-rature in ppm relative to TMS as internal standard.(90% solution in $CDCl_3$)

Carbon atom number	Previous work* DMSO-d_6 solution	Present work** 90% $CDCl_3$ solution Room temperature
2	156.6	156.605
3	122.5	122.380
4	136.0	135.895
5	117.5	117.465
6	126.3	126.472
7	110.9	110.000
8	152.4	151.828
9	137.8	137.628
10	126.9	126.895
CH_3	24.6	24.576

*Ref. 3 on Bruker WH-90 pulsedf FT NMR spectrometer

** on JEOL FX-90Q pulsed FT NMR spectrometer.

= 1n Z against t where Io is height of signal at t > $5T_1$ and it is height of signal after a time t in SR pulse sequence [5]. C-13 spectra both in chemical shift and T_1 measurement were completely noise decoupled at 1kHz. The 90° pulse width for C-13 was 25 μs.

Calculation of NOE and other parameters were done by the same method as outlined in [4].

Results

The results of carbon-13 chemical shifts in 2-methyl-oxine (I) in 90% $CDCl_3$ solution at room temperature are summarized in Table-1. The spectrum is shown in Fig. 1. The assignment were checked by off resonance spectra.

Table-2: carbon-13 spin lattice releaxation Time T_1 for 2-Methyl- 8-Hydroxyquinoline (degassed) at 80°C in neat form using saturation recovery (SR) method*.

Carbon atom number	Spin-lattice-relaxation time T_1 (second)	η	T_1^{DD} (seconds)
2	47.9257 ± 0.0026	1.000	95.276
3	2.9450 ± 0.0178	1.666	3.512
4	3.8515 ± 0.0025	1.667	4.593
5	3.375 ± 0.0014	1.667	4.025
6	3.0465 ± 0.0099	1.571	3.855
7	3.1766 ± 0.0162	1.667	3.788
8	40.1796 ± 0.0004	1.333	59.923
9	72.4453 ± 0.0010	1.333	108.043
10	56.4472 ± 0.0013	1.000	112.217
CH_3	6.5529 ± 0.0006	1.000	13.027

* 90° pulse = 25 μs

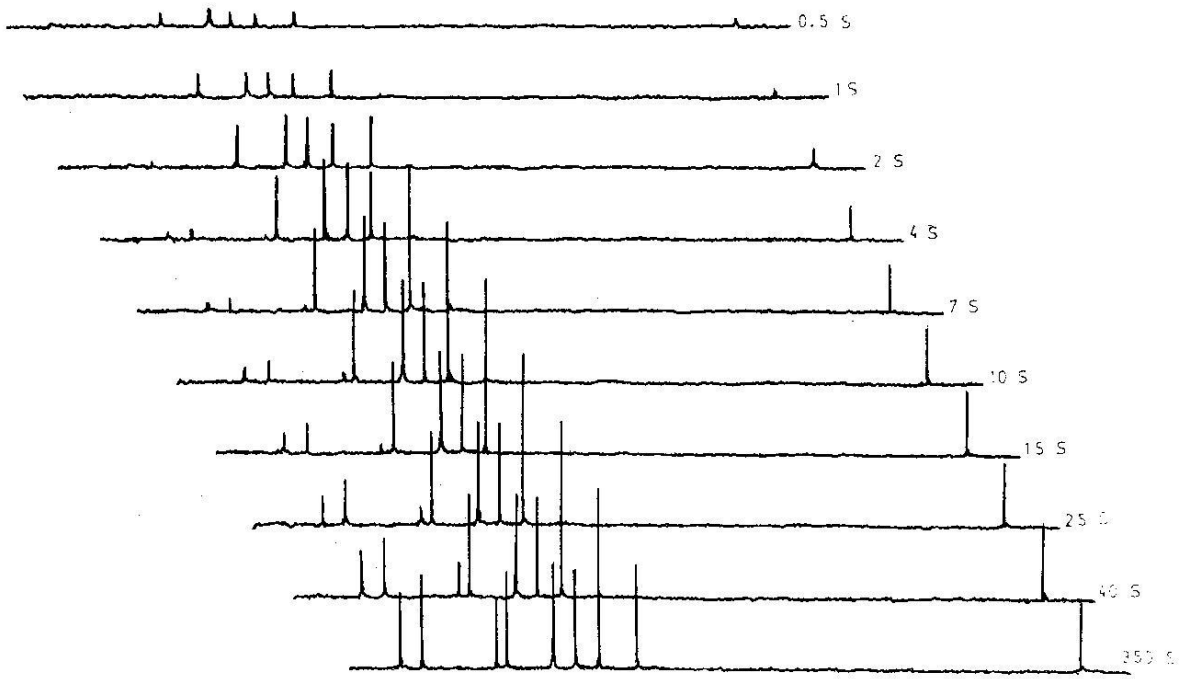


Fig.2: Carbon-13 saturation recovery (SR) T_1 spectra of neat 2-Methyl-8-Hydroxyquinoline at 80°C (90° pulse = 25 us).

The results of T_1 at 80°C of neat liquid sample are summarized in Table-2. The spectrum of T_1 measurement at various time interval t are shown in Fig. 2. For carbon-13 [4].

$$\eta_o = 0.5\,[\gamma^1H/\gamma^{13}C] = 1.988 \qquad (1)$$

$$T_1^{DD} = [\eta_o/\eta]T_1 \qquad (2)$$

η is calculated from the method outlined in [4]. The result of η is also given in Tabl 2. T_1^{DD} is calculated from Eq. (2) and the results of calculations are summarized in Tabl-2.

Discussion

The results of chemical shifts are in agreement with those of [3] with slight differences. This difference may be due to solvent used. In present case the solvent is $CDCl_3$, while Howie, Bosserman and Sawyer [3] used DMSO-d_6 as solvent. There is quite difference from oxine shifts [4] due to substitution of CH_3 group at position 2.

The T_1 results are done at 80°C for neat compound instead of doing it in solution. The compound melts before 80°C (m.p. 73°C) and is liquid at this temperature. Clearly dipole-dipole relaxation mechanism is the most effective relaxation mechanism for carbon atoms 3 to 7. The other mechanisms are involved in case of carbon atoms 2,8,9,10 and methyl carbon. These relaxation mechanisms may be spin rotation relaxation in case of quaternary carbon atoms, which do not have proton relaxing paths. Carbon number 8 and 2 are bonded to quadrupole oxygen and nitrogen respectively, thus providing additional relaxing path for these atoms. A detailed variable temperature work is necessary for these studies.

References

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