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NUCLEAR MAGNETIC RESONANCE STUDIES OF INTERNAL HYDROGEN BONDS IN NITROPHENOLS

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Badano zależność pomiędzy częstością absorpcji w widmach w podczerwieni a przesunięciem chemicznym w widmach magnetycznego rezonansu jądrowego (N.M.R.) dla protonu grupy OH w nitrofenolach. Badano również zależność pomiędzy przesunięciem chemicznym i stężeniem roztworów związków, które zawierają silne wewnątrzcząsteczkowe wiązanie wodorowe.

Исследована зависимость между частотой абсорбции в инфракрасных спектрах и химическим сдвигом в спектрах магнитного ядерного резонанса для OH-протона в нитрофенолах. Кроме того исследована зависимость между химическим сдвигом и концентрацией растворов соединений, в которых выступает сильная внутримолекулярная водородная связь.

The correlation between the infra-red frequencies and the N.M.R. chemical shift parameters of the OH-proton in nitrophenols was investigated. The dependence of the chemical shift on concentration in compounds containing strong intramolecular hydrogen bonds was also studied.

Allan, Reeves, and Strømme[1-3] correlated the change in chemical shift caused by formation of an intramolecular hydrogen bond in phenols with the frequency shift in the infra-red spectrum. The present authors investigated the chemical shifts of a number of intramolecularly hydrogen-bonded *o*-substituted nitrophenols: *o*-nitrophenol, 2,4-dinitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, and picric acid. For comparison we investigated the intramolecularly non-bonded *m*- and *p*-nitrophenols.

EXPERIMENTAL

Nuclear magnetic resonance data were determined with a 60 mc/s Varian spectrometer. Measurements were carried out in carbon tetrachloride solutions using cyclohexane as internal reference. Because of the low solubility of the compounds in carbon tetrachloride we investigated highly dilute solutions (0.05—0.005 moles/l.). Only *o*-nitrophenol was investigated at concentrations of 0.2—0.005 moles/l. Chemical shifts were measured by the usual side band technique. Shift measurements were usually reproducible to within 0.5 c/s. Experimental data are collected in Table 1.

Table 1

Concentration moles/l.		Chemical shift Δ(c/s)	Chemical shift τ (ppm)
o-Nitrophenol	0.20	556	—0.71
	0.10	556	—0.71
	0.05	555	—0.69
	0.02	554	—0.67
	0.01	554	—0.67
	0.005	554	—0.67
m-Nitrophenol	0.01	211	5.05
	0.0075	209.5	5.07
	0.005	208	5.09
p-Nitrophenol	0.0075	229	4.74
	0.005	227	4.78
2,4-Dinitrophenol	0.05	582	—1.14
	0.02	581	—1.12
	0.01	581	—1.12
2,5-Dinitrophenol	0.05	560	—0.77
	0.02	559	—0.76
	0.01	559	—0.76
2,6-Dinitrophenol	0.05	599	—1.42
	0.02	598	—1.41
	0.01	598	—1.41
Picric acid	0.05	463.5	0.84
	0.01	463	0.84

DISCUSSION

In agreement with the results obtained by Reeves and co-workers[1–3] we observed a similar correlation between the chemical shift of the intramolecularly hydrogen-bonded OH-proton and the OH- infra-red stretching frequency, i.e. the changes of τ_{OH} were nearly proportional to those of ν_{OH} (see Table 2). Only for picric acid did the result deviate from this relationship. The values of infra-red frequencies were taken from our earlier paper[4].

Table 2

Compound	Chemical shift τ_{OH} (ppm) (extrapolated to infinite dilution)	Infra-red wave numbers ν_{OH} (cm^{-1})
o-Nitrophenol	—0.67	3250
2,4-Dinitrophenol	—1.12	3210
2,5-Dinitrophenol	—0.76	3270
2,6-Dinitrophenol	—1.41	3170
Picric acid	+0.84	3100
m-Nitrophenol	+5.13	3615
p-Nitrophenol	+4.86	3615

Table 2 shows the monomer chemical shifts determined from the graphs in Figs. 1, 2 and 3. It can be seen that the chemical shift values τ for the intramolecular hydrogen-bonded species are much lower than those for the non-bonded *m*- and *p*-nitrophenols.

All compounds investigated show a single OH-resonance peak only, its position being dependent on concentration. As well known[5] rapid exchange of protons between hydrogen-bonded species results in an weighed average frequency. In solution, the lifetime of individual hydrogen-bon-

ded species is generally very short and we observe a single line. Its position depends on the proportion of polymers, dimers and monomers and hence on the concentration of the sample. As expected this dependence is almost undetectable in our compounds with strong intramolecular hydrogen bond (Fig. 1) in very dilute solutions ($c < 0.05$ moles/l.). Only for

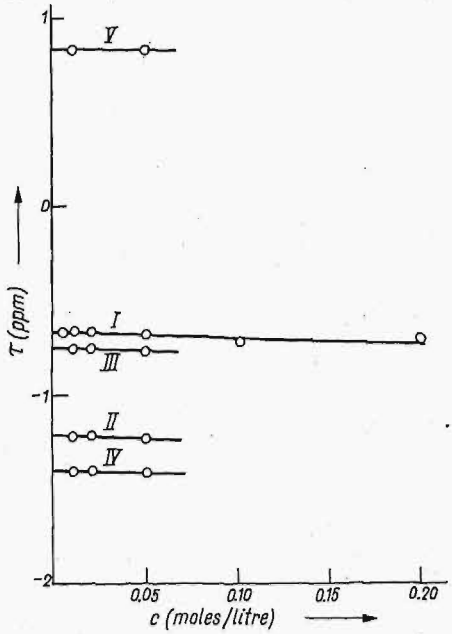

Fig. 1. *I* — o-nitrophenol, *II* — 2,4-dinitrophenol, *III* — 2,5-dinitrophenol, *IV* — 2,6-dinitrophenol, *V* — picric acid

o-nitrophenol, when more concentrated solutions could be investigated, we observed, a very slight dependence on concentration (Fig. 1, *I*).

A high dependence of τ on concentration for compounds with intermolecular hydrogen bond is also well known. This effect occurred in *m*- and *p*-nitrophenol spectra (Figs. 2, 3). The slopes (tang α) are 8.0 and 16.0, respectively.

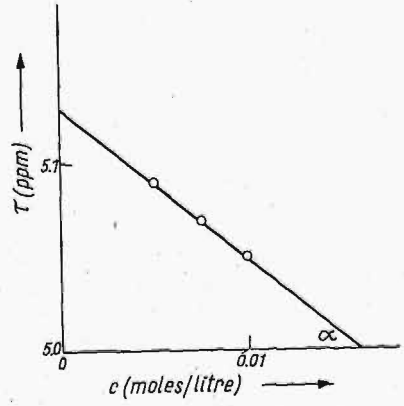

Fig. 2. *m*-Nitrophenol

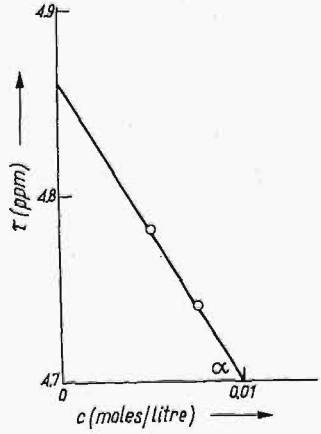

Fig. 3. *p*-Nitrophenol

It is also interesting that there is no difference in the infra-red OH--frequencies for *m*- and p-nitrophenols, whereas at infinite dilution the shifts τ are distinctly different: 5.13 and 4.86 ppm, respectively.

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BADANIA WIĄZANIA WODOROWEGO W NITROFENOLACH ZA POMOCĄ MAGNETYCZNEGO REZONANSU JĄDROWEGO

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Badano widma magnetycznego rezonansu jądrowego N.M.R. szeregu nitrofenoli: *o*-, *m*- i *p*-nitrofenoli, 2,4-, 2,5- i 2,6-dwunitrofenoli oraz kwasu pikrynowego.

Stwierdzono liniową zależność pomiędzy częstością absorpcji w widmach w podczerwieni a przesunięciem chemicznym protonu grupy OH w widmach magnetycznego rezonansu jądrowego nitrofenoli.

Badano zależność pomiędzy przesunięciem chemicznym i stężeniem roztworów i znaleziono, że w przypadku nitrofenoli z silnym wewnątrzcząsteczkowym wiązaniem wodorowym (tj. nitrofenoli z grupą lub grupami NO_2 w pozycji lub pozycjach *orto* do grupy OH) zależność taka w zakresie stężeń $< 0{,}2$ mola/litr jest prawie niewykrywalna, w przeciwieństwie do związków z wiązaniem wodorowym tylko międzycząsteczkowym, takich jak *m*- i *p*-nitrofenole, w przypadku których obserwujemy wyraźną zależność przesunięcia chemicznego od stężenia badanego roztworu.