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^{15}N NMR Study of Azo–Hydrazone Tautomerism of Some Water-soluble Dyes

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ABSTRACT

The ^{15}N NMR spectra of some water-soluble dyes and their intermediates were measured in natural abundance. Azo dyes derived by coupling to analogues of α-naphthol were found to exist in the hydrazone form, whereas dyes obtained by coupling to analogues of naphthylamine existed in the azo form. Within the range of dyes investigated, the azo–hydrazone tautomerism is concluded to depend on the structure of the coupling components.

1 INTRODUCTION

The azo–hydrazone tautomerism[1] of azo compounds is an important factor which influences the color of the dyes, and various analytical methods[2–12] have been developed to investigate this equilibrium. Of these methods, ^{15}N NMR[8–12] is thought to be the best way to investigate the equilibrium because of its wide chemical shift (high resolution) and straight reflection of the electronic states of the nitrogen atoms involved in the azo groups.

However, because of low sensitivity, most of the ^{15}N NMR studies have been carried out using ^{15}N-labelled compounds, and the structures used were relatively simple compared with those of commercially available azo dyes. In this study, the ^{15}N NMR spectra of some water-soluble azo dyes and their intermediates were measured in natural abundance and the structural dependency of azo–hydrazone tautomerism was determined.

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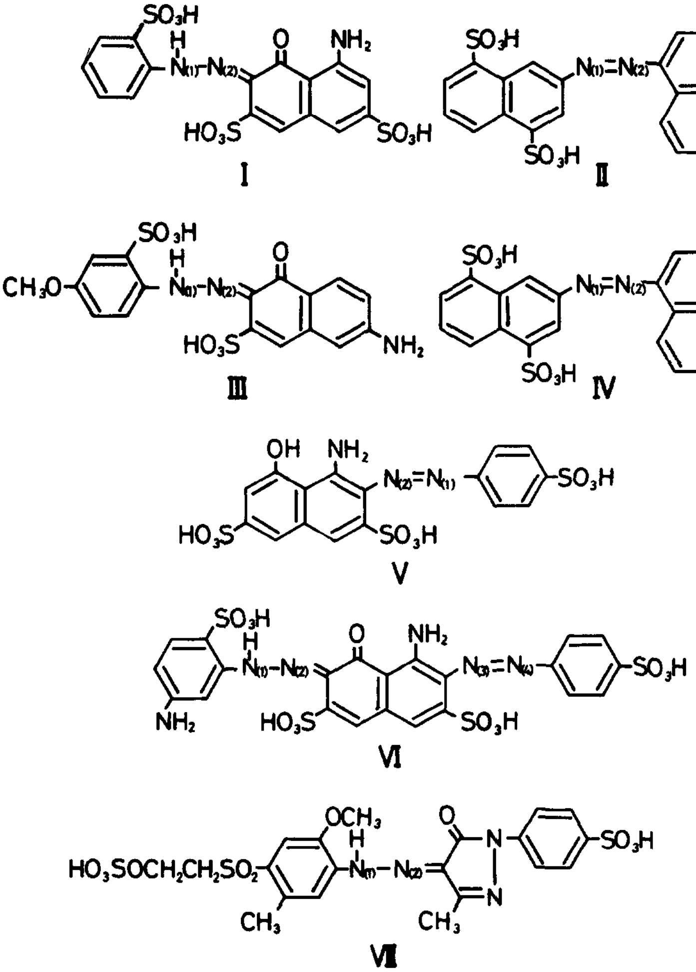
2 EXPERIMENTAL

The azo compounds **I–VII** (Scheme 1) were investigated in this study. They were synthesized by conventional azo-coupling reactions using technical grade reagents and were purified by recrystallization and by salting-out techniques.

The ^{15}N NMR spectra were measured on a JOEL GX-270 spectrometer at 27·2 MHz. Each compound was dissolved in 90% DMSO–10% DMSO-d6, to give a concentration of *c.* 1–5%. The ^{15}N chemical shifts were related to external nitromethane (0 ppm, 50% soln in DMSO-D6). Typical spectrometer conditions were: spectral width 20 000 Hz, pulse width 30°, pulse repeti-



Scheme 1

tion 3 s with proton noise decoupling. Each measurement was carried out at room temperature.

3 RESULTS AND DISCUSSION

The ^{15}N NMR spectra of compounds **I** and **II** are shown in Fig. 1. The chemical shifts of the amino groups in both of these compounds were about − 300 ppm, and they were detected as strong negative signals because of the negative nuclear Overhauser effect (NOE).

However, the chemical shifts of the azo groups were significantly different. In the case of compound **II**, two peaks with a positive phase, corresponding to two azo nitrogen atoms, were observed at 90 and 110 ppm respectively, and these values are very similar to that observed with azobenzene[13] (129 ppm), indicating that compound **II** exists in the azo form. On the other hand, the positive signal of one of the azo nitrogens showed a considerably lower shift (close to 0 ppm) in the case of compound **I**, and the signal of the other azo nitrogen was observed at −200 ppm with negative phase, which indicates proton attachment to the nitrogen atom.

From these results, it is concluded that compound **I** exists, in solution in dimethyl sulphoxide, in the hydrazone form, and that compound **II** exists in the azo form (as shown in Scheme 2).

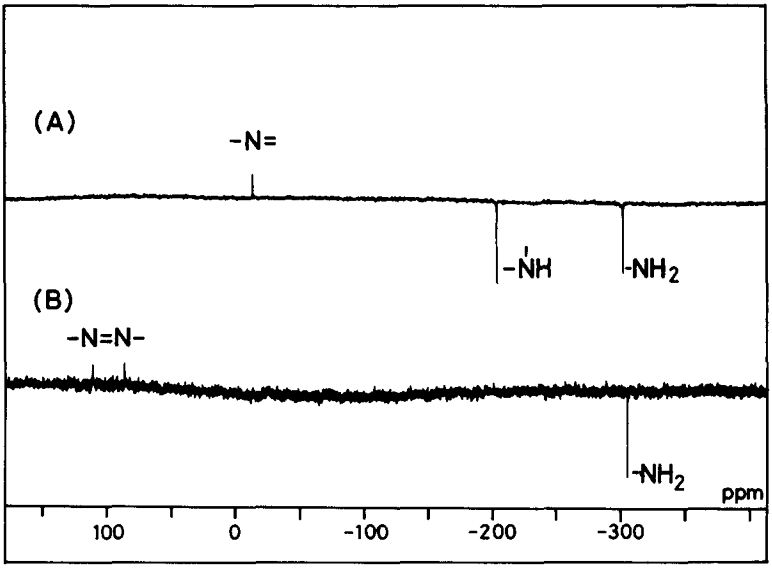
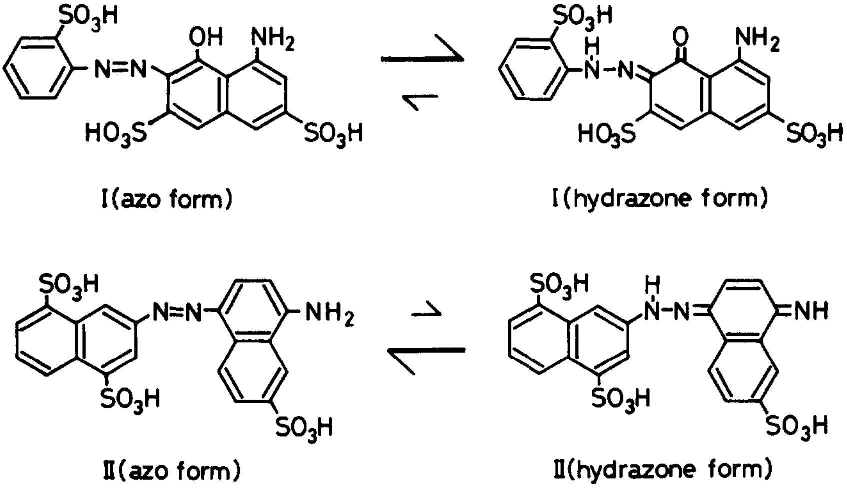


Fig. 1. 27·2 MHz ^{15}N NMR spectrum of compound I(A) and compound II(B).



Scheme 2

Table 1 gives the ^{15}N chemical shifts of compounds **I–VII**. By analogy with the above results for compounds **I** and **II**, compounds **III** and **VII** exist in the hydrazone form and compounds **IV** and **V** exist in the azo form. Those results are in agreement with those of Lyčka and co-workers[8,10–12] and the signal assignment was presumed from their data. Compound **VI** has two azo groups and, as expected from the results for compounds **I–V**, the azo group originating from coupling to *ortho* to the hydroxy group exists in the hydrazone form, and that originating by coupling *ortho* to the amino group exists in the azo form.

These results indicate that tautomerism in azo compounds **I–VI** can give the hydrazone or azo forms, depending on the nature of the coupler, and the presence within it of hydroxy or amino groups.

TABLE 1
^{15}N Chemical Shifts of Compounds I–VII in DMSO

Compound	δ (*N1*)	δ (*N2*)	δ (*N3*)	δ (*N4*)
I	−203·8	14·1	—	—
II	86·7	112·2	—	—
III	−195·1	−4·2	—	—
IV	74·7	107·3	—	—
V	54·0	127·2	—	—
VI	−196·2	−5·4	82·2	137·8
VII	−217·8	−25·7	—	—

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