Dyes and Pigments **15** (1991) 23–29

High-Field ^{1}H NMR Spectra of Some Azo Dyes Derived from 1- and 2-Naphthols

Antonín Lyčka, Josef Jirman & Miroslav Nečas

Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví, Czechoslovakia

(Received 24 January 1990; accepted 7 March 1990)

ABSTRACT

The ^{1}H NMR spectra of nine dyes derived from 1- and 2-naphthols have been measured at 400·13 MHz. The proton chemical shift assignments have been based on the application of 2D NMR spectra, mainly on the homonuclear shift-correlated H,H-COSY technique.

1 INTRODUCTION

In a previous paper[1] we reported on a concerted application of the two-dimensional high-field ^{1}H and ^{13}C NMR spectra in the assignment of ^{1}H and ^{13}C chemical shifts of some azo dyes containing amino or acetamido groups. We have also reported[2,3] data on the ^{13}C and ^{15}N NMR spectra of some azo dyes derived from 1- and 2-naphthol derivatives. These data were measured at a low field and unambiguous assignment of ^{1}H chemical shifts of aromatic protons was therefore impossible (except for protons in the peri position with respect to a substituent or in the ortho position to the hydroxy group) because of the strong overlap of the proton signals. To conclude the assignment of ^{1}H chemical shifts in some azo dyes derived from 1- and 2-naphthols in a similar manner to that described in Ref. 1 we present here the results of the analysis of the high-field ^{1}H NMR spectra measured for the compounds shown in Fig. 1.

Dyes and Pigments 0143-7208/90/$03·50
Printed in Great Britain

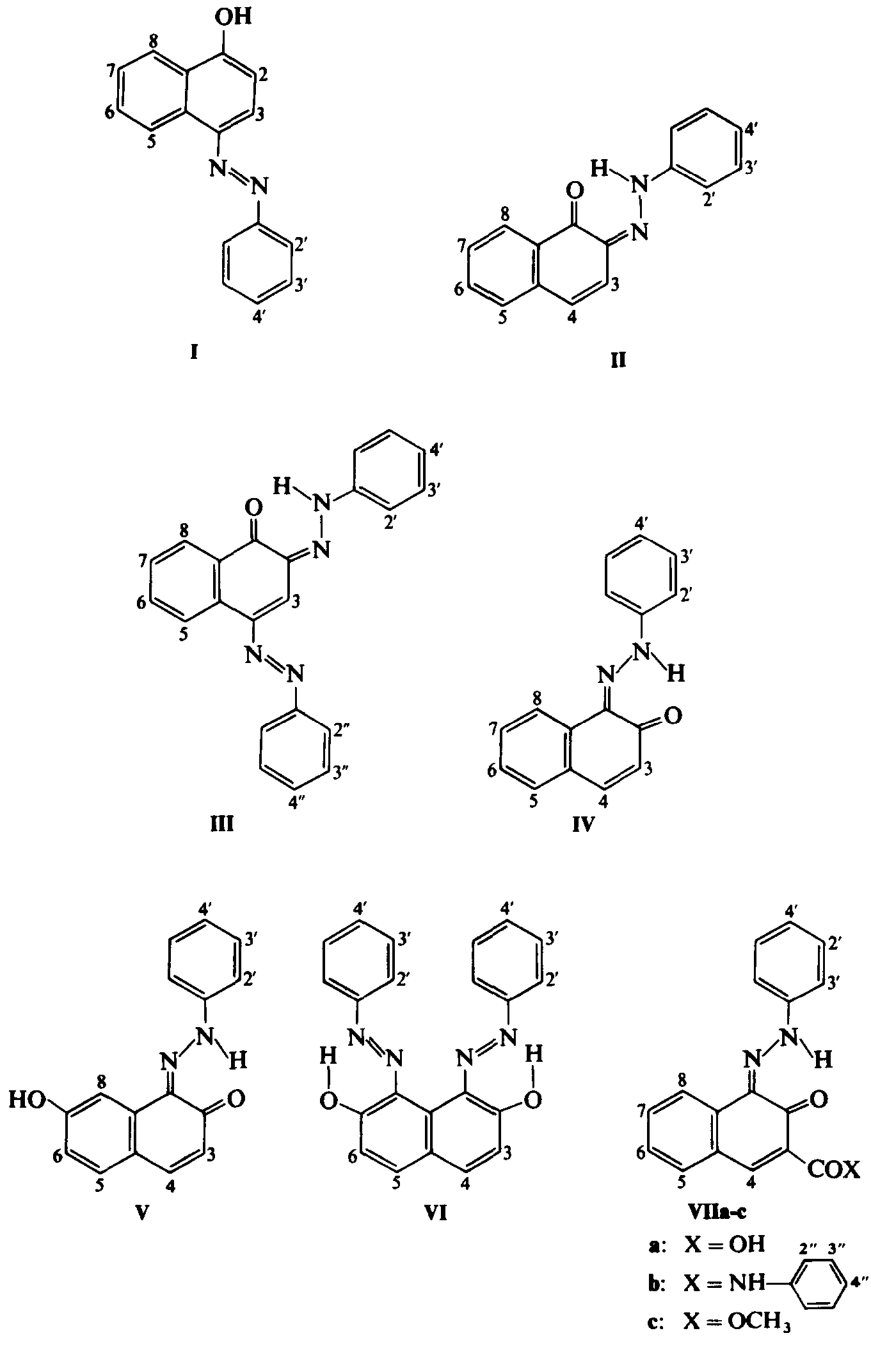

Fig. 1. Formulae of compounds measured. Only dominant tautomeric forms are shown.

2 EXPERIMENTAL

Compounds **I–VII** (Fig. 1) were prepared as described previously[2,3] and purified by column chromatography.

The ^{1}H and ^{13}C NMR spectra were measured at 400·13 and 100·61 MHz, respectively, on a Bruker AM400 spectrometer using 5 mm $^{1}H/^{13}C$ dual probe at 300 K.

The spectra were recorded for *c.* 5% (w/w) or saturated (in case of poor solubility of a dye) solutions in deuteriochloroform or hexadeuteriodimethyl sulphoxide. The chemical shifts were referenced to internal tetramethylsilane ($\delta = 0{\cdot}00$). One-dimensional ^{1}H and ^{13}C NMR spectra were measured in the standard manner at digital resolution of *c.* 0·2 Hz/point (^{1}H) and 1 Hz/point (^{13}C), respectively. The two-dimensional chemical shift-correlated experiments[4,5] were measured using the standard pulse sequences H,H-COSY (COSY[6]) and H,C-COSY (XHCORRDC[6]). Typical experimental conditions are given in Figs 2 and 3.

3 RESULTS AND DISCUSSION

The values of ^{1}H chemical shifts in compounds **I–VII** are summarized in Table 1.

Carbon–carbon connectivity in compounds **II** and **IV** was determined as a result of application of the SEMINA technique.[7] To the unambiguously assigned ^{13}C chemical shifts in these two compounds appropriate proton chemical shifts can readily be determined from the heteronuclear shift-correlated spectra, as demonstrated for compound **IV** in Fig. 2.

H,H-COSY were measured of other compounds, and connectivities of protons were determined. The application of this technique was especially important for the protons of the non-substituted naphthalene ring and for those of the phenyl groups in compound **III**. The H,H-COSY technique enabled the determination to be made of the mutual relation between neighbouring protons, but it was crucial to assign unambiguously at least one of these protons. Once this was established, the assignment of the remaining protons was then straightforward. For example, a sequence 8·89–7·75–7·63–8·27 for H(5)–H(8) for compound **I** was obtained, the signal at 8·89 being ascribed to the proton H(5), after comparison with $\delta(^{1}H) = 8{\cdot}90$ of H(8) in 1-phenylazonaphthalene.[8] The ^{1}H chemical shift of H(8) (8·27) in compound **I** is in good agreement with the value $\delta(^{1}H) = 8{\cdot}19$ for the same proton in 1-naphthol.[8] The protons H(2) and H(3) gave an AX system doublet, shifted to the higher field belonging to H(2). The same approach was used for other compounds. The assignment of protons H(2′)–H(4′) and

TABLE 1

^{1}H and Selected ^{13}C Chemical Shifts in Compounds I–VII

H No.[a]	Compound									
	I[b]	II[c]	III[c,d]	IV[b]	IV[c]	V[c]	VI[c]	VIIa[c,e]	VIIb[c,f]	VIIc[c,g]
2	7·02	—	—	—	—	—	—	—	—	—
3	7·99	7·19	7·74	6·96	6·81	6·70	6·93	—	—	—
4	—	6·98	—	7·99	7·63	7·62	7·64	8·88	8·97	8·34
5	8·89	7·53	8·71	7·82	7·53	7·49	7·64	7·75	7·73	7·57
6	7·75	7·57	7·78	7·50	7·33	6·91	6·93	7·48	7·43	7·32
7	7·63	7·44	7·58	7·65	7·51	—	—	7·69	7·62	7·53
8	8·27	8·40	8·51	8·58	8·49	7·92	—	8·46	8·43	8·37
NH/OH	[h]	16·10	16·31	15·81	16·05	16·27	15·67	16·56	16·89	16·81
2′	7·95	7·60	7·68	7·90	7·67	7·70	7·52	7·70	7·71	7·61
3′	7·61	7·42	7·47	7·59	7·43	7·46	7·26	7·52	7·50	7·41
4′	7·49	7·23	7·30	7·43	7·25	7·29	7·26	7·37	7·31	7·24
C—OH/C=O[i]	157·8	174·0	174·5	168·8	171·6	[j]	164·3	[j]	[j]	171·1
δ(C(2′))	122·6	117·6	118·1	119·0	118·3	[j]	120·9	[j]	[j]	118·3

[a] See Fig. 1.

[b] Hexadeuteriodimethyl sulphoxide.

[c] Deuteriochloroform.

[d] δ(H(2″)) = 8·00; δ(H(3″)) = 7·54; δ(H(4″)) = 7·49; [e] δ(COOH) = 13·67.

[f] δ(CONH) = 11·60; δ(H(2″)) = 7·81; δ(H(3″)) = 7·38; δ(H(4″)) = 7·13.

[g] $\delta(\mathrm{OCH_3})$ = 3·94.

[h] Not found.

[i] $\delta(^{13}\mathrm{C})$ of C—OH resp. C=O involved in tautomerism.

[j] Not measured because of very low solubility in deuteriochloroform.

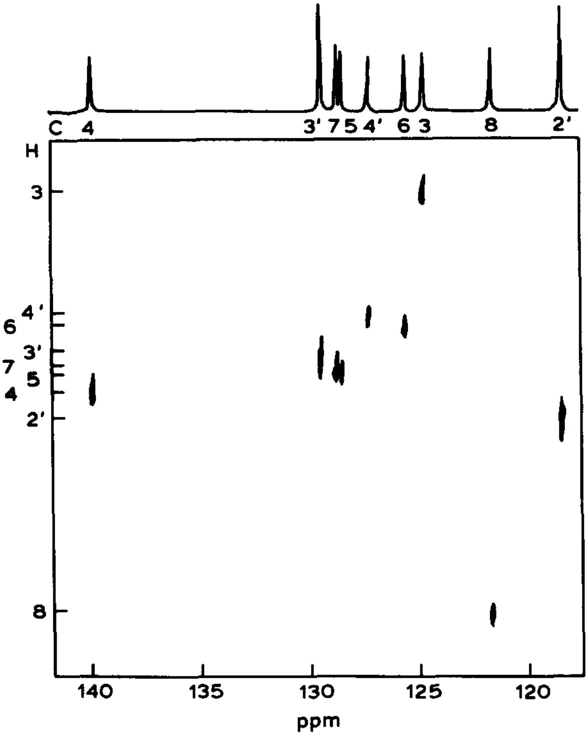

Fig. 2. H,C-COSY spectrum of compound **IV** in C^2HCl_3. Measuring conditions: relaxation time 2 s, spectral width SW1 = ±436·0 Hz, spectral width SW2 = 2439·0 Hz, data matrix 1024 × 128, 32 scans during 64 time increments (zero filled in F1), polarization time = refocusing time = 3·1 ms.

H(2″)–H(4″) in compound **III** is based on the analysis of the H,H-COSY spectrum (Fig. 3) and on the fact that the protons H(2″) are shifted downfield with respect to δ(H(2′)).

It is well known that ^{13}C and ^{15}N chemical shifts[1−3,9−12] are very useful in azo-hydrazone tautomerism characterization. The results reported here, together with those previously reported,[1] afford a suitable basis for consideration as to whether ^1H chemical shifts could also be used for such a purpose. The ^{13}C chemical shifts of C═O/C—OH and C(2′) are reported for comparison in Table 1. Higher values of δ(C═O/C—OH) and lower values of δ(C(2′)) correspond to a higher content of the hydrazone form.[2,9,11] From the results of the ^{13}C and ^{15}N NMR measurements, compound **I** exists essentially in the azo form,[3] whilst compounds **VIIa,b** are predominantly in the hydrazone form.[13] Other compounds measured exist as equilibrium mixtures of azo and hydrazone forms, the establishment of the equilibrium being fast on the NMR time scale. By analogy with $\delta(^{13}C)$,[2] ^1H chemical shifts of H(2′) and H(4′) were evaluated. The differences in the ^1H chemical

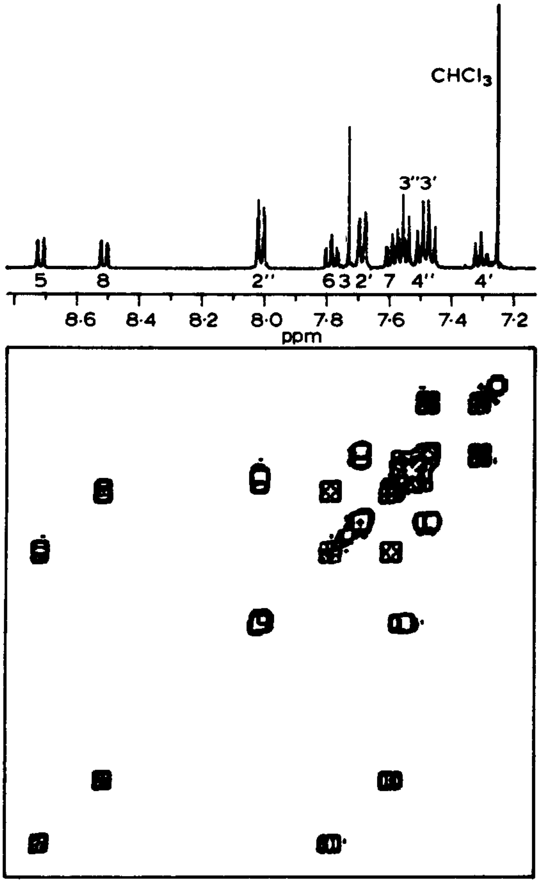

Fig. 3. H,H-COSY spectrum of compound **III** in C^2HCl_3. Measuring conditions: relaxation time 2 s, spectral width SW1 = ±339·7 Hz, spectral width SW2 = 679·4 Hz, data matrix 512 × 256, 8 scans during 128 time increments (zero filling in F1), 2 dummy scans.

shifts are relatively very small and the correlation between $\delta(^1H)$ and $\delta(C{=}O/C{-}OH)$ or $\delta(C(2'))$, respectively, is poor. NMR spectra of compound **IV** were measured in both deuteriochloroform and hexadeuteriodimethyl sulphoxide. According to $\delta(^{13}C)$, there is almost negligible change in the azo–hydrazone equilibrium on changing from $CDCl_3$ to DMSO as solvent, which is in contrast to the rather larger changes in ^1H chemical shifts. Solvation effects thus play a very important role. A similar situation was observed for some azo dyes containing amino or acetamido groups, these dyes existing exclusively in the azo form, under NMR experimental conditions. The differences in $\delta(^1H)$ of protons H(2') and H(4') resulting from the above change of solvent are up to 0·38 and 0·18 ppm, respectively, for 2-phenylazo-1-naphthylamine.[1] On the other hand, even in the ^{1}H NMR spectrum, the differences between $\delta(^1H)$ of the phenyl groups, in a different arrangement from the viewpoint of tautomerism, are clearly apparent, as can be seen in Fig. 3 for compound **III**. In this compound, the substituent in the 4-position exists completely in the azo form, whereas that in the 2-position is predominantly in the hydrazone form.

We conclude that ^{1}H chemical shifts of the phenyl group cannot be taken as values suitable for the assessment of azo–hydrazone tautomerism, in contrast to the $\delta(^{13}C)$ values. The reason for this is that protons are on the periphery of the dye molecules and are thus accessible to various effects, such as solvation, ring current effects, chemical shifts anisotropy, etc.

Haessner *et al.*[14] have reported a correlation of δ(H(3)) and δ(H(8)) in 1-substituted phenylazo-2-naphthols, with values of the equilibrium constant (K = [azo]/[hydrazone]) being influenced by substitution. Similar correlations may be found for other suitable protons, in particular compounds shown in Fig. 1.

Nevertheless, ^{1}H chemical shifts are very useful for the characterization of azo dyes derived from 1- and 2-naphthols.

REFERENCES

1. Lyčka, A., Jirman, J. & Hansen, P. E., *Dyes and Pigments*, **10** (1989) 259.
2. Lyčka, A., Šnobl, D., Macháček, V. & Večera, M., *Org. Magn. Reson.*, **15** (1981) 390.
3. Lyčka, A. & Macháček, V., *Dyes and Pigments*, **7** (1986) 171.
4. Ernst, R. R., Bodenhansen, G. & Wokaun, A., *Principles of Nuclear Magnetic Resonance in One and Two Dimensions.* Clarendon Press, Oxford, 1987.
5. Kessler, H., Gehrke, M. & Griessinger, C., *Angew. Chem., Int. Ed. Engl.*, **27** (1988) 490.
6. Bruker Software Library, DISR, 1985.
7. Hansen, P. E. & Lyčka, A., *Magn. Reson. Chem.*, **24** (1986) 772.
8. Freeman, H. S., Hsu, W. N., Esancy, J. F. & Esancy, M. K., *Dyes and Pigments*, **9** (1988) 67.
9. Kelemen, J., Moss, S., Sauter, H. & Winkler, T., *Dyes and Pigments*, **3** (1982) 27.
10. Lyčka, A., Šnobl, D., Macháček, V. & Večera, M., *Org. Magn. Reson.*, **16** (1981) 17.
11. Fedorov, L. A., *NMR Spectroscopy of Organic Analytical Reagents and Their Complexes with Metal Ions.* Nauka, Moscow, 1987, Chapter 1.
12. Mustroph, H., *Z. Chem.*, **27** (1987) 281.
13. Lyčka, A., Nečas, M., Jirman, J., Straka, J. & Schneider, B., *Collect. Czech. Chem. Commun.*, **55** (1990) 193.
14. Haessner, R., Mustroph, H. & Borsdorf, R., *J. Prakt. Chem.*, **327** (1985) 555.