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^{19}F-NMR Study of Azo–Hydrazone Tautomerism of Some Fluorine-Containing Azo Dyes

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ABSTRACT

The temperature dependence of the ^{19}F chemical shifts of some fluorine-containing azo dyes prepared by azo coupling with 2- and 4-fluorobenzenediazonium chlorides was measured in deuteriochloroform solutions. It is shown that ^{19}F chemical shifts can be used for azo–hydrazone content estimation in these compounds. The main advantage of this method consists in the high sensitivity of ^{19}F-NMR measurements which enables 1×10^{-4} M or even more dilute solutions of dyes to be used in a high-field NMR instrument.

INTRODUCTION

Nuclear magnetic resonance (NMR) is a powerful technique for the characterization of azo–hydrazone tautomerism.[1,2] The ^{1}H, ^{13}C and ^{15}N chemical shifts and the one-bond coupling constants $^{1}J(^{15}N_{\alpha}, H)$ and $^{1}J(^{15}N, ^{15}N)$ are used most frequently for quantitative purposes.[1–5] Relative low sensitivity of ^{13}C- and especially ^{15}N-NMR measurements is the main disadvantage of these methods. The measurement of $^{1}J(^{15}N_{\alpha}, H)$ coupling constants in ^{15}N-labelled dyes using ^{1}H-NMR represents a sensitive method but in many cases $^{1}J(^{15}N_{\alpha}, H)$ cannot be obtained because of fast intermolecular exchange of $N_{\alpha}H$ protons on the NMR time scale.[6]

It would be of great interest to have an NMR method that enables comparison to be made of azo–hydrazone content data obtained by means of electronic absorption spectra under similar concentration conditions. In this paper, the application of fluorine as a 'spy nucleus' is proposed for this

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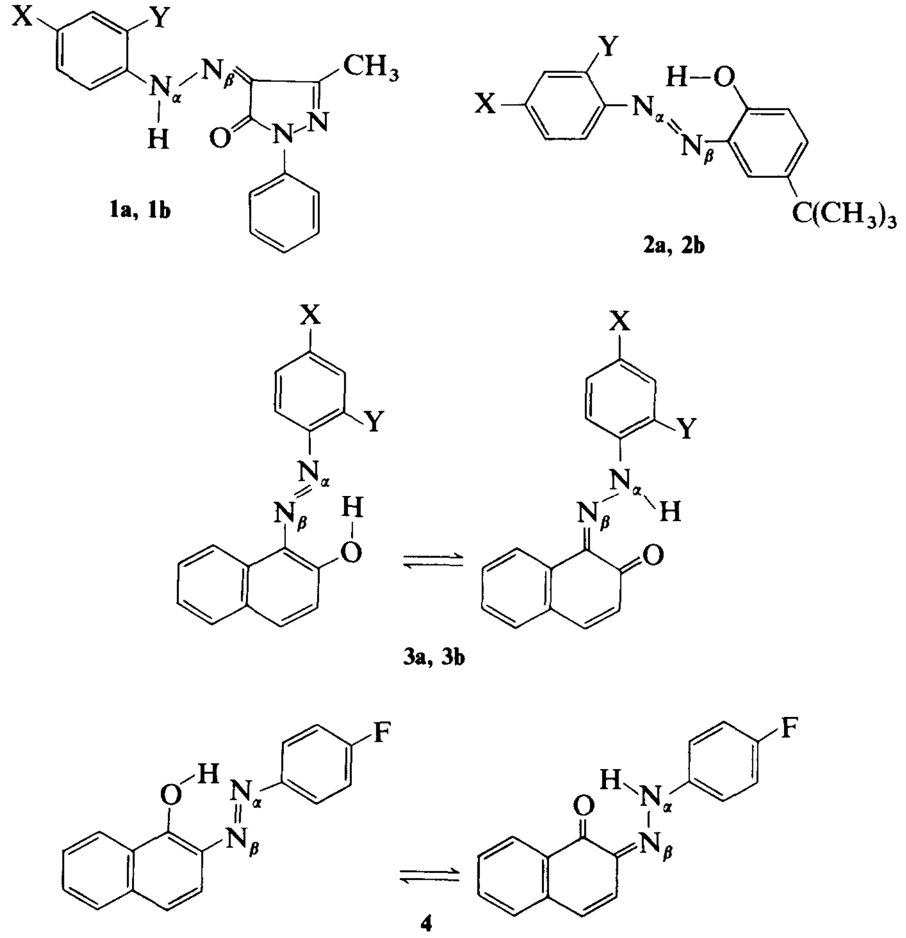
purpose because ^{19}F-NMR spectra can be measured in very dilute solutions, especially when high-field NMR instruments are used. Fluorine atoms are not directly involved in the tautomeric system and thus fast exchange of acidic protons on the NMR time scale cannot affect the measurement as in ^{1}H-NMR.

EXPERIMENTAL

The compounds **1a, 1b** (Scheme 1) were prepared by coupling using 4- and 2-fluorobenzenediazonium chlorides in acidic medium,[7] compounds **2a, 2b**



a: X = F; Y = H **b**: X = H; Y = F

Scheme 1

and **3a, 3b** in alkaline medium[8] and compound **4** by coupling in methylene chloride.[9] The products were crystallized from ethanol and their purities checked by ^{1}H-NMR and TLC.

The ^{19}F-NMR spectra were measured at 93·66 MHz using decoupling coils of a multinuclear tunable probe of a JEOL JNM-FX 100 spectrometer. The spectra were recorded for 5×10^{-2} M solutions in deuteriochloroform (C^2HCl_3). The ^{19}F chemical shifts were referred to internal $CFCl_3$ ($\delta = 0{\cdot}00$) and negative values denote upfield shifts. The measurement parameters were as follows: 10 mm NMR tube, spectral width 14 000 Hz, 32K memory (digital resolution better than 0·01 ppm/point), 45° pulse, pulse repetition 2s, proton–noise decoupling. The temperatures of the cooling or heating gas were measured with a thermocouple with an accuracy ± 1K. The ^{19}F-NMR spectra of 1×10^{-3} and 1×10^{-4} M solutions of compounds **1a**, **2a**, **3a** were taken at 376·5 MHz on a Bruker AM 400 using a 5 mm selective fluorine probe. The ^{15}N-NMR spectra of compounds **2a** and **3a** were measured at 40·55 MHz on a Bruker AM 400 at 300K at the natural abundance level of ^{15}N. Approximately 15% (w/w) solutions of compounds in C^2HCl_3 were used for the measurement. The ^{15}N chemical shifts, referred to external neat nitromethane (25% ^{15}N), of N_α and N_β in **2a** and N_β in **3a** were obtained under inverse gated decoupling (decoupler on during acquisition time): spectral width 15 000 Hz, 32K memory, 45° pulse, pulse repetition 6 s. The ^{15}N chemical shift of N_α in **2a** together with the $^1J(^{15}N_\alpha, H)$ coupling constant was measured using the INEPT pulse sequence[10] optimized for $^1J(^{15}NH) = 50$ Hz.

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the ^{19}F chemical shifts in compounds **1–4** and calculated hydrazone contents in **3** and **4**. The data given in Tables 1 and 2 were measured at 93·66 MHz using 5×10^{-2} M solutions of fluorine-containing compounds in deuteriochloroform. Two methods were used for the measurements. Fluorine chemical shifts of compounds **1a**, **2a**, **3a** and **4** were measured separately for each compound and appropriate temperature. The second method consists in the measurement of $\delta(^{19}F)$ for a mixture of standard azo compound, a compound representing a mixture of azo and hydrazone form and standard hydrazone compound (e.g. compounds **1b**, **3b** and **2b**). The latter method seems to be better because it eliminates small temperature differences (*vide infra*).

Model azo compounds (**1**) and hydrazone compounds (**2**), all with intramolecular hydrogen bonds, were taken as standards for azo–hydrazone content estimation (for reasons see Ref. 3, where non-fluorinated derivatives

TABLE 1
Temperature Dependence of the ^{19}F Chemical Shifts and Hydrazone Contents in Compounds **1a**–**3a** and **4** in Deuteriochloroform

Temp. (*K*)	**1a** $\delta(^{19}F)$	**2a** $\delta(^{19}F)$	**3a** $\delta(^{19}F)$	**3a** %[a]	**3a** K[b]	**4** $\delta(^{19}F)$	**4** %[a]	**4** K[b]
330	−116·76	−109·77	−113·00	46·2	0·859	−114·11	62·1	1·639
310	−116·60	−109·56	−113·03	49·3	0·972	−114·13	64·9	1·849
290	−116·47	−109·39	−113·03	51·4	1·058	−114·17	67·5	2·077
270	−116·38	−109·27	−113·07	53·4	1·146	−114·24	69·9	2·322
250	−116·24	−109·10	−113·18	57·1	1·331	−114·35	73·5	2·774
230	−116·10	−108·88	−113·38	62·3	1·653	−114·54	78·4	3·630

[a] Percentage of hydrazone form.
[b] K = [hydrazone form]/[azo form].

were used for a similar purpose). Hydrazone contents in compounds **3** and **4** were calculated according to eqn (1):

$$\% \text{ Hydrazone} = \frac{\delta(^{19}\mathrm{F})_2 - \delta(^{19}\mathrm{F})_X}{\delta(^{19}\mathrm{F})_2 - \delta(^{19}\mathrm{F})_1} \times 100 \qquad (1)$$

where $\delta(^{19}\mathrm{F})_X$ represented fluorine chemical shifts in compounds **3a**, **3b** and **4**. The thermodynamic data were calculated according to eqn (2):

$$-\frac{\Delta G^{\neq}}{RT} = \ln K = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} \qquad (2)$$

where K = [hydrazone form]/[azo form], and are shown in Table 3. Smaller standard deviations and better correlation coefficients were obtained for

TABLE 2
Temperature Dependence of the ^{19}F Chemical Shifts and Hydrazone Contents in Compounds **1b**–**3b** in Deuteriochloroform

Temp. (*K*)	**1b** $\delta(^{19}F)$	**2b** $\delta(^{19}F)$	**3b** $\delta(^{19}F)$	**3b** %[a]	**3b** K[b]
330	−132·94	−125·31	−129·47	54·5	1·198
310	−132·88	−125·18	−129·53	56·5	1·299
290	−132·81	−125·06	−129·60	58·6	1·415
270	−132·74	−124·91	−129·74	61·7	1·615
250	−132·61	−124·73	−129·85	65·0	1·857
230	−132·50	−124·53	−130·00	68·6	2·185

[a] % of hydrazone form.
[b] K = [hydrazone form]/[azo form].

TABLE 3

Thermodynamic Data for Azo–Hydrazone Tautomerism of Compounds **3a**, **3b** and **4** in Deuteriochloroform Calculated According to Equation (2)

	Compound[a]		
	3a	**3b**	**4**
$K^{b,c}$	0·97	1·30	1·85
$\Delta G^{\neq}$ (kJ mol^{-1})	0·07[d]	−0·67[d]	−1·58[d]
$\Delta H^{\neq}$ (kJ mol^{-1})	(3·93 ± 0·21)	(3·83 ± 0·07)	(4·85 ± 0·22)
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−(13·14 ± 0·75)	−(10·23 ± 0·08)	−(10·64 ± 0·83)
N^e	6	6	6
r^f	0·994 8	0·999 3	0·995 8

[a] See Scheme 1.
[b] K = [hydrazone form]/[azo form].
[c] 310 K.
[d] Calculated from $-\Delta G = RT \ln K$.
[e] Number of temperature measurements.
[f] Correlation coefficient.

compound **3b** in the case when $\delta(^{19}F)$ for both standard compounds and compound studied were measured together in one sample. Hydrazone contents in compounds **3a**, **3b** and **4** are slightly lower than those in compounds where fluorine is substituted by hydrogen.[3,4,11]

It was tempting to compare hydrazone contents obtained by the above method and other methods used for azo–hydrazone estimation. Therefore, we measured ^{15}N chemical shifts in compounds **2a** [$\delta(^{15}N_\alpha) = 63{\cdot}9$, $\delta(^{15}N_\beta) = 122{\cdot}6$] and **3a** [$\delta(^{15}N_\alpha) = -78{\cdot}7$, $\delta(^{15}N_\beta) = 47{\cdot}0$ together with $^1J(^{15}N_\alpha, H) = 46{\cdot}9$ Hz, all at 300 K]. The data for compound **1a** [$\delta(^{15}N_\alpha) = -207{\cdot}6$, $\delta(^{15}N_\beta) = -19{\cdot}8$] were taken from Ref. 12. Hydrazone content in compound **3a** was calculated according to procedures reported in Refs 4, 13 using $\delta(^{15}N_\alpha)$, $\delta(^{15}N_\beta)$ and $^1J(^{15}N_\alpha, H)$, and the following data were obtained: 52·5% (from N_α), 53·1% (from N_β) and 48·9% (from $^1J(^{15}N_\alpha, H)$. Comparing with data in Table 1 we can say that reasonable agreement in hydrazone contents was reached between ^{19}F-NMR and ^{15}N-NMR data.

High-field NMR instruments enable the use of much more diluted solutions for ^{19}F-NMR studies. Figure 1 shows a 376·5 MHz ^{19}F-NMR spectrum obtained on a Bruker AM 400 of a mixture of compounds **1a**, **2a** and **3a** measured as a 1×10^{-4} M solution in deuteriochloroform. This spectrum was obtained as a result of application of 250 pulses within *c*. 10 min. Of course, ^{19}F-NMR of even more dilute solutions can be measured in the case when more pulses are applied. It is important to say that practically no difference ($\leq 0{\cdot}01$) in ^{19}F chemical shifts was observed within the

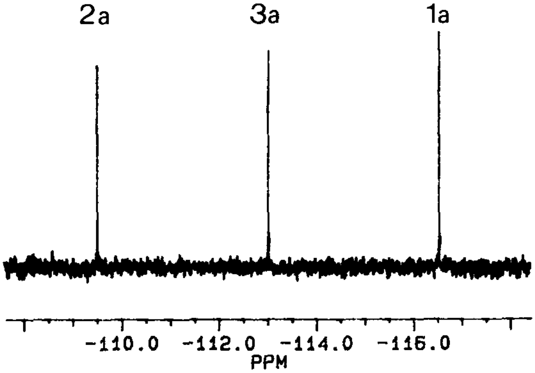
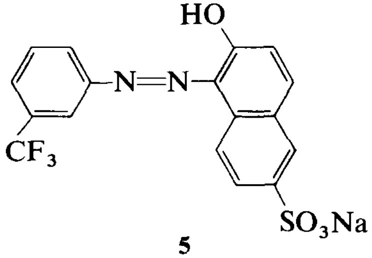


Fig. 1. ^{19}F-NMR spectrum of 1×10^{-4}M solution of compounds **1a**–**3a** in deuteriochloroform measured at 376·5 MHz in a 5-mm NMR tube using 250 45° pulses.

concentration range from 5×10^{-2} to 1×10^{-4}M in deuteriochloroform. From this fact it follows that association of dyes measured can be neglected in this range contrary to the situation reported in Ref. 14 in which ^{19}F-NMR characteristics [$\delta(^{19}F)$ and $w_{1/2}$] were successfully used as a proof of concentration-dependent aggregation of dye **5** in water.



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The above-mentioned standards can be used for azo–hydrazone content estimation in *ortho*-hydroxy derivatives only. For *para*-hydroxy compounds, standards without intramolecular hydrogen bonds should be used [compare the ^{19}F chemical shift in compound **2a** and those in 4-fluoro-4′-hydroxyazobenzene (−110·86) and 4-fluoro-4′-methoxyazobenzene (−111·06)].

REFERENCES

1. Fedorov, L. A., *NMR Spectroscopy of Organic Analytical Reagents and Their Complexes with Metal Ions*. Nauka, Moscow, 1987, Chapter I.
2. Mustroph, H., *Z. Chem.*, **27** (1987) 281.
3. Lyčka, A., Šnobl, D., Macháček, V. & Večeřa, M., *Org. Magn. Reson.*, **15** (1981) 390.

4. Lyčka, A., Šnobl, D., Macháček, V. & Večeřa, M., *Org. Magn. Reson.*, **16** (1981) 17.
5. Lyčka, A., Jirman, J. & Podstata, J., *Dyes and Pigments*, **8** (1987) 465.
6. Lyčka, A. & Mustroph, H., *J. Prakt. Chem.*, **331** (1989) 11.
7. Michaelis, A. & Schäfer, A., *Justus Liebigs Ann. Chem.*, **407** (1915) 259.
8. Schündenhütte, H. K., in *Methoden der Organischen Chemie (Houben-Weyl)*, ed. R. Stroh, Vol. 10/3. Stuttgart, Thieme, 1965.
9. Bredereck, K. & Karaca, S., Ger. Offen. 2931807 (1981).
10. Morris, G. A., *J. Am. Chem. Soc.*, **102** (1980) 428.
11. Lyčka, A. & Macháček, V., *Dyes and Pigments*, **7** (1986) 171.
12. Lyčka, A., Jirman, J. & Liptaj, T., *Coll. Czech. Chem. Commun.*, **52** (1987) 727.
13. Lyčka, A. & Šnobl, D., *Coll. Czech. Chem. Commun.*, **46** (1981) 892.
14. Skrabal, P., Bangerter, F., Hamada, K. & Iijima, T., *Dyes and Pigments*, **8** (1987) 315.