Dyes and Pigments **10** (1989) 259–268

Two-dimensional ^1H- and ^{13}C-NMR Spectra of some Azo Dyes Containing Amino or Acetamido Groups

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(Received 17 March 1988; accepted 29 April 1988)

ABSTRACT

The ^1H- and ^{13}C-NMR spectra of 12 azo dyes containing amino or acetamido groups have been measured. Two-dimensional H,H-COSY, NOESY, H,C-COSY and COLOC spectra and one-dimensional selective INEPT spectra have been used in the assignment of ^1H and ^{13}C chemical shifts. Hydrogen bonding has also been studied in these compounds.

1 INTRODUCTION

About 15% of azo dyes[1] are prepared by coupling diazonium salts with anilines and naphthylamines as the passive components. The coupling products can be very well characterized by their ^1H-,[2] ^{13}C- and ^{15}N-NMR spectra.[3,4] Minimal temperature dependence of $\delta(^{15}N)^3$ and $^1J(^{15}N^{15}N)^3$ allows a conclusion that these compounds exist practically fully in their azo forms in a broad temperature range, in deuteriochloroform or hexadeuteriodimethyl sulphoxide solutions, under NMR measurement conditions. It is very difficult to assign unambiguously all ^{13}C and ^1H chemical shifts at a

Dyes and Pigments 0143-7208/89/$03·50 © 1989 Elsevier Science Publishers Ltd, England. Printed in Great Britain

low magnetic field ($\leq 2{\cdot}35$ T). High-field (≥ 7 T) NMR measurements and application of two-dimensional NMR spectroscopy[5,6] should provide unambiguous assignment of both ^1H and ^{13}C chemical shifts in such azo dyes.

The aim of this work was to assign by two-dimensional NMR methods ^1H and ^{13}C chemical shifts in 12 azo dyes containing amino or acetamido groups, in order to complete and/or inspect the previously published data.[3] Unambiguous assignments of both ^1H and ^{13}C chemical shifts will serve for better understanding of spectral and physical properties of these compounds.[7,8] Furthermore, ^1H and ^{13}C chemical shifts can be used to gauge the hydrogen-bond structure of these compounds.

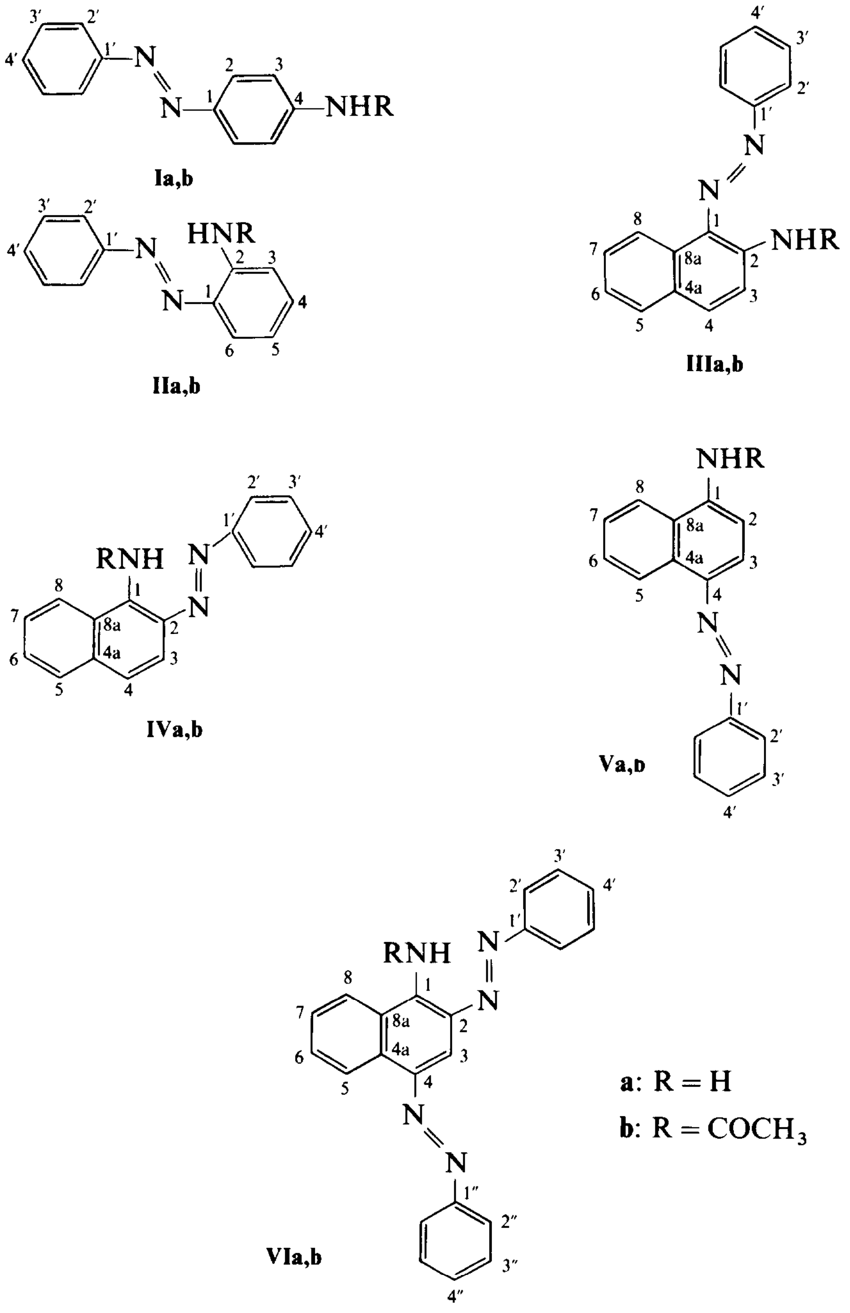
2 EXPERIMENTAL

Compound **Ia** (Scheme 1) was prepared from the corresponding triazene by a rearrangement in acidic medium.[9] Compound **IIa** was isolated by column chromatography as a by-product from crude **Ia**. Compounds **IIIa**, **Va** and **VIa** were prepared by coupling benzenediazonium chloride with naphthylamines.[9] Compound **IVa** was obtained by coupling benzenediazonium fluoroborate with 1-naphthylamine in methylene chloride.[10] Compounds **Ib**–**VIb** were prepared by acetylation using acetic anhydride.[11]

^1H- and ^{13}C-NMR spectra were measured at 400·13 MHz and 100·61 MHz, respectively, using a Bruker AM 400 spectrometer. The spectra were recorded for *ca.* 15% or saturated (in case of poor solubility) solutions in hexadeuteriodimethyl sulphoxide ($[^2H_6]$-DMSO) or deuteriochloroform (C^2HCl_3) at 300 K. The deuterated solvents were used as internal lock substances. The ^1H and ^{13}C chemical shifts were referred to the signal of solvent ($[^2H_6]$-DMSO: $\delta(^1H) = 2{\cdot}55$, $\delta(^{13}C) = 39{\cdot}6$) or internal tetramethylsilane in C^2HCl_3 ($\delta = 0{\cdot}00$). One-dimensional ^1H- and ^{13}C-NMR spectra were measured in a standard manner at digital resolution *ca.* 0·2 Hz/point (^1H) and 1 Hz/point (^{13}C), respectively. The measurement conditions of two-dimensional H,H-COSY, NOESY, H,C-COSY and COLOC were described in Ref. 12 (they were slightly modified when necessary). The one-dimensional selective INEPT spectra were measured according to Ref. 13, measurements being optimized for $^3J(^{13}CH)$. These are in the range 4–12 Hz according to Ref. 14.

3 RESULTS AND DISCUSSION

The values of ^1H and ^{13}C chemical shifts in compounds **Ia,b**–**VIa,b** are collected in Tables 1–4. The ^1H chemical shifts were, in general, assigned



Scheme 1.

TABLE 1

^1H Chemical Shifts in Compounds **Ia–VIa** and **Ib–VIb**

Compound	*Proton no.*										
	2	*3*	*4*	*5*	*6*	*7*	*8*	*2'*	*3'*	*4'*	*NHR*[c]
Ia[a]	7·85	6·72	—	—	—	—	—	7·89	7·51	7·43	4·04
Ia[b]	7·77	6·77	—	—	—	—	—	7·82	7·55	7·46	6·18
IIa[a]	—	6·49	7·02	6·68	7·79	—	—	7·73	7·31	7·23	5·71
IIa[b]	—	7·04	7·29	6·76	7·82	—	—	7·99	7·58	7·48	7·14
IIIa[a]	—	6·75	7·57	7·26	7·28	7·51	8·85	7·86	7·45	7·33	7·38
IIIa[b]	—	7·23	7·81	7·78	7·36	7·58	8·80	7·98	7·58	7·45	8·90
IVa[a]	—	7·88	7·13	7·65	7·42	7·30	7·77	7·79	7·40	7·32	6·34
IVa[b]	—	8·14	7·28	7·87	7·65	7·65	8·73	8·17	7·62	7·50	8·04
Va[a]	6·63	7·86	—	9·01	7·56	7·41	7·63	7·95	7·46	7·36	4·43
Va[b]	7·03	8·14	—	9·13	7·76	7·61	8·43	8·04	7·59	7·45	7·11
VIa[b]	—	8·42	—	9·00	7·84	7·70	8·70	[d]	[d]	[d]	8·32
Ib[b,e]	7·93	7·87	—	—	—	—	—	7·90	7·62	7·58	10·38
IIb[a,f]	—	8·62	7·40	7·10	7·78	—	—	7·80	7·49	7·47	10·04
IIb[b,g]	—	8·34	7·56	7·25	7·75	—	—	8·07	7·66	7·63	10·14
IIIb[a,h]	—	8·83	7·81	7·73	7·44	7·55	8·81	7·84	7·53	7·49	12·84
IIIb[b,i]	—	8·72	8·16	8·03	7·62	7·73	8·89	8·14	7·73	7·67	12·30
IVb[b,j]	—	8·66	8·03	7·93	7·55	7·67	8·81	8·01	7·67	7·61	12·01
Vb[b,k]	8·09	7·92	—	9·02	7·81	7·76	8·35	8·09	7·69	7·64	10·25
VIb[b,l]	—	8·17	—	9·02	7·92	7·86	8·38	[m]	[m]	[m]	10·55

[a] C^2HCl_2.

[b] $[^2H_6]$-DMSO.

[c] R = H or $COCH_3$ (see Scheme 1).

[d] 8·12; 7·58; 7·52 or 8·04; 7·63; 7·52.

[e] $\delta(COCH_3) = 2{\cdot}16$.

[f] $\delta(COCH_3) = 2{\cdot}20$.

[g] $\delta(COCH_3) = 2{\cdot}27$.

[h] $\delta(COCH_3) = 2{\cdot}20$.

[i] $\delta(COCH_3) = 2{\cdot}30$.

[j] $\delta(COCH_3) = 2{\cdot}24$.

[k] $\delta(COCH_3) = 2{\cdot}32$.

[l] $\delta(COCH_3) = 2{\cdot}38$.

[m] 7·65–8·15 for both H(2')–H(4') and H(2'')–H(4'').

TABLE 2
^{13}C Chemical Shifts in Compounds **Ia** and **IIa**

Carbon no.	*Compound*			
	Ia[a,c]	**Ia**[b,c]	**IIa**[a]	**IIa**[b]
1	145·3	143·3	136·7[e,g,i]	135·9[e,g,i]
2	125·0	125·5	142·8[f,h]	145·1[f,h]
3	114·5	114·5	116·8[g,i]	117·2[g,i]
4	149·5	149·5	132·0	132·6
5	—	—	117·0[e]	115·7[e]
6	—	—	127·2[f]	125·5[f]
1′	152·8	152·7	152·6	152·6
2′	122·2	122·1	121·9	122·1
3′	128·9	129·4	128·8	129·2
4′	129·7	129·6	129·7	129·9

[a] C^2HCl_3.
[b] $[^2H_6]$-DMSO.
[c] Data from Ref. 21.
[d–i] Most important correlations in COLOC spectrum via ^3J(CH): H(2)[d]; H(3)[e]; H(4)[f]; H(5)[g]; H(6)[h]; NH_2[i].

TABLE 3
^{13}C Chemical Shifts in Compounds III[a]–VIa

Carbon no.	*Compound*						
	IIIa[a]	**IIIa**[b]	**IVa**[a]	**IVa**[b]	**Va**[a]	**Va**[b]	**VIa**[b]
1	127·0[c,i]	125·3[d,i]	141·6	144·2[i]	146·2[i]	150·4[i]	148·3[d]
2	138·4[e]	140·2[e,f]	132·5[e]	131·3[e]	109·0[j]	107·6	129·9
3	119·5	120·1	121·5	120·4	113·9	112·5	104·2
4	133·6	133·8	117·8	116·4[f]	140·3[c,f]	137·2[c,f]	137·0[f]
4a	127·4[g,i]	126·5[d,g,i]	135·6[i]	135·6[i]	133·1[i]	133·5[i]	133·8[d,g,i]
5	128·0	128·1	128·6[e]	128·3[e]	124·0	122·9	123·3
6	123·2	122·8	128·1	128·5[i]	127·0[i]	127·5[i]	129·6
7	127·6	127·6	125·3	125·2	125·2[f]	124·4[f]	125·8[f]
8	122·1	121·0	121·9	124·1	120·5	122·8	124·2
8a	134·8[e,f]	134·3[e,f,h]	124·1[e]	124·2[e,f]	122·3[c,f,j]	121·5[c,f]	123·5[f]
1′	153·7	153·3	153·4	153·1	153·6	153·4	[k]
2′	121·9	121·4	122·1	122·1	122·6	122·0	[k]
3′	129·1	129·3	129·0	129·1	129·0	129·2	[k]
4′	128·9	128·7	129·5	129·3	129·7	129·1	[k]

[a] C^2HCl_3.
[b] $[^2H_6]$-DMSO.
[c–j] Most important correlations in COLOC or selective INEPT spectra via ^3J(CH): H(2)[c]; H(3)[d]; H(4)[e]; H(5)[f]; H(6)[g]; H(7)[h]; H(8)[i]; NH[j].
[k] 153·0/152·6 [C(1′) or C (1″)]; 122·5/122·3 [C(2′) or C(2″)]; 129·0/129·2 [C(3′) or C(3″)]; 130·0/129·9 [C(4′) or C(4″)].

TABLE 4
^{13}C Chemical Shifts in Compounds **Ib**–**Vb**

Carbon no.	*Compound*						
	Ib^{a}	**IIb**^{a}	**IIb**^{b}	**IIIb**^{a}	**IIIb**^{b}	**IVb**^{a}	**Vb**^{a}
1	147·0	141·0^{d,f}	138·6^{d,f}	130·4^{d,i}	129·6^{d,i,j}	130·4^{d}	137·6^{d,i}
2	123·8	137·2^{g}	135·8^{g}	129·5	129·4	129·3	120·0
3	119·3	122·6^{f}	120·1^{f}	120·0	119·4^{j}	119·8	111·9
4	142·5	132·3	132·7	133·3^{f}	133·8	133·0^{f}	143·5^{f}
4a	—	—	—	130·0^{d,g,i}	130·2^{d,i}	129·8^{d,i}	131·5^{d,i}
5	—	123·9^{d}	123·2^{d}	128·0	127·8	127·8	123·1
6	—	116·4	121·0	125·5^{i}	125·2^{i}	125·3	127·3^{i}
7	—	—	—	128·1^{f}	127·5	127·8	126·4^{f}
8	—	—	—	123·0	123·3	122·9	122·9
8a	—	—	—	131·2^{e,f}	133·2^{f}	131·1^{f}	127·2^{f}
CONH	169·0	168·9	168·5	169·8	170·0^{j}	169·6	169·3
CH_3	24·2	24·3	25·2	25·2	25·7	25·0	23·8
1′	152·2	152·2	152·2	152·0	152·3	152·0	152·7
2′	122·4	123·2	122·5	122·4	122·2	122·2	122·8
3′	129·4	129·4	129·2	129·6	129·3	129·4	129·5
4′	131·0	131·6	131·2	131·5	130·9	131·2	131·3

[a] [$^{2}H_6$]-DMSO.
[b] $C^{2}HCl_3$.
[c–j] Most important correlations in COLOC or selective INEPT spectra via ^{3}J(CH): H(2)^{c}; H(3)^{d}; H(4)^{e}; H(5)^{f}; H(6)^{g}; H(7)^{h}; H(8)^{i}; N$\underline{H}^{j}$.

after analysis of homonuclear shift-correlated spectra[5,6] (H,H-COSY). With compounds having protons in the peri position of the naphthalene residue, NOESY[5,6] spectra were measured showing cross-peaks formation between H(4) and H(5). Heteronuclear shift-correlated spectra[5,6] (H,C-COSY) were used for the assignment of appropriate C–H pairs, whilst COLOC spectra[15] or one-dimensional selective INEPT spectra[13] [both via $^{3}J(^{13}CH)$] were measured for assignment of ^{13}C chemical shifts of quaternary carbons. The results were mutually compared and inspected. Some applications of the above-mentioned two-dimensional NMR techniques in analysis of ^{1}H- and ^{13}C-NMR spectra of azo dyes are given in Refs 12 and 16.

The assignment of both ^{1}H and ^{13}C chemical shifts in **Ia** was straightforward, whilst H,C-COSY had to be used for differentiation of $\delta(^{1}H)$ of H(2) and H(3) in **Ib**, the assignment of $\delta(^{13}C(2))$ and $\delta(^{13}C(3))$ being clear. The COLOC spectra based on proton–carbon long-range couplings [mostly ^{3}J(CH) in aromatic systems as ^{2}J(CH) and ^{4}J(CH) are likely to be much smaller[14]] are extremely useful for assignment of quaternary carbon signals.[15] In running such COLOC spectra, peaks caused by one-bond C–H coupling appear in these spectra for carbons bearing hydrogen atoms.[17] These direct C–H cross-peaks provide additional fix-points for the orientation in the spectra, as they are known from a previously performed H,C-COSY spectra. The COLOC spectrum of **IIa** is shown in Fig. 1. For

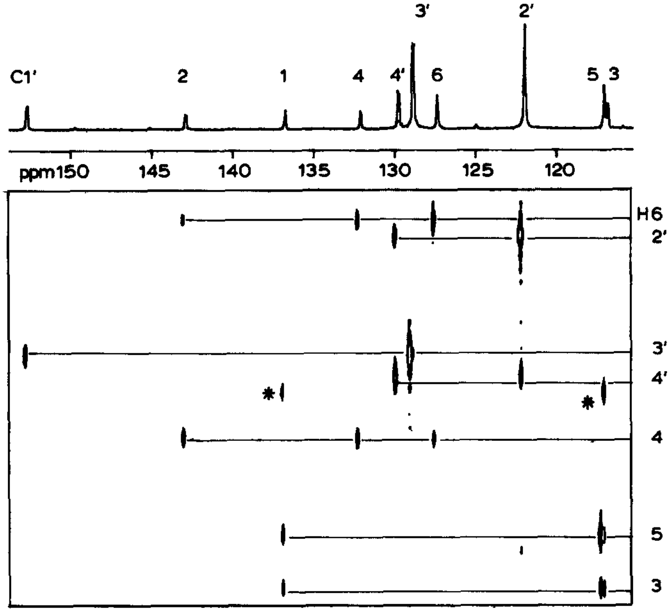


Fig. 1. COLOC spectrum of compound **IIa** via $^3J(CH)$ in C^2HCl_3. Signals marked with asterisks correspond to correlation with folded NH_2-group protons. Measuring conditions: spectral width SW1 = 590·3 Hz, spectral width SW2 = 4098·4 Hz, data matrix 1024 × 128, 32 scans during 64 time increments (zero filling in F1), $\Delta_1 = 53{\cdot}4$ ms, $\Delta_2 = 31{\cdot}0$ ms.

example, for proton H(4) we can see cross-peaks with carbon C(2) and C(6) [via $^3J(CH)$] and C(4) [direct cross-peak via $^1J(CH)$]. The different intensities of the cross-peaks can be ascribed to the fact that substituents cause a change in the magnitude of the three bond coupling constants. The spectrum depicted in Fig. 1 was optimized for a long-range coupling of *ca.* 9 Hz. Another typical feature is the existence of cross-peaks corresponding to interactions of NH_2-group protons with carbons C(1) and C(3) in **IIa**. Carbon C(1′) correlates with H(3′), carbon C(2) with H(4) and H(6), carbon C(1) with H(3), H(5) and $N\underline{H}_2$, all via $^3J(CH)$. The different number of cross-peaks and their positions enabled us to assign unambiguously the three quaternary carbons. Couplings to $N\underline{H}_2$ or $N\underline{H}COCH_3$ protons were also observed in compounds **IIIb** and **Va** for which COLOC spectra were measured. A similar approach was used in the analysis of quaternary carbon chemical shifts in other azo dyes using one-dimensional selective INEPT spectra.

This approach revealed, compared with the previous assignment[3] of $\delta(^{13}C)$ in **IIIa**, that the chemical shifts of three carbons had to be reassigned. H,H-COSY and consecutively H,C-COSY showed that signals for C(4) and C(5) had to be interchanged and, based on selective INEPT spectra, the signal with $\delta(^{13}C) = 134{\cdot}84$ had to be attributed to C(8a) [previously[3] C(1)]. The reassignment of C(1) is also confirmed by study of the deuterium isotope effect on ^{13}C chemical shifts.[8] The assignment of two previously unassigned signals[3] was also achieved. The situation was similar for $\delta(^{13}C)$ in **IIIb**. Two-dimensional NMR spectra confirmed the ^{13}C-NMR data[3] for **Va** and **Vb** and enabled completion to be made of the assignment of carbons C(6) and C(7).

Compounds **IVa** and **IVb**, as well as **VIa** and **VIb**, are reported for the first time. The ^{13}C-NMR spectrum of **VIb** was not measured because of the extremely low solubility of this compound both in C^2HCl_3 and $[^2H_6]$-DMSO.

The compounds in this study provide a unique opportunity to study hydrogen bonds between either NH_2 or $NHCOCH_3$ groups and an azo moiety.

The ^1H-NMR spectra of **Ia**–**Va** in C^2HCl_3 and $[^2H_6]$-DMSO show large differences in the chemical shifts in the two solvents especially for the amino protons; but protons close to the NH_2 group, in particular the *ortho* aromatic protons, also show quite clearcut differences, except for **Ia**. An interesting case is **IVa** and **Va**. Both compounds show a very large change in the chemical shift of H(8) upon change of solvent (Table 1). Compound **IVa** shows, in addition, a large shift for H(2′). This is not the case for **Va** in which the —N=N—C_6H_5 group is far from the NH_2 group. The finding that only the nearest aromatic protons are markedly influenced is also confirmed by the ^{13}C-NMR spectra of **IIIa** and **IVa** (Table 3). In these compounds C(1), C(2), C(3) and C(8) experience changes in addition to C(4a) of **IIIa** and C(4) of **IVa**. As the change in solvent causes changes in the chemical shifts of those nuclei close to the NH group, it is appropriate to associate these changes with hydrogen bonding. The fact that ^3J(C, C, N, H) couplings could be established via COLOC spectra or selective INEPT spectra supports this suggestion.

Several interesting points concerning the hydrogen bonding can be raised. How strong is the hydrogen bond in these compounds, in which compounds is the hydrogen bond strongest and are the intramolecular hydrogen bonds of different strength in the two solvents?

The chemical shifts of the phenolic protons have been correlated with hydrogen-bond strength[18] and an extension to amino protons is indirectly found for aromatic amines.[19] This approach has some difficulties in general[20] as the chemical shifts may be influenced by factors other than hydrogen bonding.[20] A clearcut example is found in **IVa** in which one NH hydrogen is hydrogen-bonded and the other is pointing towards H(8), thus experiencing steric compression. This will likely lead to a field shift. NH chemical shifts can be used to obtain a rough picture of hydrogen bonding despite such limitations. A comparison of NH chemical shifts of **Ia**–**Va** shows that they increase both in C^2HCl_3 and in $[^2H_6]$-DMSO in the order **Ia**, **Va**, **IIa**, **IVa** and **IIIa**. The amides are mostly only soluble in DMSO, in which we get the order **IIb**, **Vb**, **Ib**, **VIb**, **IVb** and **IIIb**. From these data, and bearing in mind the objections raised in Refs. 18 and 19, it can be safely concluded that **IIIa** and **IVa** are more strongly hydrogen-bonded in both solvents than the other dyes and that **IIIa** has the stronger hydrogen bond of the two. This also implies that the solvent is not changing the strength of the intramolecular hydrogen bond to any great extent. Among the amides, **IIIb** and **IVb** are again in their own class, as the amides only have intramolecular hydrogen bonds even in DMSO.

A picture of the hydrogen-bond pattern is thus established, a feature very important in assessing the physico-chemical properties of these compounds. The nature of the hydrogen bond will be further investigated in a paper dealing with deuterium isotope effects on ^{13}C chemical shifts.[8]

A low-temperature study of **IIIa** and **IIIb** in C^2HCl_3 reveals only moderate changes in the chemical shifts, supporting the findings of Ref. 3. However, some interesting changes are seen. Changes of the order of 0·1–0·3 ppm/50°C are observed for C(1), C(1′) and C(4a) in both compounds and for C(3) in **IIIb**. The CO carbon chemical shift of **IIIb** also shows a temperature effect. C(2) is only tentatively identified at all temperatures, but a temperature dependence most likely exists, as well as a difference between the two compounds. The differences in chemical shifts of C(2) and C(3) can probably be ascribed to a conformational change of the acetyl group of **IIIb**. Similar changes observed at C(1) and C(1′) are also found for **IIa**. A major conformational change due to breaking of hydrogen bonds is not likely, as it would be expected to change the chemical shift of C(8) dramatically, and no such effect is observed.

Concentration effects on ^1H chemical shifts of NHR protons were studied in compounds **Ia**, **Ib**, **IIa** and **IIb**. It was found that the changes of these chemical shifts in **Ib** (C^2HCl_3 and $[^2H_6]$-DMSO) and in **IIb** ($[^2H_6]$-DMSO) after tenfold dilution from *ca.* 0·25M to 0·025M solutions are lower than 0·03 ppm. Similar changes for **Ia** and **IIa** were lower than 0·12 ppm in C^2HCl_3 and $[^2H_6]$-DMSO.

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