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NMR Investigation of Azo Disperse Dyes

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ABSTRACT

The ^{13}C-NMR spectra of a series of monoazo disperse dyes derived from diethylaminoazobenzene were measured and analysed. Depending on the nature and orientation of the substituent in the dyes, different conformers, resultant from inner rotation around the C—N bonds, could be identified.

The structural data provide a new tool for studies on dye–substrate interactions.

1 INTRODUCTION

NMR investigation of azo dyes provides important information about their structure,[1,2] but NMR studies of azo disperse dyes have not yet received adequate attention. NMR data on many derivatives of *p*-amino-*trans*-azobenzene, both in solution and in the solid state are available.[3–6] Nevertheless, there are many structural problems, which have still not been taken into consideration.

In recent investigations[7–9] we have studied a wide series of azo disperse

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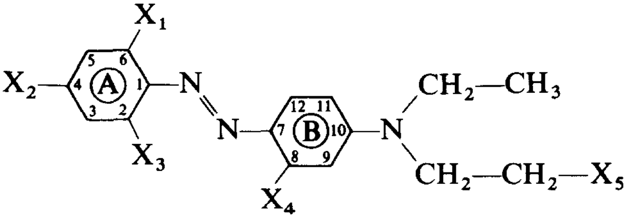
TABLE 1

Carbon-13 Chemical Shifts (ppm)

Dye	X_1	X_2	X_3	X_4	X_5	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-10*	*C-11*	*C-12*	*C-13*	*C-14*	*C-15*	*C-16*
Subclass **Ia**																					
1		CN				154·70	122·40	133·57	110·81	133·57	122·40	142·30	126·13	111·21	151·12	111·21	126·13	44·27	12·57	44·27	12·57
2		NO_2				156·33	122·27	124·78	146·71	124·78	122·27	142·50	126·15	111·26	151·31	111·26	126·15	44·17	12·41	44·17	12·41
3	NO_2					146·95	118·35	133·01	129·26	123·72	144·66	142·33	126·14	111·23	151·16	111·23	126·14	44·25	12·50	44·25	12·50
4	Cl					148·53	117·37	127·85	130·33	130·33	132·55	142·59	125·77	111·11	150·67	111·11	125·77	44·16	12·52	44·16	12·52
5	Br					149·40	117·57	128·47	130·64	133·46	123·44	142·48	125·81	111·15	150·67	111·15	125·81	44·19	12·55	44·19	12·55
6	Cl		Cl			148·48	126·08	129·21	128·24	129·21	126·08	142·01	125·64	110·98	151·18	110·98	125·64	44·25	12·49	44·25	12·49
7	NO_2	OMe				137·81	119·13	118·91	159·78	108·02	148·64	142·20	125·61	111·18	150·68	111·18	125·61	44·19	12·52	44·19	12·52
8	Br	NO_2	Cl			154·31	126·15	127·33	145·57	126·41	116·11	141·97	125·17	111·31	152·00	111·31	125·17	44·47	12·57	44·47	12·57
Subclass **Ib**																					
9					OH	152·56	121·82	129·24	129·47	129·24	121·82	142·23	125·08	111·16	150·65	111·16	125·08	45·15	12·08	52·20	58·41
10		CN			OH	154·98	122·40	133·70	110·84	133·70	122·40	142·40	125·98	111·41	151·67	111·41	125·98	45·31	12·08	52·23	58·44
11		NO_2			OH	156·33	122·42	124·95	146·74	124·95	122·42	142·61	126·20	111·50	151·91	111·50	126·20	45·34	12·07	52·25	58·44
12	NO_2				OH	146·97	118·40	133·09	129·34	123·80	144·68	142·44	126·05	111·45	151·80	111·45	126·05	45·34	12·07	52·25	58·46
13	NO_2	NO_2			OH	148·12	119·92	127·31	146·09	119·24	145·48	143·14	127·65	112·07	153·16	112·07	127·65	45·65	12·10	52·38	58·52
Subclass **Ic**																					
14					CN	152·48	121·96	129·33	129·81	129·33	121·96	142·91	125·04	111·73	149·73	111·73	125·04	44·58	12·18	45·52	15·86
15		OMe			CN	146·61	123·62	114·44	160·72	114·44	123·62	142·91	124·51	111·70	149·11	111·70	124·51	44·51	12·15	45·52	15·83
16		CN			CN	154·82	122·51	133·61	111·24	133·61	122·51	143·01	125·84	111·86	150·71	111·86	125·84	44·64	12·15	45·49	15·83
17		NO_2			CN	156·15	122·63	125·03	147·07	125·03	122·63	143·17	126·08	111·94	150·97	111·94	126·08	44·68	12·16	45·49	15·83

18	NO_2				CN	146·92	118·44	133·20	129·73	123·86	144·61	143·06	125·92	111·91	150·84	111·91	125·92	44·69	12·15	45·50	15·81
19	Cl				CN	148·41	117·47	127·95	130·78	130·54	132·76	143·32	125·60	111·81	150·26	111·81	125·60	44·64	12·16	45·50	15·83
20	Br				CN	149·34	117·65	128·55	131·04	133·54	123·63	143·22	125·60	111·83	150·26	111·83	125·60	44·64	12·16	45·50	15·83
21	CN	NO_2			CN	156·84	117·57	129·54	146·25	129·05	110·90	143·50	127·20	112·41	152·38	112·41	127·20	44·95	12·21	45·55	15·83
22	Cl		Cl		CN	148·38	125·98	129·28	128·50	129·28	125·98	142·74	125·45	111·70	150·84	111·70	125·45	44·66	12·11	45·49	15·79
23	Cl	NO_2	Cl		CN	153·09	126·75	124·59	145·48	124·59	126·75	142·80	126·13	111·87	151·62	111·87	126·13	44·72	12·16	45·42	15·77
Subclass **Id**																					
24		CN		Me	CN	155·22	122·53	133·56	110·84	133·56	122·53	142·54	141·31	112·54	150·71	110·35	117·23	44·53	12·28	45·34	15·88
25	Br			Me	CN	149·73	117·84	128·50	130·67	133·44	123·49	141·54	141·54	112·56	150·16	110·34	117·78	44·51	12·24	45·36	15·86
26	Cl	NO_2	Cl	Me	CN	152·95	127·01	124·65	145·20	124·65	127·01	143·43	141·57	112·44	151·74	110·56	117·50	44·68	12·24	45·37	15·88
27	Br	NO_2	Br	Me	CN	155·04	115·41	127·99	145·65	127·99	115·41	143·24	141·12	112·25	151·63	110·57	117·62	44·68	12·26	45·35	15·85
28	Br	NO_2	Cl	Me	CN	154·31	126·57	127·70	145·75	125·53	116·53	143·66	141·63	112·75	152·00	110·85	117·86	44·97	12·57	45·67	16·17
Subclass **Ie**																					
29		CN		NHAc		154·96	122·53	133·40	110·29	133·40	122·53	131·13	139·48	101·04	151·06	107·60	122·53	44·56	12·60	44·56	12·60
30		NO_2		NHAc		156·36	122·21	124·57	146·30	124·57	122·21	131·35	139·30	100·96	152·32	107·68	123·39	44·42	12·41	44·42	12·41
31	NO_2			NHAc		146·37	118·80	133·02	128·79	123·78	144·44	130·95	138·62	100·72	152·27	107·68	125·81	44·66	12·60	44·66	12·60
32	NO_2	OMe		NHAc		138·19	119·95	119·14	159·47	107·98	147·67	130·67	137·90	100·88	151·57	107·42	124·75	44·53	12·58	44·53	12·58
33	Cl		Cl	NHAc		146·92	126·63	129·24	128·01	129·24	126·63	130·05	138·55	100·07	151·98	106·95	123·49	44·30	12·26	44·30	12·26
34	CN			NHAc		153·96	119·60	134·21	128·87	134·09	107·19	130·72	139·28	100·67	152·55	107·94	124·61	44·79	12·71	44·79	12·71
35	Br	NO_2	Cl	NHAc		153·68	127·17	127·65	145·14	125·45	116·87	130·90	139·85	100·55	153·00	108·33	124·17	45·03	12·70	45·03	12·70
Subclass **If**																					
36	NO_2	OMe		NH_2		139·14	119·69	118·44	157·98	107·95	146·37	129·78	146·37	94·14	151·23	103·83	119·69	44·11	12·89	44·11	12·89
37	CN			Me		154·28	117·96	133·95	128·94	133·82	109·30	142·90	140·66	111·78	151·36	110·14	117·60	44·17	12·65	44·17	12·65
38		CN		Me		155·43	122·35	133·48	110·37	133·48	122·35	142·67	140·68	111·76	151·15	109·90	117·41	44·11	12·63	44·11	12·63

dyes of formula **I** containing substituents in the rings A and B, and we found some relationships between structural features of the dyes and their technological properties. For instance, their lightfastness has been correlated with some common NMR parameters.[8]



I

In this present paper we report, in more detail, further NMR data on the dyes **I**, which have been divided into a series of subclasses, **Ia–If**, to facilitate NMR analysis. These subclasses are characterized by increasing substitution in the B ring and on the alkyl chain. The gradual complication of the structures not only allowed a reliable assignment of NMR signals, but also made it possible to establish some structural trends. The chemical shift values of the ^{13}C-NMR spectra are reported in Table 1.

2 EXPERIMENTAL

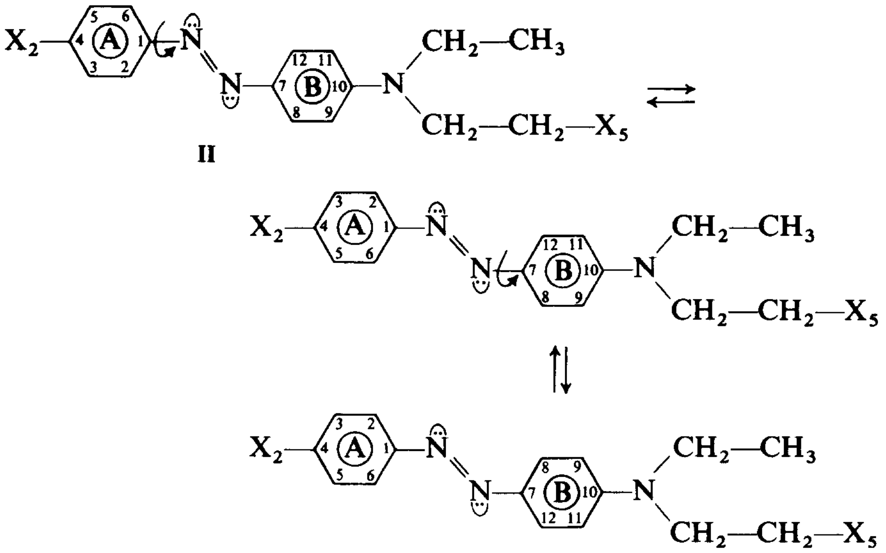
^{13}C$^-$ and ^{13}C-$\{^1$H$\}$-NMR spectra were recorded in DMSO-d_6 solution (dye concentration 0·2 M) on a JEOL GX-270 spectrometer, using the solvent signal (39·60 ppm) as internal standard. The conditions of measurement were as follows: number of data points, 32 K; spectral width, 18 kHz; cycle times, 2–3 s; number of transients 1000–5000; flip angles, 45°; line broadening factor 0·8; sample speed rotation, 15 Hz.

3 RESULTS AND DISCUSSION

Compounds of types **II** and **III** [see eqns (3) and (4) below] show substituent influences on ^{13}C shifts of the carbons in rings A and B which are, on the whole, in agreement with literature data.[1] Important deviations are observed for polysubstituted azo dyes, due to their structural complexity.

^{13}C-NMR spectra of some derivatives of *p,p'*-diethylamino-*trans*-azobenzene (**II**, $X_5 = H$) have been measured in solution[3–6] and in the solid state (**II**, $X_2 = NO_2$, $X_5 = CN$; Disperse Orange 25).[4]

Our results are in agreement with the literature data, allowing for small



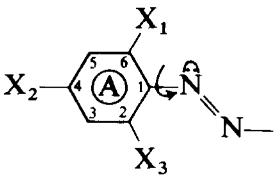
differences due to solvation effects. In this present work all measurements were performed in DMSO solution in order to ensure the same solvation effects for the whole series (for compounds **Ie** other solvents could not be used for solubility reasons).

The chemical shifts of the carbon atoms 1–12 in the A and B rings (**II**) can be easily estimated by a simple additive scheme involving the mutual influences of *para* substituents, as observed in Refs 10 and 11.

The chemical shifts of the carbon atoms 1–6 in the ring A of compounds **II** appear to be more markedly influenced by the nature of the X_2 substituent, whereas the X_5 substituent seems to exert a smaller effect, in agreement with previously observed data.[12] Although the X_2—C_6H_4—N=N moiety is not linear in the crystal state,[13] in the liquid[3] or in the gas state,[14] in the ^{13}C-NMR spectra of compounds **II** in solution the magnetic equivalence (one signal) of *ortho* (C-2 and C-6) and of *meta* (C-3 and C-5) nuclei is observed. The same behaviour is shown by the corresponding protons in ^{1}H-NMR spectra. This is the consequence of the inner rotation [eqn (1)] of ring A around the C—N bond, which takes place very fast in the time scale of NMR spectroscopy.

The same happens for ring B, in which the inner rotation (2) is also very fast and may be slowed down only at low temperatures in particular conditions. The splitting of the signals has been observed for compound **II**, $X_2 = NO_2, X_5 = H$, in solution,[3] and for compound **II**, $X_2 = NO_2, X_5 = CN$, in the solid state.[4]

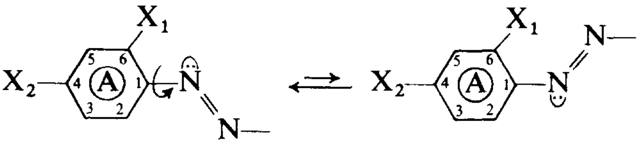
Also for more complex compounds of structure **III**, containing two equivalent *ortho* Cl or Br substituents in ring A ($X_2 = H$ or $X_2 \neq H$), the



III

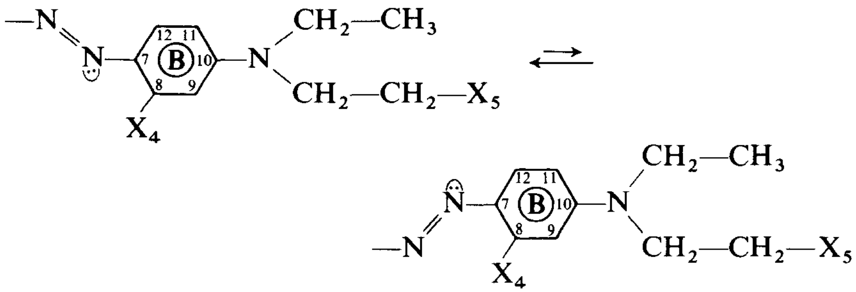
experimental chemical shift values of carbon atoms 1–6 can be easily estimated.

Important features are found in azo dyes **I** containing only one *ortho* substituent in ring A and/or B (systems **IV** and **V**, $X_1 \neq H$, and/or $X_4 \neq H$). In this case, *ortho* substituents X_1 and X_4 produce changes in the chemical shifts of carbon atoms in both rings as a consequence of rotational isomerism. Therefore, it is not possible to calculate the chemical shifts by simple additive schemes, without knowing which are the preferential isomers.



(3)

IV



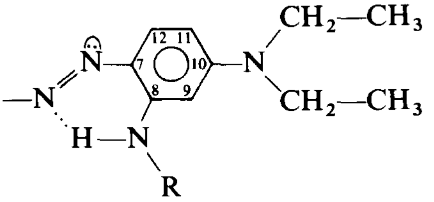
(4)

V

Indeed, in the presence of *ortho* substitutents, the distribution of the rotational isomers is not statistical, but the equilibria (3) and (4) are shifted towards the more stable isomers, in which the substituent X_1 or X_4 faces the lone pair of the nearest nitrogen atom.

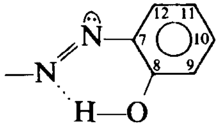
The substituents Cl, Br, NO_2, CN at X_1 and CH_3 at X_4 exert electronic and steric effects, contributing to the stabilization of rotational isomers of types **IV** and **V**. On the contrary, substituents NH_2 and $NHCOCH_3$ at X_4 strongly affect the rotational isomerism with the possible formation of intramolecular hydrogen bonds N···H—N with the azo moiety (system **VI**).

The formation of hydrogen bonds has been previously demonstrated by NMR spectroscopy in system **VII**.[15] In our case, the use of DMSO as solvent for the measurements (because of the above-mentioned low solubility of compounds **Ie**) lowers the possibility of confirming the hydrogen bonds in systems **VI**.



VI

(**a**) $R = COCH_3$
(**b**) $R = H$



VII

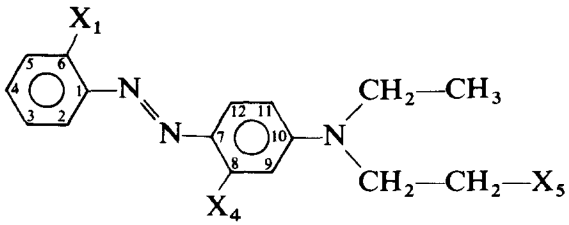
Let us consider the problem of the rotational isomerism (3) and (4) in more detail. As can be seen in Table 1, the substituents in X_1 listed above give rise to an upfield shift of the C-2 signal from $\delta = 121{\cdot}8$–$123{\cdot}6$ ppm to $\delta = 117{\cdot}4$–$119{\cdot}9$ ppm. The electronic influence of these substituents usually produces C-2 downfield shifts in the range 0·9–1·7 ppm[1] and the observed effects must therefore be explained in terms of fixation of the preferred isomer **IV** in which C-2 faces the N=N double bond. In conditions of such a fixation in conformation **IV**, upfield shifts of C-2 signals of 8–9 ppm from the average position have been reported.[2,3] Considering the electronic effects of X_1 substituents, the observed C-2 signals lie in the expected region. Analogously, the observed downfield shifts of C-6 signals are in agreement with the electronic effects of X_1 substituents and with the fixation of conformation **IV**.

Similar effects are observed for compounds **Id**. Table 1 shows highfield shifts of the C-12 signal from $\delta = 124{\cdot}5$–$127{\cdot}7$ ppm, which is characteristic of **Ia–Ic**, to $\delta = 117{\cdot}2$–$117{\cdot}9$ ppm.

Again a $\Delta\delta$ of 8–9 ppm (expected considering the negligible electronic *meta* effect of CH_3) is obtained, thus indicating the prevalence of conformer **V**, with C-12 facing the N=N double bond. Accordingly, the chemical shift value of C-8 shows the existence of the two effects, i.e. the electronic influence of CH_3 at X_4 and the fixation of the conformer **V**.

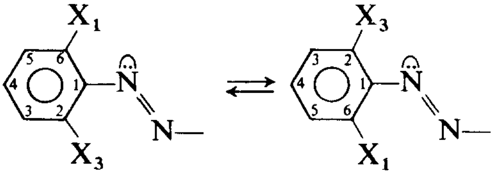
Furthermore, our ^{13}C-NMR data allow an easy identification of the conformational structure of compounds **25** and **37**, containing two 'inert' substituents in the *ortho* positions of the A and B rings. In this case, the position of the C-2 and C-12 signals ($\delta \approx 117{\cdot}6$–$118{\cdot}0$ ppm) supports the fixation of structure **VIII**, in solution.

Let us examine, finally, compounds containing two equivalent or different



VIII

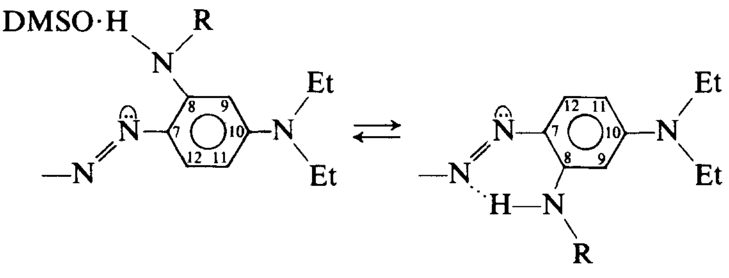
ortho substituents in ring A. In the case of equivalent substituents ($X_1 = X_3$ = Cl or Br) no conformational peculiarity is to be expected and both the rotational isomers have the same occurrence [equilibrium (5)].



(5)

In the case of $X_1 \neq X_3$, a shift of the equilibrium (5) towards the conformer in which the larger Br substituent faces the unbonded electron pair of the nearest nitrogen atom, could be expected. Apparently, in the compounds examined, the volume difference between Br and Cl is not very marked. Actually, ^{13}C-NMR data for ring A carbons in compound **28** are intermediate between data for comparable compounds **26** and **27** (Table 1).

In dyes **Ie**, containing the substituent X_4 = NHCOCH$_3$ the NMR data in Table 1 indicate a new phenomenon. The formation of the hydrogen bond (system **VI**) should shift the C-12 signal towards low field compared with the position of the signal in compounds **Ia–Ic**, X_4 = H, and a δ value around 132 ppm should be expected. A similar situation is observed with **VII** in chloroform,[15] i.e. in conditions where the hydrogen bond is more stable. The observed values of the C-12 chemical shift ($\delta \approx 122\cdot5$–$125\cdot8$) for compounds **Ie** (Table 1) indicate that isomer **VI** has only a partial occurrence and that equilibrium (6) must also be considered.



(6)

IX **VI**

In this equilibrium the substituent oscillates between the two possible planar situations **VI** and **IX**. The stability of structure **VI** may be provided only by the formation of hydrogen bond N ··· H—N, as this conformation is sterically less stable. Sterically favoured is the conformation **IX**, with the substituent facing the unbonded electronic pair of the nearest nitrogen atom. For C-12, a chemical shift value of ≈132 and ≈117 ppm would correspond to structures **IX** and **VI**, respectively. The intermediate values found for compounds **Ie** indicate that equilibrium (6) is not sharply shifted towards one or another side, as inversely observed for compounds **Id**.

Analysis of the NMR data of compounds **Ie** (Table 1) permits the effect of the substituents in ring A on the stability of the hydrogen bond in ring B (structure **VI**) to be established. The order of increasing stability is:

$$X_2 = CN < X_2 = NO_2 < X_1 = X_3 = Cl < X_1 = Br$$
$$X_2 = NO_2, \quad X_3 = Cl < X_1 = CN < X_1 = NO_2$$
$$X_2 = OCH_3 < X_1 = NO_2$$

In conclusion, the existence of the hydrogen bond in compounds **Ie**, even in strong solvating solvents, can be related to the acidity of the NH proton in the $NHCOCH_3$ group. The less acidic protons of the NH_2 group do not assist the fixation of hydrogen bond for a long enough time. However, compound **36** shows a $\delta = 119{\cdot}7$ ppm for C-12 (Table 1), thus indicating a partial shift of equilibrium (6) to the right, i.e. a partial hydrogen bond formation. In this compound, equilibrium (4) is not completely shifted to the left, unlike compounds **Id** and **37** and **38** which show, for C-12, a δ value of 117·2–117·9 ppm.

It can be expected that in less solvating solvents the shift of equilibrium (6) to the right would be much more marked.

The structural NMR data and the related conclusions about the conformational characteristics of disperse azo dyes having the general formula **I** are important not only from a theoretical, but also from a practical, point of view. In principle, the conformational arrangements shown in solution should be maintained during the various steps of the dyeing processes and important information on dye–substrate interactions could be derived.

ACKNOWLEDGEMENT

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