^{1}H AND ^{13}C NMR SPECTRA OF 2,2′-DISUBSTITUTED *trans*-AZOBENZENES SUITABLE FOR PREPARATION OF METALLIZED AZO DYES

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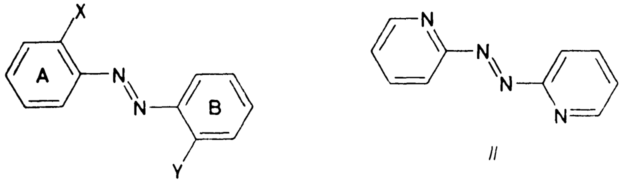
The ^{1}H and ^{13}C NMR spectra have been measured of six *trans*-azobenzenes substituted at 2 and 2′ positions with substituents favourable for complex formation with a metal (OH, NH_2, $NHCOCH_3$, COOH). From the standpoint of NMR such substituted *trans*-azobenzenes are present in solution in a rapid equilibrium following from rotation around the bond between C-1 of phenyl group and N atom of azo linkage. The predominant form has the substituent in the *syn*-position with respect to the free electron pair of the nearer azo nitrogen atom. The equilibrium is affected by dipolar aprotic solvents (such as hexadeuteriodimethyl sulfoxide) by decreasing the presence of the predominant form by 1 to 11%.

Metallized azo dyes represent an important group of dyestuffs. Structure of these complex compounds is unknown in many cases. Beside the estimation of crystal structure by means of X-ray diffraction analysis another advantageous method is the nuclear magnetic resonance (NMR)[1-5]. Some authors[2,5] used selective labelling



II

I	X	Y
a	OH	OH
b	NH_2	NH_2
c	$NHCOCH_3$	$NHCOCH_3$
d	COOH	COOH
e	NH_2	$NHCOCH_3$

SCHEME 1

of the compounds with ^{15}N to find the site of complex formation of the metal with the azo linkage. This method is advantageous but, in some cases where the parent azo dye cannot be obtained by azo coupling, rather difficult to carry out.

One possible approach to establishing the structure of metallized azo dyes consists in comparing their ^1H and ^{13}C NMR spectra with those of the precursors or model substances. The aim of the present communication is to measure the ^1H and ^{13}C NMR spectra of compounds suitable for formation of complexes with metals, i.e. azo dyestuffs having *ortho* substituents (to the azo linkage) able to supply electron pairs into the complexes with metals (see Scheme 1).

EXPERIMENTAL

Compound *Ia* was prepared by decomposition of its Cu^{II} complex formed from the diazonium salt derived from 2-aminophenol[6]. Compound *Ib* was prepared by hydrolysis of compound *Ic* by 10 h boiling in 70% aqueous ethanol with catalysis with sodium hydroxide at pH ≈ 10. The m.p. of product is 135°C in accordance with ref.[7]. Compound *Ic* was prepared by reducing 2-nitroacetanilide with zinc powder in the presence of ammonium chloride[8]. Compound *Id* was prepared by melting 2-nitrobenzaldehyde with sodium hydroxide[9]. Compound *Ie* was prepared together with *Ib* by partial hydrolysis of compound *Ic* accomplished by 3 h boiling and subsequent 40 h standing at 25°C in 70% aqueous ethanol at pH ≈ 10 (sodium hydroxide). Compounds *Ib* and *Ie* were separated by column chromatography (silica gel, benzene–ethyl acetate 3 : 1) and exhibit the R_F values of 0·75 (*Ib*) and 0·50 (*Ie*) during TLC on Silufol (Kavalier Czechoslovakia) with the same solvent system. Compound *Ie* melts at 138—140°C and exhibits the following mass spectrum (EI ionization; *m*/*z*, rel. intensity): 254 (100, M^+), 92 (78), 210 (38), 134 (25), 120 (22), 65 (19). Compound *II* was prepared from 2-aminopyridine by action of calcium hypochlorite[10].

The mass spectrum of compound *Ie* was measured with an MS 25 RFA (Kratos) apparatus with direct inlet. The ion source temperature 220°C, the ionization energy 70 eV.

The ^1H and ^{13}C NMR spectra were measured with an AM 400 (Bruker) apparatus at 400·13 and 100·61 MHz, respectively. For the measurements the substances were dissolved in hexadeuteriodimethyl sulfoxide or in deuteriochloroform. The measurements were carried out in a 5 mm NMR cell using a dual C/H probe at 300 K.

The chemical shifts with respect to TMS were related to the solvent signals, hexadeuteriodimethyl sulfoxide $\delta(^1H) = 2{\cdot}55$, $\delta(^{13}C) = 39{\cdot}60$, deuteriochloroform $\delta(^1H) = 7{\cdot}25$, $\delta(^{13}C) = 77{\cdot}00$. The twodimensional experiments H,H-COSY, H,C-COSY and the onedimensional J-modulated ^{13}C experiments were measured with application of the microprograms of pulse to the sequence given in ref.[12].

The NOE difference spectra of compounds *Ia*, *Ie*, and *Ic* in deuteriochloroform were measured in 5 mm cells according to the NOEDIFF program supplied by Bruker[11]. A 6 s presaturation of the proton signal in hydrogen bond was used. Decoupling power 45 dB under 0·2 W. Separated free induction decays were accumulated for the on-resonance and the control spectrum. After subtracting the FIDS, the result was transformed by means of FT. During the measurements of NOE difference spectra the samples were temperated at 305 K in order to increase the stability and decrease the residual dispersion signals in the difference spectrum.

RESULTS AND DISCUSSION

The ^1H and ^{13}C NMR chemical shifts of compounds *I* and *II* are presented in Tables I and II. The chemical shifts were ascribed on the basis of measurements of the proton spectra, estimation of mutual correlation between the protons (H,H-COSY), the differentiation of CH signals and quaternary carbon atoms was carried out by the APT (Attached Proton Test) method[13] and correlation of carbon atoms with hydrogen atoms (H,C-COSY). The signals of quaternary carbon atoms were assigned on the basis of the selective INEPT with the polarization transfer through three bonds. The experiments were supplemented by the calculation of approximative ^{13}C chemical shifts using the substituent chemical shifts (SCS) from ref.[14] and values of ^{13}C chemical shifts of solid *trans*-azobenzene[15].

Compound *Ic* is very little soluble in current solvents, hence the assignment of their signals was carried out in analogy to compound *Ie* (the ring B) and literature data on NMR parameters of its analogues[16].

At room temperature and above, *trans*-azobenzene in solution exhibits a set of signals[17] with equivalent pairs of carbon atoms C-2 with C-6 and C-3 with C-5 due

TABLE I

^1H NMR chemical shifts (δ, ppm) of compounds *I* and *II* at 300 K

Compound	Proton No.					
	3	4	5	6	X[a]	Y[a]
Ia[b]	7·04	7·35	7·03	7·70	12·21	12·21
Ia[c]	7·13	7·42	7·04	7·89	11·60	11·60
Ib[b]	6·76	7·17	6·78	7·67	5·48	5·48
Ib[c]	6·87	7·15	6·63	7·90	6·42	6·42
Ic[b]	8·66	7·50	7·16	7·63	[d]	[d]
Ic[c]	8·27	7·57	7·28	7·96	[e]	[e]
Id[c]	7·91	7·61	7·69	7·55	6·22	6·22
Ie[b,f]	6·78	7·23	6·76	7·59	5·43	—
Ie[b,g]	8·60	7·38	7·11	7·67	—	[h]
Ie[c,f]	6·92	7·25	6·69	7·82	6·89	—
Ie[c,g]	8·10	7·46	7·25	7·85	—	[i]
II[b]	8·73	7·42	7·88	7·92	—	—
II[c]	8·78	7·65	8·11	7·80	—	—

[a] The protons in X and Y groups. [b] Measured in deuteriochloroform. [c] Measured in hexadeuteriodimethyl sulfoxide. [d] $\delta(NH) = 9{\cdot}36$, $\delta(CH_2) = 2{\cdot}29$. [e] $\delta(NH) = 10{\cdot}13$, $\delta(CH_3) = 2{\cdot}25$. [f] The protons H-3 through H-5 belong to the ring A (see Scheme 1). [g] The protons H-3 through H-5 belong to the ring B (see Scheme 1). [h] $\delta(NH) = 9{\cdot}92$, $\delta(CH_3) = 2{\cdot}24$. [i] $\delta(NH) = 10{\cdot}04$, $\delta(CH_3) = 2{\cdot}22$.

to the rotation around the bond N—(C-1) which is very fast from the standpoint of the NMR time scale. Bulky substituents (tert-C_4H_9, iso-C_3H_7, or CH_3) at the *ortho* positions to azo group will not slow down this rotation sufficiently enough to make the pairs of signals of C-2 and C-6 observable at room temperature and below[18]. On the other hand, introduction of a strong electron-donor substituent (such as $N(C_2H_5)_2$) into para position to azo group makes the pairs of signals of C-2 and C-6 observable in the NMR spectra after cooling[18]. Thereform it follows that the increase of rotational barrier around the (C-1)—N= bond of azobenzenes is affected predominantly by electronic factors and not by the steric ones[19]. The azobenzenes with one substituent *ortho* to azo group exhibit chemical shifts contradictory to the substituent chemical shifts given in literature[14]. This phenomenon is caused by rotational isomerism at the (C-1)—N bond (Eq. (*1*)).

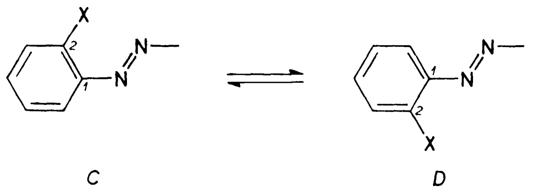
If it is X = Cl, Br, NO_2, CN, or CH_3, then the predominant arrangement is *D* (ref.[20]), which was confirmed by X-ray diffraction analysis[21] for X = NO_2 and

TABLE II

^{13}C NMR chemical shifts (δ, ppm) of compounds *I* and *II* at 300 K

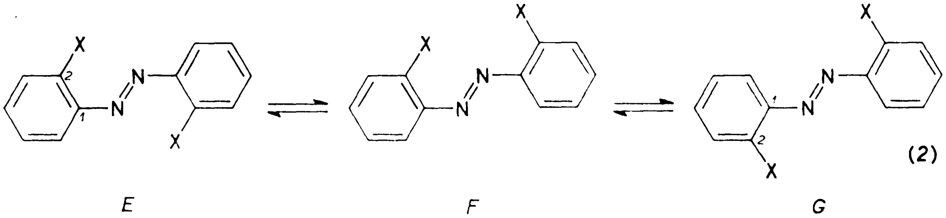
Compound	Carbon No.					
	1	2	3	4	5	6
Ia[a]	135·21	152·99	118·63	133·19	120·25	131·20
Ia[b]	137·77	154·11	118·14	133·29	119·89	123·63
Ib[a]	137·76	143·13	117·03	131·35	117·65	124·21
Ib[b]	136·74	145·31	115·69	131·28	116·60	121·91
Ic[a,c]	[d]	137·43	120·55	133·45	123·45	116·54
Ic[b,e]	141·59	137·35	122·67	132·42	123·98	117·29
Id[b,f]	151·99	130·91	130·09	131·17	132·61	118·42
Ie[a,g]	137·29	144·81	117·24	132·93	117·70	122·11
Ie[a,h,i]	139·30	135·26	120·28	131·53	123·33	119·99
Ie[b,g]	135·88	145·99	117·11	132·93	115·64	124·12
Ie[b,h,j]	142·92	136·45	123·46	130·39	124·41	116·63
II[a]	162·61	—	149·51	126·00	138·40	115·16
II[b]	162·62	—	149·65	126·63	139·23	113·99

[a] Measured in deuteriochloroform. [b] Measured in hexadeuteriodimethyl sulfoxide. [c] $\delta(CH_3) = 25\cdot31$; the signal of the CONH carbon atom was not observed due to low solubility of the substance. [d] The signal was not observed because of low solubility of the substance. [e] $\delta(CONH) = 169\cdot00$, $\delta(CH_3) = 24\cdot32$. [f] $\delta(COOH) = 168\cdot71$. [g] The carbon atoms C-1 through C-6 belong to the ring A (see Scheme 1). [h] The carbon atoms C-1 through C-6 belong to the ring B (see Scheme 1). [i] $\delta(CONH) = 168\cdot45$, $\delta(CH_3) = 25\cdot13$. [j] $\delta(CONH) = 168\cdot68$, $\delta(CH_3) = 24\cdot05$.



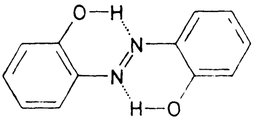
(1)

CN. The equilibrium (2) can be considered for 2,2′-di-X-substituted *trans*-azobenzenes.



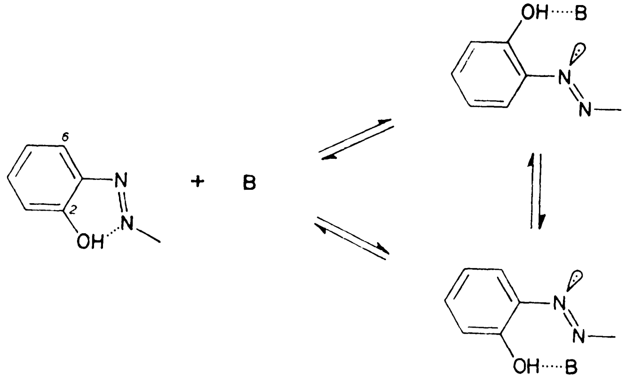
(2)

For the 2,2′-di-X-substituted *trans*-azobenzenes in which X is a group with acidic proton it is possible to include this proton in an intramolecular hydrogen bond with six-membered ring (e.g. structure *H* for X = OH),



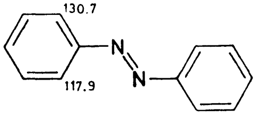
H

which arrangement is preferred in literature[22] with the presumption that the equilibrium (3) is established during interaction with a dipolar aprotic solvent *B* (e.g. DMSO).



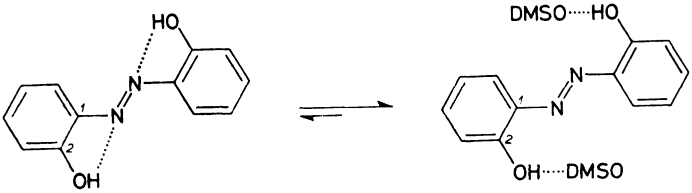
(3)

This presumption is supported by the difference between the chemical shifts of C-6 carbon atom in chloroform and dimethyl sulfoxide, viz. 8·3 ppm. If the solvation were accompanied by establishing of the equilibrium (*3*), a substantial change in chemical shift would have to be observed also at the C-2 carbon atom, since the difference between the chemical shifts of C-2 and C-6 is 12·8 ppm in solid *trans*-azobenzene[15] (where no rotation is possible) (see structure *J*).



J

As the difference between the shifts of C-2 carbon atoms in chloroform and in dimethylsulfoxide is only c. 1 ppm for compound *Ia*, the difference between the shifts of C-6 carbon atoms could also be explained in such a way that there is no substantial change in conformation at the (C-1)—N bond but only a change in solvation of OH proton which, according to Eq. (*4*), can only affect distinctly the shielding of C-6 carbon atom in the other part of the molecule.



(4)

In the present paper we have made an attempt at quantification of the state of conformational equilibrium at the (C-1)—N bond of compounds I. Theoretical chemical shifts of the C-2 and C-6 carbon atoms were calculated for two solvents on the basis of SCS of the X substituent[14] and values of the shifts of solid *trans*-azobenzene[15].

Table III gives the percentage calculated for the *D* form content in compound *I* in two solvents. The calculation was carried out on the basis of the ratio of the difference of the measured chemical shifts of C-2 carbon atoms from the calculated values in the forms *C* and *D* and the difference of the chemical shifts of C-2 carbon atom for both the forms *C* and *D*. The same calculation was also carried out for the C-6 carbon atoms.

The calculation of equilibrium (*1*) based on the chemical shifts of the C-6 carbon atoms for compounds *Ia* and *Ib* supports the theory by Fedorov[22] concerning the shift of conformational equilibrium at the (C-1)—N bond in favour of the *D* form when going to a dipolar aprotic solvent. For the other compounds *Ic*–*Ie* the results do not agree with this theory, the shifts of C-6 carbons of compounds *Ic* and *Ie*

TABLE III

The content of the form *D* in equilibrium (*1*) for compounds *I* in two solvents at 300 K. The calculation was carried out on the basis of the values of chemical shifts of C-2 and C-6 carbon atoms calculated for both the forms *C* and *D*

Compound	Calculation from C-2		Calculation from C-6	
	D, %[a]	*D*, %[b]	*D*, %[a]	*D*, %[b]
Ia	64	54	7	63
Ib	55	52	57	73
Ic	77	66	112	107
Id	—	76	—	104
Ie[c]	68	58	73	55
Ie[d]	60	59	85	112

[a] Deuteriochloroform. [b] Hexadeuteriodimethyl sulfoxide. [c] Applies to the arrangement of the ring A (see Scheme 1). [d] Applies to the arrangement of the ring B (see Scheme 1).

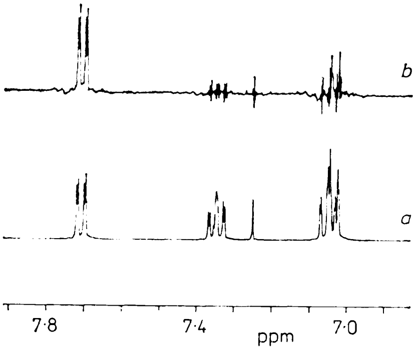


FIG. 1

a Normal ^{1}H NMR spectrum of compound *Ia* in deuteriochloroform at 305 K. *b* The NOE difference spectrum of compound *Ia* obtained by subtraction of the spectrum *a* from that measured with the presaturation of the OH proton

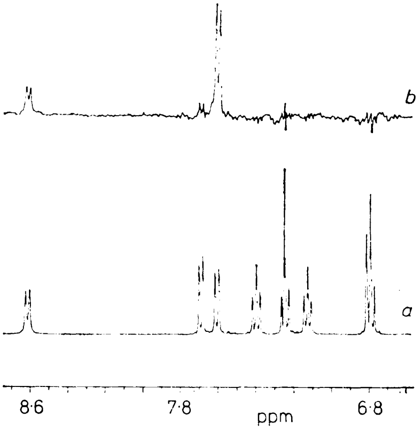
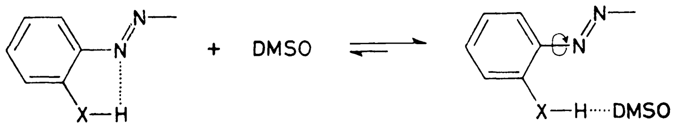


FIG. 2

a Normal ^{1}H NMR spectrum of compound *Ie* in deuteriochloroform at 305 K. *b* The NOE difference spectrum of compound *Ie* obtained by subtraction of the spectrum *a* from that measured with the presaturation of the NHCO proton being deviated from the interval of the shift values of C-6 carbons of the forms *C* and *D*. This can be explained by the fact that the calculation does not take into account the solvation effects which are distinctly felt at the C-6 carbon atom, probably much more markedly than the values of the used SCS of the groups X in *meta* position which are not distinct (and, hence, specific) for the X substituents. On the other hand the calculations of equilibrium (*1*) from the shifts of C-2 carbon atoms give a relatively more consistent picture of the fact that all the compounds *I* exists as the *D* forms both in chloroform and dimethyl sulfoxide, a transition to polar medium decreasing the content of *D* form. This result can be explained by the fact that in the conformer *D* there exists – at least partially – the hydrogen bond with the free electron pair of the nearer nitrogen atom of azo linkage, and this hydrogen bond is weakened in dimethyl sulfoxide, which makes the rotation around the (C-1)—N bond easier (see Eq. (*5*)).



(5)

No such calculation of the conformational equilibrium (*1*) can be carried out for compound *II*, however, with respect to the above-mentioned substituent effect of *trans*-azo linkage on the C-2 and C-6 carbon atoms in solid azobenzene and to the chemical shifts in pyridine[23] (δ(C-2) = 123·9) it can be presumed that the preferred arrangement in the molecule of compound *II* corresponds to that given in Scheme 1. That means that the azo linkage and the (C-1) –N(pyridine) bond form an angle of c. 180°.

The NOE difference spectra were measured with compounds *Ia*, *Ic*, and *Ie* (Figs 1 and 2). The fact that a distinct NOE was found between the proton of group X and the proton H-6 supports the statement that the forms *E* and *G* are preferred in the equilibrium (*2*), since the form *F* cannot give NOE between the proton of X and the proton H-6.

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