Substituent effects on physical properties of substituted azobenzenes

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A series of symmetrical 4,4′-disubstituted azobenzenes has been prepared. Their dipole moments vary within the range of 1.2 to 8.1×10^{-30} C m. The Raman, mass, and ^{13}C NMR spectra are reported and discussed. The properties of azobenzenes point out an electron-withdrawing character of the azo bridge. It has been claimed that the nonzero value of the azobenzene dipole moment results from the hybridization of the nitrogen atoms, intermediate between the sp^2 and sp^3 state.

Получен ряд симметричных 4,4′-дизамещенных азобензолов. Величины их дипольных моментов находились в интервале от $1{,}2 \cdot 10^{-30}$ до $8{,}1 \cdot 10^{-30}$ Кл м. Обсуждаются Рамановские, ^{13}C ЯМР и масс-спектры полученных соединений. Свойства азобензолов свидетельствуют об электронноакцепторном характере азо-мостика. Высказано предположение, что ненулевое значение дипольного момента азобензолов является следствием гибридизации атомов азота, промежуточным между sp^2 и sp^3.

Nonzero values of dipole moments of symmetrical *E*-azoarenes present some interpretation problems and the explanation given by *Bullock*, *Cumper*, and

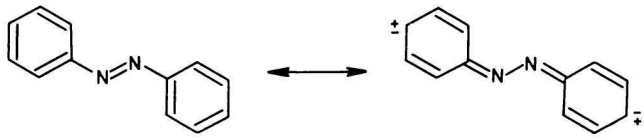
Table 1

Dipole moments of symmetrical azoarenes

Compound	$\mu/(10^{-30}$ C m)	Ref.
Azobenzene	1.73	[1]
4,4′-Dihydroxyazobenzene	8.69	[3]
2,2′-Azonaphthalene	3.56	[4]
2,2′-Azopyridine	5.89	[5]
3,3′-Azopyridine	7.99	[5]
4,4′-Azopyridine	1.20	[1]
2,2′-Azoquinoline	3.73	[1]

Vogel [1] seems to be unsatisfactory as well as the more general elucidation by *DiCarlo* and *Smyth* [2] (Table 1).

In most cases dissymmetrical conformations may be the source of dipole moments, however, such an interpretation fails in the case of azobenzene and 4,4′-azopyridine. The *E*-azobenzene molecule used to be considered as the planar and rigid conjugated system [6].



a *b*

X-Ray diffraction examination of *E*-azobenzene crystals indicates that the molecules are distorted: the angle between the N—N bond and the plane of the aromatic ring is 15°, while the angle of rotation of the ring from the position of a flat molecule is 17° [7]. Electronic spectra of *E*-azobenzene and those of derivatives with the steric hindrance which excludes the planar conformation are nearly identical [8]. The influence of substituents on the acidic dissociation of 4′-substituted 4-hydroxyazobenzenes is negligible [9], which indicates that conjugation is not transmitted through the azo bridge. These facts point out that the azobenzene molecule is neither planar nor rigid and the benzene rings are not conjugated. On the other hand, it is well known that azobenzene is very resistant to electrophiles [10] and the substituent constant of the phenylazo group ($\sigma_p = +0.64$) is comparable with that of the cyano group [11]. Obviously the azo link must be a strong electron-withdrawing group.

c *d*

If we assume that the electronic structure of the azobenzene molecule can be described as the resonance hybrid of the structures *a* and *c* the source of the dipole moment becomes apparent. The state of hybridization of the nitrogen atoms is intermediate between sp^2 and sp^3 and consequently the azo group must have a small dipole moment of its own. The aim of this work is to support the hypothesis given above with the spectral properties of symmetrically 4,4′-disubstituted azobenzenes.

Experimental

Bimolecular reduction of *p*-substituted nitrobenzenes has been carried out as described by *Badger* and *Lewis* [12]. *p*-Substituted anilines were oxidized to the corresponding azo compounds with active manganese dioxide according to *Pratt* and *McGovern* [13]. Oxidation of *p*-nitroaniline under these conditions gave pure *VI* in a very low yield. When peroxoacetic acid was used as an oxidizing agent 4,4′-dinitroazoxybenzene, m.p. = 192—194 °C was produced. In the presence of copper(II) chloride the reaction was diversed to produce *VI* (*cf.* Ref. [14]), however the compound isolated had m.p. = 212—215 °C and contained significant amount of azoxy compound. It could not be purified by crystallization.

Reduction of *VI* with sodium sulfide in boiling ethanol gave *VIIa* in a very good yield. Acetylation of *VIIa* with acetic anhydride and a drop of boron trifluoride etherate provided *VIII*. Compounds *IVc* and *IVd* were obtained from *IVa* by transesterification and alkaline hydrolysis, respectively.

All the dipole moments were determined at 25 °C for benzene solutions with the use of Dipolmeter DM-01 (WTW, Germany), according to the previously described [15] procedure. Raman spectra were recorded on a Coderg PHO using 632.8 nm radiation from a He—Ne laser (Spectra Physics); typical output power was 60 mW. Electron-impact (70 eV) mass spectra were registered on the MX 1321 instrument (Scientific Instruments, USSR). ^{1}H and ^{13}C NMR spectra were recorded on a Tesla BS 567A spectrometer (2.3 T).

4,4′-Dinitroazobenzene

p-Nitroaniline (27.62 g; 0.2 mol) was suspended in 250 cm^3 of chloroform, 30 % hydrogen peroxide (41 cm^3) and trifluoroacetic acid (1 cm^3) were added. The mixture was maintained at 40 °C and intensely stirred for 12 h. A dark-brown solution was filtered, the layers were separated, the chloroform solution was dried with sodium sulfate and evaporated to dryness. The residue was crystallized from toluene boiling with charcoal yielding 13.00 g (47.7 %) of the crude product, m.p. = 225—239 °C. Repeated crystallization from dimethylformamide gave 8.60 g (31.6 %) of 4,4′-dinitroazobenzene, m.p. = 239—240 °C.

For $C_{12}H_8N_4O_4$ w_i(calc.): 52.95 % C, 2.96 % H; w_i(found): 52.99 % C, 3.07 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 860 (aromatic CH deformations); 1340, 1530 (NO_2 stretching vibrations); 3100 (CH stretch).

4,4′-Dicyanoazobenzene

A mixture of azobenzene-4,4′-dicarboxamide (1.87 g; 7 mmol) and benzenesulfonyl chloride (3.6 cm^3; 28 mmol) in 50 cm^3 of dry pyridine was refluxed for 1 h until clear, brown solution was formed. It was cooled to −20 °C and brown needles of the crude product (1.80 g) were collected by filtration, m.p. = 268—271 °C (subl. above 200 °C).

Crystallization from toluene gave 1.11 g (68 %) of pure 4,4′-dicyanoazobenzene as orange needles, m.p. = 269—270 °C.

For $C_{14}H_8N_4$ w_i(calc.): 72.40 % C, 3.47 % H; w_i(found): 72.52 % C, 3.54 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 860 (aromatic CH deformations, 2 adjacent protons); 2230 (CN stretching vibration); 3055, 3100 (CH stretch).

Ethylation of 4,4′-diaminoazobenzene

To a solution of 4,4′-diaminoazobenzene (2.12 g; 10 mmol) in 50 cm^3 of dimethyl sulfoxide potassium hydroxide (20 g in 20 cm^3 of water) and tetrabutylammonium bromide (0.1 g) were added. The mixture was stirred at 50 °C and ethyl iodide (15 cm^3) was added dropwise during 1 h. The stirring was continued for 0.5 h and the mixture was poured on ice. A brown precipitate was collected by filtration, washed with water and crystallized from ethanol. The unchanged substrate (1.04 g, recovery 49 %) was isolated as orange plates, m.p. and mixed m.p. = 252—253 °C.

For $C_{12}H_{12}N_4$ w_i(calc): 67.90 % C, 5.70 % H; w_i(found): 68.01 % C, 5.79 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 830 (out of plane hydrogen wagging); 1585, 1610 (NH_2 deformations); 3380, 3480 (NH_2 stretching vibrations). ^{1}H NMR spectrum (DMSO-d_6), δ/ppm: 7.52, d, ^3J = 9 Hz, 4H (2,6-protons); 6.62, d, ^3J = 9 Hz, 4H (3,5-protons); 5.57, s broad, 4H (amino group).

The mother liquors were evaporated to dryness and the residue chromatographed on the 50 cm × 5 cm column packed with silica gel (Kieselgel, type 60, Merck) using benzene—ethyl acetate (φ_r = 1 : 1) as the eluent. The first coloured fraction contained 0.11 g (3 %) of 4,4′-bis(diethylamino)azobenzene, m.p. = 175—176 °C (isooctane).

For $C_{20}H_{28}N_4$ w_i(calc.): 74.03 % C, 8.70 % H; w_i(found): 74.17 % C, 8.82 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 825 (out of plane hydrogen wagging); 1350, 1390 (aliphatic C—H deformations); 2890, 2930, 2970, 3070 (C—H stretching vibrations). ^{1}H NMR spectrum (DMSO-d_6), δ/ppm: 7.72, d, ^3J = 9 Hz, 4H (3,5-protons); 6.72, d, ^3J = 9 Hz, 4H (2,6-protons); 3.37, q, ^3J = 7 Hz, 8H and 1.10, t, ^3J = 7 Hz, 12H (*N*-ethyl group).

Further elution gave some minor constituents, which were not separated and identified, and then 4,4′-bis(ethylamino)azobenzene. After recrystallization from ethanol it was obtained (0.80 g, 30 %) as brown rods, m.p. = 198—200 °C.

For $C_{16}H_{20}N_4$ w_i(calc.): 71.61 % C, 7.51 % H; w_i(found): 71.78 % C, 7.60 % H. IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 820 (out of plane hydrogen wagging); 1330, 1480 (aliphatic C—H deformations); 2870, 2980 (aliphatic C—H stretch); 3330 (N—H stretching vibration). ^{1}H NMR spectrum (DMSO-d_6), δ/ppm: 7.55, d, ^3J = 9 Hz, 4H (3,5-protons); 6.57, d, ^3J = 9 Hz, 4H (2,6-protons); 3.07, q, ^3J = 7 Hz, 4H and 1.13, t, ^3J = 7 Hz, 6H (*N*-ethyl group).

Results

A series of azobenzene derivatives has been prepared by the bimolecular reduction of the corresponding nitro compounds (procedure *A*) or by the

Table 2

Preparation of 4,4′-disubstituted azobenzenes[a]

Compound	Substituent	Method of preparation	Formula	M_r	M.p. °C (Solvent)	M.p. °C	Ref.	Mass spectra, m/z (I_r/%)
I	H	*A*	$C_{12}H_{10}N_2$	182.22	67—68 (MeOH)	67—68	[16]	182 (12), 105 (6), 77 (100), 51 (88), 50 (13)
II	Me	*A*	$C_{14}H_{14}N_2$	210.27	148—149 (PhMe)	144—145	[16]	210 (9), 119 (8), 91 (100), 65 (71), 63 (17), 51 (12), 39 (26)
III	*tert*-Bu	*A*	$C_{20}H_{26}N_2$	294.42	184—186 (EtOH)	183	[17]	294 (38), 279 (3), 161 (14), 133 (100), 118 (22), 105 (20), 90 (20)
IVa	COOMe	*B*	$C_{16}H_{14}O_4$	298.29	252—253 (PhMe)	242	[18]	298 (9), 163 (8), 135 (55), 120 (17), 119 (12), 104 (100), 76 (76)
IVb	COOEt	*B*	$C_{18}H_{18}N_2O_4$	326.34	144—145 (PhH)	144.5	[16]	326 (34), 281 (10), 177 (15), 149 (100), 104 (15)
IVc	COOBu	from *IVa*	$C_{22}H_{26}N_2O_4$	382.44	118—120 (Hexane)	—		382 (21), 205 (9), 177 (100), 135 (23), 104 (15)
IVd	COOH	from *IVa*	$C_{14}H_{10}N_2O_4$	270.24	360 (AcOH)	350	[19]	270 (35), 149 (17), 121 (100), 76 (82), 75 (87)
IVe	$CONH_2$	*A*	$C_{14}H_{12}N_4O_2$	268.27	360 (DMF)	360—363	[20]	268 (47), 148 (49), 120 (100), 104 (19), 103 (71), 92 (15), 76 (26)
V	CN	from *IVe*	$C_{14}H_8N_4$	232.24	269—270 (PhMe)	275	[20]	232 (48), 130 (37), 103 (3), 102 (100), 75 (69), 51 (54)
VI	NO_2	*B*	$C_{12}H_8N_4O_4$	272.22	239—240 (PhMe)	212—214	[14]	272 (35), 150 (57), 122 (100), 106 (11), 92 (35), 75 (49)

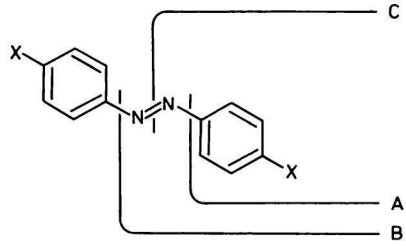
Table 2 (Continued)

Compound	Substituent	Method of preparation	Formula	M_r	M.p. °C (Solvent)	M.p. °C	Ref.	Mass spectra, m/z (I_r/%)
VIIa	NH_2	from *VI*	$C_{12}H_{12}N_4$	212.25	252—253 (aq. EtOH)	246—249	[16]	212 (63), 120 (26), 106 (6), 92 (100), 65 (33)
VIIb	NMe_2	*B*	$C_{16}H_{20}N_4$	268.35	276—277 (DMF)	271	[21]	268 (63), 148 (4), 134 (15), 120 (100), 105 (23), 91 (15), 79 (13)
VIIc	NEt_2	*B*	$C_{20}H_{28}N_4$	324.45	174—175 (PhH)	171	[22]	324 (100), 309 (31), 265 (7), 162 (7), 148 (48), 146 (20), 132 (23)
VIII	NHAc	from *VIIa*	$C_{16}H_{16}N_4O_2$	296.32	294—295 (EtOH)	295—296	[23]	296 (80), 162 (14), 134 (100), 93 (15), 92 (40), 65 (27)
IX	NHEt	from *VIIa*	$C_{16}H_{20}N_4$	268.35	198—200 (EtOH)	—		268 (61), 148 (9), 134 (7), 120 (100), 104 (34), 92 (29), 91 (19)
X	OMe	*A*	$C_{14}H_{14}N_2O_2$	242.27	166—168 (MeOH)	160	[16]	242 (14), 135 (32), 121 (4), 107 (100), 92 (50), 77 (78), 64 (38)
XI	Cl	*B*	$C_{12}H_8N_2Cl_2$	251.10	188—190 (PhMe)	185	[16]	252 (9), 250 (13), 139 (53), 11 (100)
XII	Br	*B*	$C_{12}H_8N_2Br_2$	340.02	223—224 (PhMe)	204	[16]	342 (21), 340 (40), 338 (20), 183 (52), 155 (100)
XIII	I	*B*	$C_{12}H_8N_2I_2$	434.00	247—248 (PhMe)	235	[16]	434 (65), 231 (48), 203 (91), 152 (6), 76 (100)

a) All the compounds listed gave satisfactory elemental analyses.

oxidation of properly substituted anilines (procedure *B*). Some other compounds have been obtained by transformation of the substituents already present in an azobenzene molecule. The structures of compounds were confirmed by the mass spectrometry. The most characteristic peaks are given in Table 2.

All the compounds produce molecular ions of medium intensities. The most characteristic cleavage of azobenzene involves fragmentation of the azo bridge. Decomposition of a substituent is usually negligible even in the case of butoxycarbonyl or *tert*-butyl groups.



The daughter ions of the type A form usually the base peaks, *VIIc* and *XIII* are the only exceptions. The spectrum of *VIIc* has another features: the base peak comes from the molecular ion, expulsion of the methyl radical gives another abundant peak and the fragment ion of the type B, *i.e.* ArN_2^+ is lacking. The relative intensities of the fragment ions A/B vary in a broad range from 2 to 25 %. There is no relationship between the A/B ratio and electron-donating or -withdrawing properties of substituents. Monosubstituted azobenzenes behave analogously [24]. It is well known that daughter ions of the type A are formed directly from the molecular ion and from the B fragments by expulsion of the nitrogen molecule [25]. A substituent which facilitates formation of the ArN_2^+ ion facilitates its cleavage as well, hence no simple correlation can be observed. In the mass spectra of azobenzenes containing strong electron-donating substituents (OMe, NH_2, NHEt, NR_2) fragmentation of the type C is observed. Corresponding peaks in the spectra of remaining compounds are lacking. Their intensities (4—15 % of the base peak) are too high for double charged ions. This is noteworthy since this mode of fragmentation is typical of azines [25].

Most of the 4,4′-disubstituted azobenzenes are sparingly soluble in benzene and other nonpolar solvents hence the dipole moments of nine compounds only have been measured. The results are listed in Table 3.

The azobenzenes containing regular substituents display dipole moments $\mu = (1.7 \pm 0.7) \times 10^{-30}$ C m similar to that of azobenzene itself ($\mu = 1.73 \times 10^{-30}$ C m according to Ref. [1]). Diethyl azobenzene-4,4′-dicarboxylate (*IVb*) has the dipole moment closely related to that of diethyl terephtha-

Table 3

Dipole moments of 4,4′-disubstituted azobenzenes

Substituent	a_c	a_n	a_v	a_Q	$P_{2\infty}$	R_D	$\mu_{exp}/(10^{-30}$ C m)
H	0.61	0.44	−0.22	0.17	71.15	64.76	1.30 ± 0.10
Me	0.59	0.44	−0.18	0.14	83.89	77.25	1.23 ± 0.43
Me_3C	0.42	0.28	−0.14	0.11	111.20	103.30	1.23 ± 0.27
Et_2N	1.14	0.94	−0.18	0.14	162.36	149.70	1.67 ± 0.50
Cl	0.59	0.40	−0.35	0.27	87.15	77.89	1.70 ± 0.53
Br	0.66	0.42	−0.60	0.46	97.38	81.83	2.47 ± 0.10
I	0.60	0.40	−0.60	0.46	119.86	102.70	2.57 ± 0.43
MeO	2.00	0.48	−0.32	0.24	150.50	81.04	5.97 ± 0.10
EtOOC	2.40	0.35	−0.32	0.24	227.50	101.00	8.13 ± 0.07

late ($\mu = 8.37 \times 10^{-30}$ C m) [26], analogously those of 1,4-dimethoxybenzene and 4,4′-dimethoxydiphenyl ($\mu = 6.14 \times 10^{-30}$ C m [27]) are nearly the same as that of *p*-azoanisole. Dipole moments of symmetrically substituted benzenes and diphenyls were studied in detail [2, 26, 27] and the explanations given for the compounds containing angular, *e.g.* alkoxy or alkoxycarbonyl groups are commonly accepted [28]. These compounds exist in solutions as mixtures of nonplanar forms, and the observed dipole moments come from the asymmetrical conformations. It should be also the case with 4,4′-bis(diethylamino)azobenzene, however its dipole moment is significantly lower than that of *p*-phenylenediamine ($\mu = 5.10 \times 10^{-30}$ C m) and its tetramethyl derivative ($\mu = 4.44 \times 10^{-30}$ C m) [29]. It seems reasonable to argue that the mesomeric interaction between the amino and azo groups makes the former nearly planar and decreases its contribution to the total dipole moment.

The azo linkage gives a strong Raman line. Its frequency should be influenced with the N—N bond order because it is known that azomethane displays a strong band at $\tilde{\nu} = 1576$ cm^{-1}, azoarenes in the region of $\tilde{\nu} = 1400$—1500 cm^{-1} [30] while the line assigned to the stretching vibration of a single N—N bond is shifted towards lower wavenumber, *viz.* $\tilde{\nu} = 1100$—1200 cm^{-1} [31, 32]. There is however no unequivocal assignment of a particular band to the N—N stretching mode in the Raman spectra of azoarenes. In the case of azobenzene, the vibrational spectroscopy studies pointed out the bands at $\tilde{\nu} = 1493$ cm^{-1} or 1474 cm^{-1} as the most probable but the band at $\tilde{\nu} = 1438$ cm^{-1} was not excluded [33]. The interpretation of the Raman spectra of substituted azobenzenes by *Zgierski* is based on the notion that the conjugation effect should weaken the strong Raman activity of the N—N stretch and increase the intensity of a weakly active Ar—N stretch [34].

The spectra of 19 symmetrically substituted azobenzenes were registered and the relevant lines lying between the region of C—H deformations and that of

Table 4

The Raman lines ($\tilde{\nu}$ = 1300—1500 cm^{-1}) of 4,4′-disubstituted azobenzenes

Compound	Substituent	Raman frequencies/cm^{-1} (I_r/%)		
VIIc	NEt_2	1390 (10)	1445 (1)	—
VIIb	NMe_2	1397 (9)	1447 (3)	—
IX	NHEt	1395 (9)	1435 (1)	—
VIIa	NH_2	1405 (10)	1455 (2)	—
X	OMe[a]	1407 (7)	1455 (6)	—
III	*tert*-Bu[a]	1400 (2)	1455 (7)	—
II	Me[a]	1402 (1)	1457 (5)	—
VIII	NHAc[a]	1410 (1)	1450 (5)	—
I	H	1438 (9)	1470 (5)	1490 (5)
XI	Cl	1397 (4)	1454 (10)	1483 (2)
XII	Br	1397 (2)	1454 (8)	1480 (2)
XIII	I	1391 (3)	1453 (10)	1477 (6)
IVe	$CONH_2$	1400 (3)	1460 (10)	1500 (1)
IVd	COOH	1405 (3)	1460 (9)	1500 (1)
IVa	COOMe[a]	1405 (2)	1460 (5)	1495 (1)
IVb	COOEt	1405 (3)	1456 (9)	1500 (1)
IVc	COOBu	1408 (2)	1455 (10)	1500 (1)
V	CN	1410 (2)	1465 (10)	1500 (1)
VI	NO_2[b]	1405 (5)	1457 (10)	1487 (5)

a) The line at $\tilde{\nu}$ = 1100—1145 cm^{-1} is the strongest one. *b*) Symmetrical NO_2 stretching ($\tilde{\nu}$ = = 1350 cm^{-1}) also occurs in this region.

ring vibrations are collected in Table 4; the substituents are listed in the order of increasing σ_p constant.

Two strong bands at $\tilde{\nu}$ = 1390—1410 cm^{-1} and $\tilde{\nu}$ = 1435—1465 cm^{-1}, corresponding to the bands at $\tilde{\nu}$ = 1438 cm^{-1} and 1470 cm^{-1} in unsubstituted azobenzene, are common to all the examined compounds. The third band of lower intensity appears at $\tilde{\nu}$ = 1475—1500 cm^{-1} in the spectra of azobenzenes containing electron-withdrawing ($\sigma_p \geq 0$) substituents. Another feature of these spectra is the relative intensity of the bands at $\tilde{\nu}$ = 1400—1450 cm^{-1} varying from 10 : 1 to 1 : 5. The influence of substituents can be interpreted in terms of the Zgierski's idea. The strong band near $\tilde{\nu}$ = 1450 cm^{-1} can be identified as the N—N stretching vibration while the weaker one, around $\tilde{\nu}$ = 1400 cm^{-1} as the Ar—N stretch. In the presence of a strong ($\sigma_p \leq -0.27$) electron-donating substituent in *para* position its conjugation with the azo bridge is reflected in the reversed intensities ratio of the aforementioned lines.

The next table contains the ^{13}C NMR spectra of the azobenzenes. Again some

problems with their limited solubilities were encountered. The spectra registered in various solvents are nearly identical. The signal assigned to the C-1 carbon atom displays some sensitivity to the solvent, nevertheless the differences do not exceed 1 ppm. The solubilities of compounds listed at the bottom of Table 5 were so low that the chemical shift of the quaternary carbons could not be estimated. As regards the remaining compounds it is possible to examine their spectra for the consistency with the additivity rule. The increments of the azo group in various solvents were calculated from the data given at the top of Table 5. For the compounds soluble in nonpolar solvents the increments of *para* substituents were taken from the literature [35, 36]. The others were measured by comparison of the spectra of benzene and monosubstituted benzenes registered in an appropriate solvent. The difference ($\Delta\delta$) between the calculated observed chemical shifts of aromatic carbons varies within the range of ± 3 ppm. The values of $\Delta\delta$ of the carbons C-1 connected to the azo link are given in the last column of Table 5. As shown, the peaks are shifted diamagnetically ($\Delta\delta < 0$) in the case of derivatives containing electron-releasing substituents.

Discussion

The measurements of dipole moments of symmetrically substituted azobenzenes indicate that the *E*-azobenzene system exhibits a small dipole moment of its own. The influence of substituents on the magnitude of dipole moment cannot be interpreted unequivocally hence the source of the dipole moment of *E*-azobenzene cannot be elucidated in this way.

It has been assumed that the contribution of the mesomeric forms *c* to the charge distribution in azobenzene will increase when donor substituents are bonded in conjugated positions. It was also expected that the Raman frequencies characteristic of the azo bridge would be dependent on the donor-acceptor properties of the substituents. Surprisingly, it turned out that the frequency assigned to the N—N double bond stretching mode varied in the range of $\tilde{\nu} = 1435$—$1465\ \mathrm{cm}^{-1}$. It can be explained in the following ways: The mesomeric structures *c* are incorrect and the contribution of the *b* structures should not be influenced with substituents. The mesomeric structures *c* are correct but substituents do not influence their contribution to the resonance hybrid. The Raman frequencies within the region of $\tilde{\nu} = 1300$—$1500\ \mathrm{cm}^{-1}$ are not sensitive to the contribution of *c*, *i.e.* to the N—N bond order as it changes under the influence of the *para* substituents.

The latter explanation seems to be the most convincing otherwise it should be difficult to elucidate the influence of the donor-acceptor properties of a substituent on the relative intensity of the band at $\tilde{\nu} = 1450\ \mathrm{cm}^{-1}$. Such an

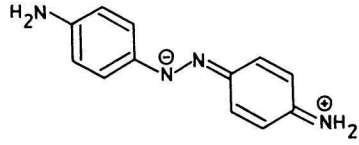
Table 5

Carbon ^{13}C NMR spectra of 4,4′-disubstituted azobenzenes

Substituent	Solvent	Chemical shifts δ/ppm					$\Delta\delta$ for C-1
		C-1	C-2	C-3	C-4	Others	
H	C_6D_6	151.2	121.3	127.2	129.0		
H	$CDCl_3$	151.2	121.2	127.1	129.3		
H	THF	151.1	121.3	127.3	129.2		
H	Pyr-d_5	151.0	121.2	127.5	129.4		
H	DMSO-d_6	150.0	120.6	127.4	129.5		
NEt_2	C_6D_6	142.7	123.0	109.6	147.1	42.4 (CH_2); 10.4 (CH_3)	−3.2
NEt_2	$CDCl_3$	141.7	122.2	109.3	147.0	42.7 (CH_2); 10.7 (CH_3)	
NHEt	$CDCl_3$	142.1	122.5	110.5	147.8	36.5 (CH_2); 14.0 (CH_3)	−3.0
NH_2	DMSO-d_6	141.3	121.8	111.5	148.9		−0.8
NHAc	DMSO-d_6	145.6	121.3	117.2	140.0	166.7 (CO); 22.1 (CH_3)	−3.3
MeO	$CDCl_3$	145.5	122.8	112.6	169.3	53.9 (CH_3)	−2.3
tert-Bu	$CDCl_3$	149.8	121.2	124.5	152.6	33.4 (C); 29.6 (CH_3)	−1.6
Me	C_6D_6	149.5	121.2	127.9	139.1	19.2 (CH_3)	−1.1
Me	$CDCl_3$	149.3	121.2	127.8	139.5	19.6 (CH_3)	
COOEt	$CDCl_3$	152.9	120.9	128.7	130.9	153.9 (CO); 59.4 (CH_2); 12.4 (CH_3)	+2.8
COOBu	C_6D_6	152.2	121.2	128.9	131.5	163.5 (CO); 63.0; 29.0; 17.4; 11.7 (n-Bu)	
CN	Pyr-d_5		121.9	131.8		124.1 (CN)	
Br	THF		122.8	130.8			
I	THF		122.9	136.9			
NO_2	DMF-d_7		122.9	124.0			

interpretation is supported with the mass spectra. Fragmentation patterns of the derivatives containing electron-releasing groups indicate a low N—N bond order.

Carbon ^{13}C NMR spectra also point out mesomeric interaction between the azo link and a donor *para* substituent. The peak of the C-1 carbon atom is shifted towards higher magnetic field as compared with its position calculated from the additivity rule. The value of the difference $\Delta\delta$ may be considered as the gauge of the enhancement of electron density around C-1 due to the conjugation. This effect indicates an electron-withdrawing character of the azo link, that can be presented with the mesomeric forms of the *c* type.



This property of the azo group is reflected in the reactivity of some azobenzene derivatives. Alkylation of aniline occurs readily in a neutral solution and quaternary salts are produced in many instances. 4,4′-Diaminoazobenzene cannot be alkylated in a neutral medium, its amino group does not display nucleophilic properties. The reaction takes place only in the presence of strong bases when formation of a nucleophilic amide anion precedes the substitution.

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