CARBON-13 AND NITROGEN-15 NMR SPECTRA OF *cis*- AND *trans*-AZOBENZENE, 4-MONOSUBSTITUTED AND 4,4′-DISUBSTITUTED *trans*-AZOBENZENES

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^{13}C and ^{15}N NMR spectra of *cis*- and *trans*-azobenzene, 4-substituted *trans*-azobenzenes ($N(CH_3)_2$; NH_2; OH; OCH_3; CH_3; Br; NO_2) and 4,4′-disubstituted *trans*-azobenzenes (OH; NO_2; NH_2; OH; $N(CH_3)_2$, CH_3; NO_2) were measured. In comparison with *trans*-azobenzene, *cis*-azobenzene exhibits a downfield shift of nitrogen and $C_{(1)}$ signals and an upfield one of the $C_{(2)}$ and $C_{(4)}$ signals. The individual coupling constants $^nJ(^{15}N^{13}C)$ in 4-substituted and 4,4′-disubstituted *trans*-azobenzenes, respectively, have characteristic values and can be used for carbon signal assignment. With 4-substituted *trans*-azobenzenes, the ^{15}N substitution chemical shifts of the nitrogen of the azo-bond were determined and their additivity in series of 4,4′-disubstituted *trans*-azobenzenes was proved.

Azocompounds are subject of interest owing to their reactivity, unusual spectroscopic properties, and interesting structure[1]. An important group of azocompounds are substituted azobenzenes. ^1H NMR spectra of these compounds are described in the ref.[2], records of ^1H NMR spectra of 4-substituted and 4,4′-disubstituted azobenzenes were published in the ref.[3]. ^{13}C, ^{14}N, and ^{15}N chemical shifts of *trans*-azobenzene were determined in various solvents[1,4−8]. Spin-lattice relaxation times were measured in ^{15}N-double labelled *trans*-azobenzene[9] and *trans*-azobenzene[10]. No ^{13}C and ^{15}N NMR spectra of *cis*-azobenzene were published. However, ^{15}N NMR spectra of *cis*- and *trans*-isomers of difluorodiazene[11], N-cumyl-N′-phenyldiazene, phenylisobutyronitril, and N-cumyl-N′-norbornyldiazene were measured[12]. Among substituted *trans*-azobenzenes were published ^{13}C (ref.[7]) and ^{15}N (ref.[8,13]) chemical shifts for 4-hydroxyazobenzene, ^{13}C chemical shifts of 4-substituted azobenzenes are given in the ref.[14]. Relaxation times of substituted azobenzenes were also published[15].

The aim of this work was to determine ^{13}C and ^{15}N chemical shifts and absolute values of coupling constants $^nJ(^{15}N^{13}C)$ in azobenzene and some its derivatives. ^{15}N chemical shifts of nitrogen atom of the azogroup in substituted azobenzenes were unambiguously assigned using ^{15}N-labelling.

EXPERIMENTAL

trans-Azobenzene (IIa) and ^{15}N-monolabelled *trans*-azobenzene, respectively, were prepared by condensation of nitrosobenzene with aniline (^{15}N-aniline)[16]. *cis*-Azobenzene (I) and [15]N- -monolabelled *cis*-azobenzene were prepared photochemically[17] in n-hexane. 4-Hydroxyazo- benzene (IId) and 4-hydroxy-4'-nitroazobenzene (IIi) were prepared by coupling of corresponding diazonium salts in alkaline media[18]. 4-N,N-Dimethylaminoazobenzene (IIb), 4-N,N-dimethyl- amino-4'-methylazobenzene (IIk) and 4-N,N-dimethylamino-4'-nitroazobenzene (III) were pre- pared by coupling of corresponding diazonium salts in acidic media[19]. 4-Aminoazobenzene (IIc) was prepared from aminoazobenzene[20]. 4-Methylazobenzene (IIf), 4-bromoazobenzene (IIg), and 4-nitroazobenzene (IIh) were prepared by condensation of 4-toluidine, 4-bromo- and 4-nitroaniline, respectively, with nitrosobenzene[21]. 4-Methoxyazobenzene (IIe) was pre- pared by alkylation of compound IId (ref.[22]). 4-Amino-4'-hydroxyazobenzene (IIj) was obtained as the product of reduction III (ref.[23]). ^{15}N-monolabelled compounds in the α-position (with IIj in β-position) were prepared by coupling using Na[15]NO$_2$. ^{15}N-monolabelled IId (β-position) was prepared by coupling using ^{15}N-aniline. Compounds IIf and IIg ^{15}N-monolabelled in the β-position were obtained by condensation[21] of ^{15}N-aniline and 4-methyl- or 4-bromo- nitrosobenzene, respectively. The ^{15}N content of ^{15}N-aniline and Na[15]NO$_2$ (Isocommerz, Berlin) was 94·8 and 97·9%, respectively. All compounds were purified by crystallization and column chromatography.
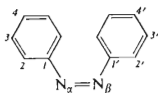
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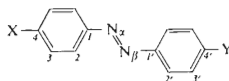
$$II$$

IIa; X = H,	X = H	IIg; X = Br,	Y = H
IIb; X = N(CH$_3$)$_2$,	Y = H	IIh; X = NO$_2$,	Y = H
IIc; X = NH$_2$,	Y = H	IIi; X = OH,	Y = NO$_2$
IId; X = OH,	Y = H	IIj; X = NH$_2$,	Y = OH
IIe; X = OCH$_3$,	Y = H	IIk; X = N(CH$_3$)$_2$, Y = CH$_3$
IIf; X = CH$_3$,	Y = H	III; X = N(CH$_3$)$_2$, Y = NO$_2$

^{13}C and ^{15}N NMR spectra were measured at 25·047 and 10·095 MHz, respectively, on a JEOL JNM-FX 100 instrument, equipped by a multinuclear tunable probe, quadrature detection and operating in the FT mode. Measurements were made in 10 mm NMR sample tubes. For ^{13}C NMR spectra measurements were used 10—15% (w/v) solutions in deuteriochloroform and hexadeuteriodimethyl sulfoxide at 30°C (at 70°C with IIi and at 60°C with III). Deuterated solvents were used as internal lock substances. The course of photochemical isomerization of *trans*-azobenzene was followed by ^{13}C NMR spectroscopy in 5% n-hexane solution of *trans*- -azobenzene using external [7]Li lock. Following parameters were used in ^{13}C chemical shifts determination: spectral width 5 000 Hz, 8 K, pulse width 7 μs (23 μs corresponds to 90°), pulse repetition 3 s, proton noise decoupling. Carbon chemical shifts are referred to internal tetramethylsilane. In the case of azobenzenes I and IIa, measured in n-hexane, the chemical shifts were related to the n-hexane methyl group and converted to the δ-scale adding a correction 13·70 (ref.[24]). Positive values denote downfield shifts. Coupling constants $^nJ(^{15}N^{13}C)$ were

measured using $2-5\%$ (w/v) solutions of ^{15}N-monolabelled compounds. Following measurement parameters were used: spectral width 1 400 Hz or smaller, 8 K, pulse width 11 µs, pulse repetition 6 s, proton noise decoupling. ^{15}N NMR spectra of ^{15}N-monolabelled compounds *I* and *II* were obtained by measurements of $2-5\%$ (w/v) solutions in deuteriochloroform or hexadeuteriodimethyl sulfoxide (spectral width 3 000 Hz, 8 K, pulse width 10 µs (30 µs corresponds to 90°), pulse repetition 15 s, inverse gated decoupling [25] (proton noise decoupling on during the acquisition time)). After completing the experiments, tris(acetylacetonato)chromium(III) (40 mg/ml) was added and the measurement was repeated (spectral width 6 500 Hz, 8 K, pulse width 12 µs, pulse repetition rate 7 s, inverse gated decoupling). ^{15}N NMR spectra of compounds *IIb*, *IIc* and *IIe*–*k* were measured at ^{15}N natural abundance level. The solutions for measurements were prepared by filtration of solutions or suspensions of 400 mg of azocompound and 80 mg of tris(acetylacetonato)chromium(III) in 2 ml of solvent. The measurement parameters were the same as with ^{15}N-monolabelled compounds after the addition of tris(acetylacetonato)chromium(III), accumulation time was 10–16 h. The effect of concentration change of tris(acetylacetonato)chromium(III), pulse width, and irradiation mode on the signal to noise ratio was not studied. ^{15}N Chemical shifts are related to the external neat nitromethane (25% ^{15}N, ref.[26]) and their positive values denote downfield shifts.

RESULTS AND DISCUSSION

^{13}C Chemical shifts of *cis*-azobenzene, *trans*-azobenzene, 4-substituted and 4,4'-disubstituted *trans*-azobenzenes are given in Table I. The ^{13}C chemical shifts of *trans*-azobenzene in deuteriochloroform agree with the published values[1] within an experimental error caused by digitalization. The changes for individual carbon atoms in *trans*-azobenzene measured in deuteriochloroform, n-hexane and hexadeuteriodimethyl sulfoxide are in the range 0·4–1·2 ppm. ^{13}C Chemical shifts in *cis*-azobenzene differ from those of the *trans*-derivative according to the expectation (with respect to marked change in geometry[27], change in pK_a (ref.[17]), etc.); the values correspond to an increase of electron density in the positions 2 and 4. The carbon signals in 4-substituted *trans*-azobenzenes were assigned as follows: *a*) by comparison with unsubstituted *trans*-azobenzene and according to the appearence of the proton-coupled spectrum *b*) the substituted ring was assigned using the values of substituent chemical shifts[28] and using the patterns of the proton-coupled spectrum. The values of $^nJ(^{15}N^{13}C)$ were used with ^{15}N-monolabelled compounds. The range of chemical shifts of carbons at the unsubstituted ring in 4-substituted *trans*-azobenzenes is 0·6 ppm for the positions $C_{(1')}$ and $C_{(3')}$ and 1·1 ppm for the position $C_{(2')}$. Most affected is the position $C_{(4')}$ ($\Delta\delta = 3\cdot1$ ppm), where the electron-donating substituents cause upfield shifts and the electron-accepting ones cause downfield shifts. Employing^{13}C substituent chemical shifts (SCS) of the individual substituents, good agreement between measured and calculated ^{13}C chemical shifts in 4-substituted azobenzenes was achieved when the SCS's were added to the corresponding chemical shifts of carbons in *trans*-azobenzene. Thus the results confirm a well known fact that substituted azobenzenes exist mainly as *trans*-derivatives[29] with negligible amount of the hydrazo-form[3,7].

Carbon signals in 4,4'-disubstituted azobenzenes were also assigned using SCS's that were added to the corresponding ^{13}C chemical shifts in 4-substituted *trans*-azobenzenes. The assignment was checked by the inspection of the spectral pattern of the proton-coupled spectra and using the magnitudes of $^nJ(^{15}N^{13}C)$.

Table II gives the absolute values of coupling constants $^nJ(^{15}N^{13}C)$ and $^nJ(^{15}NN$. $.^{13}C)$, respectively, in single ^{15}N-monolabelled *trans*-azobenzenes. Comparing their magnitudes for corresponding positions in *trans*-azobenzenes, these conclusions follow: *a)* magnitudes of $^1J(^{15}N^{13}C)$ (0·6—1·8 Hz) are smaller than $^2J(^{15}NN^{13}C)$ (5·1—6·0 Hz); *b)* magnitudes of $^2J(^{15}N^{13}C)$ and $^3J(^{15}NN^{13}C)$ are nearly equal and amount 3·8—4·6 Hz; *c)* magnitudes of $^3J(^{15}N^{13}C)$ lie in the range 1·6—2·3 Hz whereas those of $^4J(^{15}N^{13}C)$ are in all cases less than 0·5 Hz; *d)* couplings $^4J(^{15}N^{13}C)$ and $^5J(^{15}NN^{13}C)$ are less than 0·9 Hz. From this comparison it is clear that the absolute values of $^nJ(^{15}N^{13}C)$ and $^nJ(^{15}NN^{13}C)$ for the individual carbons of 4-substituted and 4,4'-disubstituted *trans*-azobenzenes, respectively, are within their

TABLE I

^{13}C Chemical shifts (δ scale; ± 0.10 ppm) of azobenzenes *I* and *IIa—IIb*

Compound	Solvent[a]	C(1)	C(2)	C(3)	C(4)	C(1')	C(2')	C(3')	C(4')
I	CDCl₃	153·3	120·5	128·6	127·3	153·3	120·5	128·6	127·3
I	DMSO	153·8	120·1	129·1	127·5	153·8	120·1	129·1	127·5
I	n-hexan	154·1	120·2	128·0	126·2	154·1	120·2	128·0	126·2
IIa	CDCl₃	152·5	122·8	129·0	130·9	152·5	122·8	129·0	130·9
IIa	DMSO	151·9	122·5	129·4	131·4	151·9	122·5	129·4	131·4
IIa	n-hexane	152·7	122·9	128·4	130·2	152·7	122·9	128·4	130·2
IIb[b]	CDCl₃	143·4	124·8	111·3	152·2	153·0	122·0	128·8	129·2
IIc	CDCl₃	145·3	125·0	114·5	149·5	152·8	122·2	128·9	129·7
IIc	DMSO	143·3	125·5	113·8	152·9	152·7	122·1	129·4	129·6
IId[c]	DMSO	145·5	125·1	116·1	161·0	152·3	122·3	129·5	130·8
IIe[d]	CDCl₃	146·8	124·6	114·1	161·9	152·6	122·5	128·9	130·2
IIf[e]	CDCl₃	150·7	122·8	129·8	141·4	152·6	122·7	129·0	130·6
IIg	CDCl₃	151·2	124·3	132·2	125·3	152·4	122·9	129·1	131·2
IIh	CDCl₃	155·5	123·3	124·6	148·5	152·2	122·3	129·2	132·3
IIi	DMSO	145·3	125·5	116·1	162·4	155·5	122·6	124·5	147·5
IIj	DMSO	143·2	123·9[f]	113·7	151·9	145·8	124·7[f]	115·9	159·2
IIk[g]	CDCl₃	143·5	124·7	111·4	152·1	151·1	122·1	129·5	139·5
III[h]	CDCl₃	144·1	126·1	111·7	153·6	157·0	122·6	124·6	147·7

[a] DMSO hexadeuteriodimethyl sulfoxide; [b] $\delta(N(CH_3)_2) = 40.06$; [c] ref.[7]; [d] $\delta(OCH_3) = 55.42$; [e] $\delta(CH_3) = 21.44$; [f] assignment could be reversed;[g] $\delta(N(CH_3)_2) = 40.21$; $\delta(CH_3) = 21.35$, $\delta(N(CH_3)_2) = 40.21$.

characteristic limits (with the exception of direct discerning of positions $C_{(2)}$ and $C_{(2')}$). ^{15}N-labelling represents a very efficient tool of the signal assignment or its confirmation in the 4-substituted or 4,4'-disubstituted *trans*-azobenzenes. The procedure is especially useful when both α and β position are ^{15}N-monolabelled (signals of $C_{(1)}$ and $C_{(1')}$, respectively, can be distinguished from those of $C_{(4)}$ or $C_{(4')}$). Absolute values of coupling constants were used to discern $C_{(1')}$ ($= 153\cdot02$; $J = 5\cdot3$ Hz) form $C_{(4)}$ ($\delta = 152\cdot19$; $J < 0\cdot5$ Hz) in compound *IIb*; the signal of $C_{(1')}$ ($\delta = 152\cdot35$; $J = 1\cdot5$ Hz) from that of $C_{(1)}$ ($\delta = 151\cdot23$; $J = 5\cdot5$ Hz) in compound *IIg*. They were used analogically for the assignment of $C_{(3)}$ in the same compounds (confirmed by selective decoupling) where $^4J(^{15}NN^{13}C) < 0\cdot5$ Hz what is sufficient to distinguish $C_{(3)}$ from $C_{(2)}$ and $C_{(2')}$ (Tables I and II). Corresponding values of coupling constants $^{15}N^{13}C$ were also obtained for the unsubstituted ring in 2-hydroxy--5-tert-butylazobenzene[7]. The values of $^nJ(^{15}N^{13}C)$ for the 2,5-disubstituted nucleus were significantly different. Coupling constants $^nJ(^{15}N^{13}C)$ also undergo changes with increasing proportion of the hydrazo form[7]. ^{15}N Chemical shifts in substituted azobenzenes are given in Table III. The ^{15}N chemical shifts in ^{15}N-monolabelled *trans*-azobenzene was determined in deuteriochloroform, n-hexane, and hexadeuterio-dimethyl sulfoxide. Difference of these chemical shift lie within 1 ppm. ^{15}N NMR signal in *cis*-azobenzene exhibits a downfield shift (17·5 ppm in deuteriochloroform, 20·5 ppm in hexadeuteriodimethyl sulfoxide) in agreement with observations on similar compounds: ^{14}N chemical shift of *cis*-difluorodiazene[11] is 60 ppm downfield from that of *trans*-difluorodiazene; the unsymmetric diazenes mentioned in the

TABLE II

Absolute values of coupling constants $^nJ(^{15}N^{13}C)$ and $^nJ(^{15}NN^{13}C)$, respectively; (Hz, $\pm0\cdot3$ Hz) in substituted *trans*-azobenzenes. Number of intervening bonds given in parentheses

Compound	Position of ^{15}N-labelling	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
IIa	α	1·8 (1)	4·0 (2)	1·8 (3)	0·6 (4)	5·2 (2)	4·0 (3)	0·5 (4)	0·6 (5)
IIb	α	0·6 (1)	4·6 (2)	2·1 (3)	0·5 (4)	5·3 (2)	4·3 (3)	0·5 (4)	0·6 (5)
IId[a]	α	1·17 (1)	4·25 (2)	2·05 (3)	0·88 (4)	5·42 (2)	4·10 (3)	0·5 (4)	0·7 (5)
IId[a]	β	5·13 (2)	4·25 (3)	0·5 (4)	0·85 (5)	1·76 (1)	3·81 (2)	1·76 (3)	0·90 (4)
IIg	β	5·5 (2)	4·2 (3)	0·5 (4)	0·5 (5)	1·5 (1)	4·0 (2)	1·6 (3)	0·5 (4)
IIi	α	0·8 (1)	4·6 (2)	2·3 (3)	0·5 (4)	5·8 (2)	3·9 (3)	0·5 (4)	0·8 (5)
IIj	β	5·1 (2)	4·3 (3)	0·5 (4)	0·8 (5)	0·6 (1)	4·3 (2)	2·1 (3)	0·7 (4)
III	α	0·8 (1)	4·3 (2)	2·2 (3)	0·8 (4)	6·0 (2)	4·0 (3)	0·5 (4)	0·8 (5)

[a] Ref.[7], $\pm0\cdot15$ Hz.

introduction to this paper[12] exhibit in the *cis*-series 7—29 ppm shift in the same direction; with *cis*-azoxybenzene, the differences of 18·1 ppm (NO) and 26·9 ppm (N) (ref.[30]), respectively, were found. In the repeated measurement of ^{15}N-monolabelled *cis*-azobenzene, after 24 h, two signals, corresponding to the mixture of *cis*- and *trans*-azobenzene, were found in the ^{15}N NMR spectrum. For an unambiguous assignment of two close ^{15}N NMR signals of unsymmetrically substituted azobenzenes it was necessary to perform the selective ^{15}N-labelling. Diazotation was performed in aqueous solution and the coupling was made immediately after its completion so that the isotope exchange between N_α and N_β nitrogen atoms in diazonium salt could be neglected[31]. One signal was observed only (besides the signal of the standard) in the ^{15}N NMR spectra of ^{15}N-monolabelled substituted azobenzenes. The measurement

TABLE III
^{15}N Chemical Shifts ($\pm 0·2$ ppm) related to external neat nitromethane (25% ^{15}N) in azobenzenes *I* and *IIa—III*

Compound	Solvent[a]	$\delta(N_\alpha)$[b]			$\delta(N_\beta)$[b]	
		A	B	C	A	C
I	CDCl$_3$	146·5	—	—	146·5	—
I	DMSO	150·6	—	—	150·6	—
IIa	CDCl$_3$	129·0	127·6	127·5	129·0	127·5
IIa	DMSO	130·1	128·7	128·4	130·1	128·4
IIa	n-hexane	129·1	—	—	129·1	—
IIb[c,]	CDCl$_3$	119·2	116·5	117·7	—	96·2
IIc[d]	CDCl$_3$	—	—	118·9	—	101·7
IIc	DMSO	—	—	118·2	—	91·4
IId[e]	DMSO	124·2	—	—	110·2	—
IIe	CDCl$_3$	—	—	121·8	—	113·7
IIf	CDCl$_3$	—	—	126·1	123·6	122·2
IIg	CDCl$_3$	—	—	122·1	130·7	128·6
IIh	CDCl$_3$	—	—	120·9	—	144·0
IIi[f]	DMSO	138·7	137·2	138·0	—	101·2
IIj	DMSO	—	—	103·6	91·8	91·1
IIk	CDCl$_3$	—	—	113·1	—	96·2
III	CDCl$_3$	132·1	—	—	—	—

[a] DMSO hexadeuteriodimethyl sulfoxide; [b] A ^{15}N-monolabelled compound, B ^{15}N-monolabelled compound with Cr(acac)$_3$ added (40 mg/ml), C measured at ^{15}N natural abundance level Cr(acac)$_3$ added (40 mg/ml); [c] $\delta(N(CH_3)_2) = -325·5$ (C); [d] $\delta(NH_2) = -318·4$ (natural abundance), ($-314·0$ method C); [e] ref.[8], $\pm 0·1$ ppm; [f] $\delta(NO_2) = -10·3$ (C).

was repeated after the addition of tris(acetylacetonato)chromium(III) (40 mg/ml, only partially soluble in hexadeuteriodimethyl sulfoxide) and the chemical shifts were determined. Their values were in all cases lower than those without addition of the relaxation agent. Resonance frequencies (in Hz) both of the sample and external CH_3NO_2 (25% ^{15}N) were determined with and without the relaxation agent. From the measured frequencies, it follows that larger frequency change upon the addition of the relaxation agent is observed with external standard (different effect

TABLE IV

^{15}N Substituent chemical shifts (ppm) of nitrogen atoms N_α (SCS$_\alpha$) and N_β (SCS$_\beta$) in 4-substituted *trans*-azobenzenes related to *trans*-azobenzene

Substituent	Solvent[a]	SCS$_\alpha$[b]	SCS$_\beta$[b]
N(CH$_3$)$_2$	CDCl$_3$	$-9\cdot8$ (A); $-12\cdot2$ (B); $-9\cdot8$ (C); $-10\cdot6$[c]	$-31\cdot3$ (C)
NH$_2$	CDCl$_3$	$-8\cdot6$ (C)	$-25\cdot8$ (C)
NH$_2$	DMSO	$-10\cdot2$ (C)	$-37\cdot0$ (C)
OH	DMSO	$-5\cdot9$ (A)	$-19\cdot9$ (A)
OCH$_3$	CDCl$_3$	$-5\cdot7$ (C)	$-13\cdot8$ (C)
CH$_3$	CDCl$_3$	$-1\cdot4$ (C)	$-5\cdot4$ (A); $-5\cdot3$ (C)
Br	CDCl$_3$	$-5\cdot4$ (C)	$+1\cdot7$ (A); $+1\cdot1$ (C); $+1\cdot4$[c]
NO$_2$	CDCl$_3$	$-6\cdot6$ (C)	$+16\cdot5$ (C)

[a] DMSO hexadeuteriodimethyl sulfoxide; [b] A, B, C measuring modes according to note[b] to Table III; [c] average value.

TABLE V

Measured and calculated (using substituent chemical shifts SCS$_\alpha$ and SCS$_\beta$) ^{15}N chemical shifts for compounds *IIi—III*

Compound	$\delta(^{15}N_\alpha)$ found/calculated	$\delta(^{15}N_\beta)$ found/calculated
IIi	138·0/139·0	101·2/101·9
IIj	103·6/ 98·3	91·1/ 85·5
IIk	113·1/112·4	96·2/ 94·8
III	132·1/134·9[a]	— / 91·1[a]

[a] Calculated for ^{15}N-labelled compound in CDCl$_3$.

of the change in magnetic susceptibility). Change of ^{15}N chemical shifts related to the internal and external standard before and after the addition of tris(acetyl-acetonato)chromium(III) was described in the ref.[32]. Both ^{15}N chemical shifts of the azo-bond nitrogen atoms were measured in natural abundance either in deuterio-chloroform or in hexadeuteriodimethyl sulfoxide (solvent with better solubility of samples was chosen) and always with tris(acetylacetonato)chromium(III) added. Tris(acetylacetonato)chromium(III) was used to shorten the relaxation times of the azo-bond nitrogens (T_1 in azobenzene amounts several tens of seconds and is temperature dependent[9]). With ^{15}N-non-labelled compounds the ^{15}N signal assignment was performed assuming analogous effects of electron-accepting and electron-donating substituents (by comparison with the labelled compounds).

Differences in ^{15}N chemical shifts between the measurement of ^{15}N-mono-labelled and non-labelled compounds (Table III) can be explained by tris(acetylacetonato)-chromium(III) acting as a weak shift reagent and by changes in the [substrate] : :[tris(aceylacetonato)chromium(III)] ratio. Table IV gives ^{15}N substituent chemical shifts obtained by comparison of ^{15}N chemical shifts of 4-substituted *trans*-azo-benzenes with *trans*-azobenzene for the α-(SCS_α) and the β-positions (SCS_β). The resonance of nitrogen atoms closer to the substituent was always shifted upfield with respect to *trans*-azobenzene. That of the second nitrogen atom was shifted upfield with electron-donating substituents and downfield with electronaccepting ones. Values of SCS's are solvent-dependent (Table IV, entries for NH_2). The additivity of SCS's is used in ^{13}C NMR spectroscopy for ^{13}C chemical shifts prediction in polysubstituted compounds. Table V gives the values of measured and calculated ^{15}N chemical shifts for 4,4'-disubstituted *trans*-azobenzenes *IIi*–*III*. Very good agreement was achieved for compounds *IIi*, *IIk* and good one for N_α in *IIII*. Second ^{15}N chemical shift in compound *IIII* could not be determined owing to its poor solubility in deuteriochloroform even at 60°C. Despite the substantial differences between measured and calculated ^{15}N chemical shifts for compound *IIj*, the assignment of signals both at lower and higher field agree with the prediction making use of SCS_α and SCS_β. Difference between the calculated and observed ^{15}N chemical shifts of nitrogens N_α and N_β in compound *IIj* are practically the same (5·3 and 5·6 ppm, respectively) and can be due to the saturation effect of two strong electron-donating substituents.

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