^{13}C, ^{15}N, AND ^{19}F NMR SPECTRA OF 4-FLUORO-(3′ OR 4′-SUBSTITUTED) AZOBENZENES

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Received December 7th, 1982

The ^{13}C and ^{19}F NMR spectra of fifteen 4-fluoro-(3′ or 4′-substituted (azobenzenes have been measured. The $\delta(^{19}F)$ values correlate with the corresponding $\sigma_{m,p}$ constants ($\delta(^{19}F) = 3{\cdot}60\sigma_{m,p} - 30{\cdot}78$). The ^{15}N NMR spectra have been measured of six compounds, and additivity of the ^{15}N substitution chemical shifts has been proved. The measured coupling constants are $^{6}J(^{19}F^{15}N) = 2{\cdot}1$ Hz and $^{7}J(^{19}F^{13}C) = 0{\cdot}7$ Hz.

The ^{13}C and ^{15}N NMR spectra of *cis*- and *trans*-azobenzenes and 4-mono- and 4,4′-disubstituted *trans*-azobenzenes have been measured recently[1]. In the 4-substituted azobenzenes the substitution affects mostly the chemical shifts of $C_{(4')}$ atom, the slope ϱ in the equation $\delta(^{13}C) = \varrho\sigma + c$ being positive. In the same compounds the ^{15}N substitution chemical shifts ($^{15}N_\alpha$—SCS and $^{15}N_\beta$—SCS) were determined which, however, show no simple dependence on the σ constants. The ^{15}N—SCS values were used for prediction of the ^{15}N chemical shifts in the 4,4′-disubstituted-*trans*-azobenzenes.

The aim of the present work was to measure and assign the ^{13}C, ^{15}N, and ^{19}F chemical shifts and to determine the $^{n}J(^{19}FX)$ coupling constants in a series of 4-floro-(3′ or 4′-substituted) azobenzenes and, furthermore, to study the substituent effects of the ^{19}F chemical shifts.

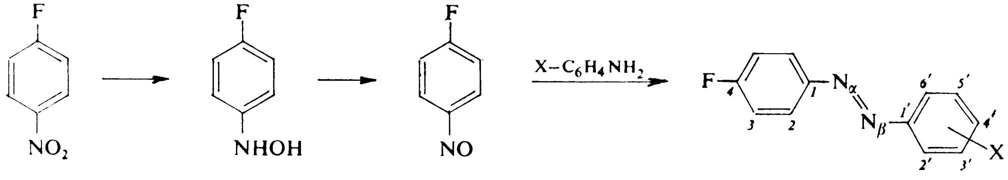
EXPERIMENTAL

The preparation method of 4-fluoro-(3′ or 4′-substituted)azobenzenes *Ia*—*Io* is given in Scheme I. 4-Fluoronitrosobenzene was prepared by reduction of 4-nitrofluorobenzene with zinc and by subsequent oxidation of the 4-fluorophenylhydroxylamine formed with ferric chloride[2]. The compounds *Ia*—*Io* were prepared by reaction of 4-fluoronitrosobenzene with the respective 3- or 4-substituted anilines in acetic acid medium[3]. The products were purified on an alumina column using cyclohexane or benzene as eluent. ($^{15}N_\beta$)-4-Fluoroazobenzene was prepared from ^{15}N-aniline (94·8% ^{15}N, Isocommerz Berlin). The condensation gave 4,4′-difluoroazoxybenzene (*II*) as a side product unless 4-fluoronitrosobenzene was purified by steam distillation.

The ^{13}C, ^{15}N, and ^{15}F NMR spectra were measured at 25·047, 10·095, and 93·708 MHz, respectively, using a JNM-FX 100 (JEOL) apparatus equipped with tunable multinuclear probe, quadrature detection, and working in FT mode. For the measurements of ^{13}C and ^{19}F NMR spectra we used 5—10% (W/V) solutions in deuteriochloroform, and the measurements were carried out in 10 mm (o.d.) NMR test tubes at 300 K. For the measurements of ^{19}F NMR spectra we also used more diluted solutions, but the found differences in chemical shifts were within experimental error. Deuteriochloroform was used as an internal lock substance. The NMR spectra were measured in the standard way; the measurement of $^{n}J(^{19}F^{13}C)$ and $\delta(^{19}F)$ was carried out at digital resolution of 0·6 Hz/point and 1 Hz/point, respectively, (±0·011 ppm). For the measurements of ^{15}N NMR spectra we used the solutions prepared by filtration of solutions or suspensions of 400 mg azo compounds and 50 mg $Cr(acac)_3$ in 2 ml deuteriochloroform. The measurement parameters were the same as in ref.[1]. The ^{13}C, ^{15}N, and ^{19}F chemical shifts are related to internal tetramethylsilane, external neat nitromethane (25% ^{15}N) or external neat trifluoroacetic acid, respectively. Positive values denote the downfield shifts.

RESULTS AND DISCUSSION

The compounds *Ia*–*Io* were prepared according to Scheme I. 4-Fluoronitrosobenzene must be steam-distilled, otherwise the residual 4-fluorophenylhydroxylamine reacts in acid medium with 4-fluoronitrosobenzene to give 4,4′-difluoroazoxybenzene *II*. $\delta(^{19}F)$ of compound *II* have the values 29·30 and 29·82. The values of ^{13}C chemical shifts of compound *II* are given in Table I. The assignment of signals was carried out with the help of ^{13}C substitution shifts for fluorine[4] and ^{13}C chemical shifts in *trans* azoxybenzene ($C_{(1-4)}$: 143·91, 125·48, 128·65, 129·57, $C_{(1'-4')}$: 148·28, 122·26, 128·65, 131·51) which were assigned on the basis of comparison of the chemical shift in *trans* azoxybenzene, 4-bromoazoxybenzene, and 3-nitroazoxybenzene[5], the assignment of the ^{13}C chemical shifts being different from the published values[4]. The ^{13}C chemical shifts of compounds *Ia*–*Io* were assigned on the basis of com-



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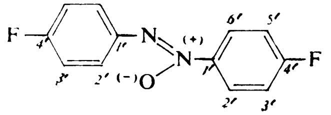

II

Ia, X = 4′-$N(CH_3)_2$
Ib, X = 4′-OCH_3
Ic, X = 4′-CH_3
Id, X = 3′-CH_3
Ie, X = H
If, X = 4′-F
Ig, X = 4′-I
Ih, X = 4′-Cl
Ii, X = 4′-Br
Ij, X = 3′-$COCH_3$
Ik, X = 3′-Cl
Il, X = 4′-$COOCH_3$
Im, X = 4′-$COCH_3$
In, X = 3′-NO_2
Io, X = 4′-NO_2

parison with other azo compounds[1] with the use of the ^{13}C substituent chemical shifts (SCS), and the assignment was checked by the appearance of the proton-coupled spectrum. The values of ^{13}C chemical shifts of compounds *Ia*–*Io* are given in Table I. The 3′- and 4′-substituents exert the largest influence on the fluor-substituted nucleus in the ^{13}C chemical shifts of $C_{(4)}$ atom which correlate with the $\sigma_{m,p}$ constants according to Eq. (*1*).

$$\delta(C_{(4)}) = (1{\cdot}12 \pm 0{\cdot}08)\,\sigma_{m,p} + (164{\cdot}16 \pm 0{\cdot}03)\,, \quad n = 15\,, \quad r = 0{\cdot}968 \qquad (1)$$

The $^{n}J(^{19}F^{13}C)$ values were obtained from the ^{13}C NMR spectra. $^{1}J(^{19}F^{13}C)$ values are given in Table II and these values correlate with the $\sigma_{m,p}$ constants of the substituents according to Eq. (*2*).

$$^{1}J(^{19}F^{13}C) = (3{\cdot}31 \pm 0{\cdot}33)\,\sigma_{m,p} + (251{\cdot}70 \pm 0{\cdot}14)\,, \quad n = 15\,, \quad r = 0{\cdot}940 \qquad (2)$$

TABLE I

The ^{13}C chemical shifts (δ scale, ±0·10 ppm) in the compounds *Ia*–*Io* and *II* in deuteriochloroform

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$
Ia[e]	149·59	123·85	115·60	163·21	143·28	124·80	111·38	152·28	111·38	124·80
Ib[b]	149·13	124·43	115·81	163·84	146·66	124·64	114·12	161·95	114·12	124·64
Ic[c]	149·13	124·62	115·91	164·12	150·49	122·78	129·72	141·58	129·72	122·78
Id[d]	149·00	124·25	115·84	164·18	152·44	122·96	138·79	131·67	128·75	120·37
Ie[e]	149·08	124·83	115·97	164·32	152·40	122·81	129·05	131·00	129·05	122·81
	(5·5)	(4·1)	(<0·5)	(0·6)	(1·2)	(3·9)	(1·6)	(<0·5)	(1·6)	(3·9)
If	148·92	124·73	115·99	164·29	148·92	124·73	115·99	164·29	115·99	124·73
Ig	148·80	124·96	116·07	164·45	151·64	124·35	138·28	97·66	138·28	124·35
Ih	148·93	124·89	116·04	164·42	150·69	124·02	129·28	136·88	129·28	124·02
Ii	148·87	124·99	116·06	164·43	151·05	121·25	132·25	125·34	132·25	121·25
Ij[f]	148·75	124·98	115·99	164·45	152·29	122·66	137·91	130·11	129·24	126·75
Ik	148·78	125·04	116·06	164·57	153·17	122·30	135·08	130·64	130·06	121·67
Il[g]	148·97	125·15	116·08	164·65	154·77	122·49	130·53	131·69	130·53	122·49
Im[h]	148·97	125·20	116·10	164·70	154·67	122·76	129·29	138·25	129·29	122·76
In	148·34	125·20	116·03	164·76	152·40	116·61	148·69	124·64	129·71	128·89
Io	148·81	125·53	116·28	165·08	155·39	123·30	124·63	148·58	124·63	123·30
II	140·19	127·92	115·60	162·43	144·10	124·44	115·60	164·38	115·60	124·44

[a] $\delta(N(CH_3)_2) = 40{\cdot}20$, [b] $\delta(OCH_3) = 55{\cdot}41$, [c] $\delta(CH_3) = 21{\cdot}52$, [d] $\delta(CH_3) = 21{\cdot}26$, [e] the values in brackets give $|^{n}J(^{15}N^{13}C)|$, [f] $\delta(CO) = 197{\cdot}17$, $\delta(CH_3) = 26{\cdot}66$, [g] $\delta(COO) = 166{\cdot}31$, $\delta(OCH_3) = 52{\cdot}25$, [h] $\delta(CO) = 197{\cdot}22$, $\delta(CH_3) = 26{\cdot}76$.

However, in this case the correlation is affected by still greater relative experimental error than that in Eq. (*1*). The $^nJ(^{19}F^{13}C)$ values ($n = 2, 3, 4$) are, within experimental error, independent of the substitution and are equal to 23·0, 9·2, 3·0, respectively, (in Hz, ±0·5 Hz). The $^nJ(^{19}F^{13}C)$ values agree well with analogous values of fluorobenzene[6,7] (−245·07, 21·02, 7·79, 3·20). For compounds *Ia*–*Io* we also measured $^7J(^{19}F^{13}C_{(1')}) = 0.7 \pm 0.2$ Hz. From the proton coupled ^{19}F NMR spectra we read the values $^3J(^{19}F^1H) = 8.2 \pm 0.2$ Hz and $^4J(^{19}F^1H) = 5.2 \pm 0.2$ Hz for all the measured compounds *I* (ref.[7] gives 9·13 and 5·72 for fluorobenzene).

The ^{15}N chemical shifts of the substituted fluoroazobenzenes *I* were obtained by ^{15}N NMR measurement at natural abundance. Unambiguaous assignment of N_α and N_β in 4-fluoroazobenzene was achieved by the measurement of the $^{15}N_\beta$ isotopomer. The calculated ^{15}N substitution chemical shifts are $^{15}N_\alpha$—SCS = −5·2 and $^{15}N_\beta$—SCS = −2·9 related to *trans* azobenzene[1] for 4-fluorosubstitution. Refs[8,9] give a rather small number of $^nJ(^{19}F^{15}N)$ coupling constants, mainly for $n = 2-5$. The $^nJ(^{19}F^{15}N)$ values ($n = 2-5$) of fluoroanilines and their derivatives vary within the limits 0 to 1·9 Hz (ref.[10]). No $^5J(^{19}F^{15}N)$ coupling constant was observed in 4-fluoroazobenzene (<0·7 Hz), but from both the ^{15}N and ^{19}F NMR

TABLE II

The values of ^{19}F chemical shifts (±0·02 ppm), ^{19}F substitution chemical shifts, coupling constants $^1J(^{19}F^{13}C)$ (±0·6 Hz), and the σ values used in the correlations

Compound	$\delta(^{19}F)$	^{19}F-SCS	$^1J(^{19}F^{13}C)$	$\sigma_{m,p}$[a]
Ia	−33·37	2·71	249·0	−0·63
Ib	−31·70	1·04	251·0	−0·28
Ic	−31·16	0·50	251·8	−0·14
Id	−30·86	0·20	251·5	−0·06
Ie	−30·66	0·00	252·7	0·00
If	−30·49	−0·17	251·5	0·06
Ig	−29·83	−0·83	252·3	0·21
Ih	−30·00	−0·66	252·9	0·22
Ii	−29·87	−0·79	252·1	0·22
*I*l	−29·65	−1·01	252·7	0·36
Ik	−29·60	−1·06	252·9	0·37
Il	−29·24	−1·42	252·9	0·44
Im	−29·06	−1·60	252·7	0·47
In	−28·41	−2·25	253·9	0·71
Io	−27·82	−3·04	254·8	0·81

[a] The values were taken from ref.[6].

spectra of (^{15}N)-4-fluoroazobenzene it was possible to obtain for the first time the value $^{6}J(^{19}F^{15}N) = 2{\cdot}1 \pm 0{\cdot}2$ Hz. Table III gives the experimental and calculated values of ^{15}N chemical shifts of compounds *I*, the calculation being carried out with the use of ^{15}N-SCS of the respective substituents[1] and with the use of $\delta(^{15}N)$ in *trans* azobenzene[1] under the corresponding experimental conditions. From the point of view of ^{15}N NMR spectroscopy a very good agreement was reached between the measured and the calculated values of ^{15}N chemical shifts.

The $\delta(^{19}F)$ and/or ^{19}F—SCS values are often used in studies of substituent effects[11,12], because the ^{19}F NMR spectra are obtained very easily, are simple and measurable with high accuracy with respect to favourable relation of experimental error to the span of values of the chemical shifts. As early as in 1952, Gutowsky and coworkers observed[13] a correlation between ^{19}F—SCS and $\sigma_{m,p}$ for 4- and 3-substituted fluorobenzenes. Ager and coworkers[14,15] correlated ^{19}F—SCS in 4-fluoro -(3′- or 4′-substituted)*trans*-stilbenes and found a dependence of ^{19}F—SCS according to Eq. (*3*).

$$^{19}\text{F—SCS} = 2{\cdot}677\sigma_{m,p}\,, \quad r = 0{\cdot}992 \qquad (3)$$

In the azo compounds measured the obtained dependence between $\delta(^{19}F)$ and $\sigma_{m,p}$ is given by Eq. (*4*).

$$\delta(^{19}F) = (3{\cdot}60 \pm 0{\cdot}11)\,\sigma_{m,p} - (30{\cdot}78 - 0{\cdot}04)\,, \quad n = 15\,, \quad r = 0{\cdot}994 \qquad (4)$$

TABLE III

The measured and calculated values of ^{15}N chemical shifts (±0·2 ppm) in the compounds *I*

Compound	$\delta(^{15}N_\alpha)$ found	$\delta(^{15}N_\alpha)$ calculated	$\delta(^{15}N_\beta)$ found	$\delta(^{15}N_\beta)$ calculated
Ie[a]	123·8	—	126·1	—
Ie[b]	—	—	126·2	—
Ia[c]	92·0	90·0	115·2	114·0
Ib[c]	109·5	108·5	119·7	118·9
Ic[c]	117·4	117·0	123·6	123·2
If[a]	121·1	120·8	121·1	120·8
Io[c,d]	139·1	138·8	118·6	118·0

[a] Measured at natural abundance of ^{15}N isotope; [b] selectively ^{15}N-labelled compound; [c] measured at natural abundance level of ^{15}N isotope with addition of Cr(acac)$_3$ (25 mg/ml); [d] $\delta(NO_2) = -12{\cdot}8$.

Comparing the slope values of the substituted fluorobenzenes[16] with those of compounds *I*, we find the slope value of the azo compounds about five times smaller, which is connected with the much greater distance between fluorine atom and the substituent. Furthermore, the substituent effects were compared, the distance between fluorine and the substituents being maintained the same. Using the ^{19}F NMR spectra, Ager and coworkers[15] studied the transfer of electronic effects of a group X through a group Z in the compounds type $4\text{-F}{-}C_6H_4{-}Z{-}C_6H_4{-}(4\text{-X})$ (*III*), where Z means substituted carbon, oxygen or sulphur atoms. The ^{19}F—SCS values of compounds *III* were correlated with respect to the ^{19}F—SCS of 4-fluoro-4′-X-*trans*-stilbenes ($Z = CH{=}CH$), and the obtained slope values varied within the limits 0·20 ($Z = CH_2\text{-}CH_2$) to 3·70 ($Z = C{=}\overset{+}{O}{-}H$). The same correlation was carried out for the substituted fluoroazobenzenes *I* to give the slope value about 1·3 which is almost equal to that observed for substituted 4-fluorobiphenyls[15] (1·36 ± 0·20).

To explain the difference between the slopes of *trans* azobenzenes *I* and *trans* stilbenes *III* ($Z = CH{=}CH$), we carried out a calculation using the *F* and *R* values by Swain and Lupton[17]. The correlations for the compounds *I* and for the substituted 4-fluoro-*trans*-stilbenes (the ^{19}F—SCS values measured in chloroform were taken from ref.[15]) are given in Eqs (*5*) and (*6*), respectively.

$$^{19}\text{F—SCS} = (-2{\cdot}01 \pm 0{\cdot}09)\,F + (-3{\cdot}60 \pm 0{\cdot}23)\,R \qquad (5)$$

$$n = 10\,, \quad \text{the F test value} = 431{\cdot}6$$

$$^{19}\text{F—SCS} = (-1{\cdot}45 \pm 0{\cdot}12)\,F + (-2{\cdot}19 \pm 0{\cdot}18)\,R \qquad (6)$$

$$n = 9\,, \quad \text{the F test value} = 209{\cdot}2$$

The negative values of the coefficients are given by the calculation method of ^{19}F—SCS and choice of the standard in the measurement of ^{19}F chemical shifts. The larger numerical values of ^{19}F—SCS of the azo compounds *I* are due to both the increased significance of the field constants *F* and increased significance of the resonance constants *R*, the participation of the resonance effect being relatively more important.

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Translated by J. Panchartek.