

^{13}C AND ^{15}N NMR SPECTRA OF 3-METHYL-1-PHENYLPYRAZOLE-4,5-DIONE 4-(4'-SUBSTITUTED PHENYL)HYDRAZONES

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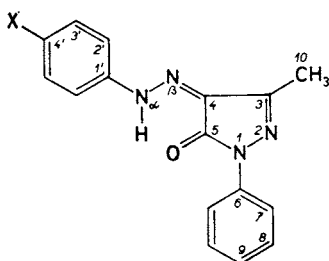
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^{13}C and ^{15}N NMR spectra have been measured of eleven 3-methyl-1-phenylpyrazole-4,5-dione 4-(4'-substituted phenyl)hydrazones (*I*). The ^{13}C chemical shifts of the non-substituted compound *I* have been assigned with the use of the $^1J(^{13}\text{C}, ^{13}\text{C})$ coupling constants obtained from the 1D-INADEQUATE spectrum. The greatest changes in chemical shifts of the compounds *I* connected with the substituent at 4'-position have been observed for the nitrogen atoms N_α , N_β , N_2 and carbon C(4). These substitution chemical shifts have been correlated with the substituent constants by means of the equations $\text{SCS} = \rho_1\sigma_1 + \rho_R\bar{\sigma}_R + \text{const.}$, where $\bar{\sigma}_R$ means one of the values σ_{R}^0 , $\sigma_{\text{R}}^{\text{BA}}$, σ_{R}^- , or σ_{R}^+ . The best correlations have been obtained for the combinations $\text{N}_\alpha - \sigma_{\text{R}}^{\text{BA}}$, $\text{N}_\beta - \sigma_{\text{R}}^-$, $\text{N}_2 - \sigma_{\text{R}}^0$, and $\text{C}(4) - \sigma_{\text{R}}^0$. The ^{15}N substituent chemical shifts of the nitrogen atoms N_α and N_β of compounds *I* have been compared with the analogous values of 4-substituted *trans*-azobenzenes.

The azo coupling products of benzenediazonium salts with 3-methyl-1-phenylpyrazole-5-one represent a significant group of pyrazolone dyestuffs¹. These compounds can be very well characterized by their ^{13}C and ^{15}N chemical shifts²⁻⁵. The assignment



- | | |
|----------------------------------|--------------------------------------|
| <i>Ia</i> , X = NH ₂ | <i>Ig</i> , X = Br |
| <i>Ib</i> , X = OCH ₃ | <i>Ih</i> , X = I |
| <i>Ic</i> , X = CH ₃ | <i>Ii</i> , X = CH ₃ COO |
| <i>Id</i> , X = H | <i>Ij</i> , X = CF ₃ |
| <i>Ie</i> , X = F | <i>Ik</i> , X = NO ₂ |
| <i>If</i> , X = Cl | <i>Il</i> , X = CH ₃ CONH |

of ^{13}C chemical shifts in the non-substituted compound *Id* agrees with refs^{2,4,5} except for the assignment of C_3 and C_4 carbon atoms. The measurements of ^{13}C chemical shifts in 3-tert-butyl-1-phenylpyrazole-5-one and 3-tert-butyl-1-phenylpyrazole-4,5-dione 4-phenylhydrazone⁶ support the assignment given in refs^{4,5}. The 3-methyl-1-phenylpyrazole-4,5-dione 4-(4'-substituted phenyl)hydrazones *I* exist completely in their hydrazone form with intramolecular hydrogen bridge²⁻⁵ and represent a suitable model for a study of substituent effects on the N_α and N_β nitrogen atoms in the $4\text{-X-C}_6\text{H}_4\text{-N}_\alpha\text{H-N}_\beta=$ grouping and make it possible to compare these effects with the ^{15}N substituent chemical shifts in $\text{trans-4-X-C}_6\text{H}_4\text{-N}_\alpha=\text{N}_\beta\text{-C}_6\text{H}_5$.

EXPERIMENTAL

3-Methyl-1-phenylpyrazole-4,5-dione 4-(4'-substituted phenyl)hydrazones *Ib-II* were prepared by azo coupling of the respective diazonium salts with 3-methyl-1-phenylpyrazole-5-one in acetic acid medium⁷. Compound *Ia* was prepared by acid hydrolysis of compound *II*⁸. The compounds were recrystallized from ethanol. The ^{15}N -enriched compounds (*Ia* - N_β , N_1 , N_2 : 95% ^{15}N ; *Id* - N_α : 10% ^{15}N , N_β , N_1 , N_2 : 95% ^{15}N ; *Ik* - N_α : 10% ^{15}N , N_β , N_1 , N_2 : 95% ^{15}N) were prepared similarly by azo coupling with [$^{15}\text{N}_2$]-3-methyl-1-phenylpyrazole-5-one⁹.

The ^{13}C and ^{15}N NMR spectra were measured with a JNM-FX 100 (JEOL) apparatus at 25.047 and 10.095 MHz, resp., in the pulse mode. The samples for the measurements were about 20% (w/v) or saturated (in the case of the little soluble derivatives *Ia* and *Ik*) solutions in C^2HCl_3 in 10 mm NMR test tubes, temperature 300 K. The experimental conditions of the measurements of ^{13}C NMR spectra were as follows: spectral width 5 000 Hz, 8 K, 30° pulse, pulse repetition 3 s. The ^{13}C chemical shifts are related to the solvent signal ($\delta = 77.0$) and transformed to the δ scale. The 1-D INADEQUATE (ref.¹⁰) ^{13}C NMR spectra of compound *Id* and *trans*-azobenzene were measured on a Bruker AM-300 NMR spectrometer at 75.54 MHz with the use of the pulse program INADCOMP (Bruker; VS. 831101) which utilizes composite 90° and 180° pulses and Ernst-type double-quantum phase cycling for suppression of the artefacts. The length of mixing period for transfer of the double-quantum coherences into observable magnetization was optimized for coupling constant $^1J(^{13}\text{C}, ^{13}\text{C}) = 60$ Hz. The relaxation delay was 6 s, and accumulations were carried out overnight. The observation offset, spectral width, and number of memory points were chosen so that digital resolution in spectra were better than 0.1 Hz/point.

The ^{15}N NMR spectra of the N_α nitrogen atoms were measured in the following way: spectral width 5 000 Hz, 8 K, 45° pulse, pulse repetition 5 s, the proton noise decoupling. After the measurement of ^{15}N chemical shifts of the N_α nitrogen atoms, the solutions of compounds *I* were treated with $\text{Cr}(\text{acac})_3$ (20 mg/ml) as the relaxation agent, and the measurement of ^{15}N chemical shifts was carried out at the above-given conditions. The ^{15}N chemical shifts were related to external neat nitromethane (25% ^{15}N).

RESULTS AND DISCUSSION

The $^1J(^{13}\text{C}, ^{13}\text{C})$ coupling constants obtained from the 1-D INADEQUATE spectrum of compound *Id* enable an unambiguous assignment of the ^{13}C chemical shifts of this compound. The results are given in Table I, and the assignment of ^{13}C

chemical shifts agrees with published data⁴⁻⁶. The compound *Id* was used as the model standard for estimation of the content of azo and hydrazo forms in azo dye-stuffs^{2,3}. In order to appreciate the possibility of the $^1J(^{13}\text{C}, ^{13}\text{C})$ coupling constants to the same purpose, we measured, by the 1-D INADEQUATE method, the $^1J(^{13}\text{C}, ^{13}\text{C})$ coupling constants in *trans*-azobenzene ($^1J(^{13}\text{C}, ^{13}\text{C}) = 64.3$ (C(1)—C(2)); 56.7 (C(2) C(3)); 55.8 (C(3) C(4)) Hz; ± 0.1 Hz). From the comparison with $^1J(^{13}\text{C}, ^{13}\text{C})$ of the C(1')—C(4') carbon atoms of compound *Id* it follows that, due to practical coincidence of the corresponding values, the $^1J(^{13}\text{C}, ^{13}\text{C})$ values are almost useless for appreciation of the azo-hydrazone tautomerism. This conclusion is also confirmed by the corresponding $^1J(^{13}\text{C}, ^{13}\text{C})$ values of phenyl group in the azo coupling product of benzenediazonium chloride and 2-naphthol ($^1J = 65.0, 58.2, \text{ and } 56.0$)¹¹.

The ^{13}C chemical shifts of compounds *Ia–Ik* (compound *Il* exhibits slight solubility in C^2HCl_3) are given in Table II. The assignment was carried out with the help of the ^{13}C substituent chemical shifts¹² and was checked with respect to the ^{13}C proton coupled spectrum and/or by means of the selective decoupling.

The ^{15}N NMR chemical shifts of compounds *Ia–Ik* are presented in Table III. First we measured the ^{15}N chemical shift of N_αH group, then the relaxation agent (see Experimental) was added and the ^{15}N chemical shifts of all nitrogen atoms were measured. A typical ^{15}N NMR spectrum obtained by overnight accumulation

TABLE I
 ^{13}C NMR chemical shifts and $^1J(^{13}\text{C}, ^{13}\text{C})$, $^1J(^{13}\text{C}, \text{H})$, and $^nJ(^{15}\text{N}, ^{13}\text{C})$ coupling constants of compound *Id* in C^2HCl_3 at 300 K

Carbon	$\delta(^{13}\text{C})^a$	$^1J(^{13}\text{C}, ^{13}\text{C})^b$	$^1J(^{13}\text{C}, \text{H})^a$	$^nJ(^{15}\text{N}_\alpha, ^{13}\text{C})^a$	$^nJ(^{15}\text{N}_\beta, ^{13}\text{C})^a$
3	148.30	63.7 (C(3) C(4))	—	$^3J = 2.90$	$^2J = 8.64$
4	128.31	66.9 (C(4) C(5))	—	$^2J = 0.60$	$^1J = 5.13$
5	157.55	—	—	$^3J = 1.68$	$^2J < 0.5$
6	137.91	64.4 (C(6) C(7))	—	—	—
7	118.28	57.8 (C(7) C(8))	163.2	—	—
8	128.75	55.9 (C(8) C(9))	161.4	—	—
9	124.91	—	161.0	—	—
10	11.66	52.6 (C(3) C(10))	129.4	—	—
1'	140.94	65.2 (C(1') C(2'))	—	$^1J = 18.77$	$^2J = 5.71$
2'	115.60	59.0 (C(2') C(3'))	161.4	$^2J = 1.83$	$^3J = 2.34$
3'	129.48	56.0 (C(3') C(4'))	161.4	$^3J = 2.44$	$^4J < 0.5$
4'	125.59	—	161.5	$^4J < 0.5$	$^5J < 0.5$

^a Ref. 2; ^b Hz, ± 0.1 Hz.

TABLE II
 ^{13}C NMR chemical shifts of compounds Ia—Ik in C^2HCl_3 at 300 K

Compound	Carbon												
	3	4	5	6	7	8	9	10	1'	2'	3'	4'	
Ia	148.2	126.7	158.1	138.3	118.5	128.9	124.9	11.7	133.1	117.5	115.8	145.1	
Ib ^a	147.8	127.0	157.5	138.0	117.9	128.5	124.5	11.4	134.4	116.7	114.5 ^b	157.5	
Ic ^c	147.8	127.4	157.3	137.9	117.8	128.5	124.4	11.4	138.5	115.2	129.7	135.2	
Id	148.3	128.3	157.6	137.9	118.3	128.8	124.9	11.7	140.9	115.6	129.5	125.6	
Ie ^d	148.2	128.3	157.5	137.9	118.2	128.7	124.9	11.6	137.3	117.0	116.4	160.3	
If	148.1	128.7	157.3	137.8	118.0	128.7	124.9	11.5	139.5	116.5	129.4	130.5	
Ig	148.3	128.9	157.5	137.8	118.2	128.8	125.1	11.6	140.1	117.0	132.5	118.4	
Ih	148.0	128.8	157.3	137.7	118.0	128.6	124.9	11.6	140.6	117.2	138.2	89.0	
Ii ^e	147.9	129.4	157.1	137.4	117.5	128.4	124.6	11.4	144.1	114.5	130.8	126.1	
Ij ^f	148.5	129.9	157.5	137.7	118.2	128.8	125.2	11.6	143.7	115.4	126.8	126.9	
Ik	148.6	131.5	157.2	137.5	118.4	129.0	125.5	11.8	146.1	115.3	125.7	144.4	

^a $\delta(\text{OCH}_3) = 55.1$; ^b the assignment according to selective decoupling, $\delta(\text{C}(3')\text{H}) = 6.84$; ^c $\delta(\text{CH}_3) = 20.6$; ^d $^nJ(^{19}\text{F}, ^{13}\text{C}) = 246.6$ Hz ($n = 1$), 23.2 Hz (2), 8.5 Hz (3), 2.4 Hz (4); ^e $\delta(\text{COO}) = 165.6$, $\delta(\text{OCH}_3) = 51.7$; ^f $\delta(\text{CF}_3) = 123.9$, $^nJ(^{19}\text{F}, ^{13}\text{C}) = 271.6$ Hz ($n = 1$), 33.0 (2), 3.7 Hz (3).

after addition of chromium(III) acetylacetonate ($\text{Cr}(\text{acac})_3$) is presented in Fig. 1. Compounds *Ia* and *Ik*, which are very little soluble in C^2HCl_3 , and compound *Id* (for the purposes of comparison and calculation of the substituent chemical shifts,

TABLE III
 ^{15}N Chemical shifts of compounds *Ia–Ik* in C^2HCl_3 at 300 K

Compound	$\delta(\text{N}_\alpha)$	$\delta(\text{N}_\alpha)^a$	$\delta(\text{N}_\beta)^a$	$\delta(\text{N}_1)^a$	$\delta(\text{N}_2)^a$
<i>Ia</i>	-199.9		-17.4 ^b	-191.3 ^b	-80.4
<i>Ib</i>	-203.6	-204.4	-19.0	-192.4	-79.2
<i>Ic</i>	-204.5	-205.8	-19.8	-192.9	-78.1
<i>Id</i>	-205.6	-206.4	-18.9	-192.4	-76.1
<i>Id</i>	-205.4 ^c		-17.4 ^c	-191.5 ^c	-75.3 ^c
<i>Ie</i>	-207.6	-208.6	-19.8	-192.1	-75.8
<i>If</i>	-208.7	-209.4	-20.8	-192.3	-74.2
<i>Ig</i>	-208.2	-209.3	-20.8	-192.5	-74.7
<i>Ih</i>	-208.6	-209.2	-21.3	-192.1	-73.9
<i>Ii</i>	-209.8	-210.8	-22.7	-192.9	-72.3
<i>Ij</i>	-210.9	-212.1	-22.2	-192.8	-72.1
<i>Ik</i>	-212.9 ^c		-22.4 ^c		
<i>Ik</i>		-213.2 ^d	-22.7 ^d	-191.9 ^d	-67.4 ^d

^a Measured with the addition of $\text{Cr}(\text{acac})_3$ (20 mg/ml); ^b the $^{15}\text{N}_3$ -labelled compound measured without $\text{Cr}(\text{acac})_3$; ^c the $^{15}\text{N}_4$ -labelled compound measured without $\text{Cr}(\text{acac})_3$; ^d the $^{15}\text{N}_4$ -labelled compound measured with addition of $\text{Cr}(\text{acac})_3$.

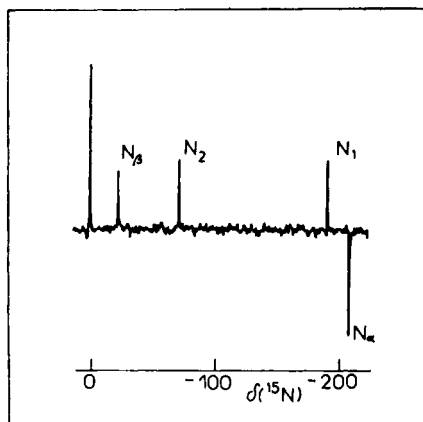


FIG. 1
The ^{15}N NMR spectrum of compound *Id* measured with addition of $\text{Cr}(\text{acac})_3$ at 300 K

TABLE IV
 ^{15}N and ^{13}C substituent chemical shifts (SCS) of compounds Ia–Ik and of 4-substituted *trans*-azobenzenes^a II

Substituent	Ia–k					II		
	$^{15}\text{N}_\alpha$ -SCS	$^{15}\text{N}_\beta$ -SCS	$^{15}\text{N}_1$ -SCS	$^{15}\text{N}_2$ -SCS	$^{13}\text{C}_4$ -SCS	$^{15}\text{N}_\alpha$ -SCS	$^{15}\text{N}_\beta$ -SCS	$^{15}\text{N}_\beta$ -SCS
N(CH ₃) ₂	—	—	—	—	—	—10.6	—	—31.3
NH ₂	5.7	0.0	0.2	—5.1	—1.6	—8.6	—	—25.8
OCH ₃	2.0	—0.1	0.0	—3.1	—1.3	—5.7	—	—13.8
CH ₃	1.1	—0.9	0.5	—2.0	—0.9	—1.4	—	—5.4
H	0.0	0.0	0.0	0.0	0.0	0.0	—	0.0
F	—2.0	—0.9	0.3	0.3	0.0	—5.2 ^b	—	—2.9 ^b
Cl	—3.1	—1.9	0.1	1.9	0.4	—	—	—
Br	—2.6	—1.9	—0.1	1.4	0.6	—5.4	—	1.4
I	—3.0	—2.4	0.3	2.2	0.5	—	—	—
CH ₃ COO	—4.2	—3.8	—0.4	4.0	1.1	—	—	—
CF ₃	—5.3	—3.3	—0.5	3.8	1.6	—	—	—
NO ₂	—7.5	—5.0	—0.5	8.7	3.2	—6.6	—	16.5

^a Ref. 17, ^b ref. 23

see below) were measured after being enriched in the ^{15}N isotope. The ^{15}N -enriched compounds enable the measurement of $^1J(^{15}\text{N}_1, ^{15}\text{N}_2)$ coupling constants. The following values were found: $Ia - ^1J(^{15}\text{N}_1, ^{15}\text{N}_2) = 12.0$; $Id - ^1J(^{15}\text{N}_\alpha, ^{15}\text{N}_\beta) = 11.1$; $^1J(^{15}\text{N}_1, ^{15}\text{N}_2) = 12.2$; $Ik - ^1J(^{15}\text{N}_1, ^{15}\text{N}_2) = 12.4$; $^1J(^{15}\text{N}_\alpha, ^{15}\text{N}_\beta) = 11.1$ (Hz; ± 0.3 Hz). The $^1J(^{15}\text{N}_\alpha, ^{15}\text{N}_\beta)$ values found correspond to hydrazone compounds¹³, and the $^1J(^{15}\text{N}_1, ^{15}\text{N}_2)$ agree with the analogous values found for [$^{15}\text{N}_2$]-1-phenylpyrazole and 3-methyl-1-phenylpyrazol-5-one⁹. The assignment of N_α and N_β nitrogen atoms was carried out unambiguously by measuring the ^{15}N -monolabelled compounds *Id* (ref.³). The assignment of the N_α atom agrees with high negative value of the nuclear Overhauser effect which remains partially maintained also in the spectra measured after the addition of $\text{Cr}(\text{acac})_3$ (Fig. 1). The ^{15}N chemical shifts of the N_1 and N_2 nitrogen atoms were differentiated by comparison with those in 1-phenylpyrazole and 3-methyl-1-phenylpyrazol-5-one⁹. The signals with the ^{15}N chemical shifts about -192 ppm were assigned to the N_1 nitrogen atom (pyrrole type of nitrogen¹⁴) and those about -76 ppm to N_2 (pyridine type of nitrogen¹⁴). The ^{15}N substituent chemical shifts (SCS) were calculated from Eq. (1):

$$^{15}\text{N}\text{-SCS} = \delta(^{15}\text{N})_x - \delta(^{15}\text{N})_H. \quad (1)$$

TABLE V

The constants of correlation equation (2) for N_α , N_β , N_2 , and C(4) atoms in compounds *I* and N_α , N_β atoms in *trans*-4-X-C₆H₄-N₂=N_β-C₆H₅ (*II*) and nitrogen atoms of other model compounds

Nucleus	ϱ_1	$\varrho_R \bar{\sigma}_R$	Const.	λ^a	f^b	n^c
$\text{N}_\alpha\text{-I}$	$-(10.19 \pm 0.48)$	$-(7.95 \pm 0.33) \sigma_R^{\text{BA}}$	$-(0.02 \pm 0.20)$	0.78	0.070	11
$\text{N}_\beta\text{-I}$	$-(3.74 \pm 0.71)$	$-(3.76 \pm 0.49) \sigma_R^-$	$-(0.99 \pm 0.28)$	1.01	0.141	11
$\text{N}_2\text{-I}$	(10.01 ± 0.93)	$(11.91 \pm 0.91) \sigma_R^0$	$-(0.41 \pm 0.40)$	1.19	0.138	11
C(4)- <i>I</i>	(3.63 ± 0.37)	$(4.27 \pm 0.36) \sigma_R^0$	$-(0.23 \pm 0.16)$	1.18	0.159	11
$\text{N}_\alpha\text{-II}$	$-(7.93 \pm 2.40)$	$(4.61 \pm 0.86) \sigma_R^+$	$-(0.37 \pm 1.10)$	-0.58	0.190	8
$\text{N}_\beta\text{-II}$	(18.38 ± 2.20)	$(18.27 \pm 0.78) \sigma_R^+$	(0.04 ± 0.78)	0.99	0.067	8
$\text{N}^{d,e}$	12.11	$21.64 \sigma_R^-$		1.79		9
$\text{N}^{d,f}$	4.42	$8.61 \sigma_R^-$		1.95		7
$\text{N}^{d,g}$	0.61	$5.27 \sigma_R^-$		8.64		5
N^h	-6.0	$-1.0 \sigma_R^0$		0.17	0.09	11
N^i	$-(2.73 \pm 0.51)$	$-(2.67 \pm 0.44) \sigma_R^0$	$-(9.75 \pm 0.92)$	1.02		10

^a $\lambda = \varrho_R/\varrho_1$; ^b see the text; ^c number of points; ^d ref.²¹; ^e 4-X-C₆H₄-NH₂; ^f 4-X-C₆H₄-NHSO₂C₆H₅; ^g 4-X-C₆H₄-NHCOCH₃; ^h 4-X-C₆H₄NO₂, ref.¹⁸; ⁱ 2-substituted 5(6)-nitrobenzimidazoles, ref.²².

The ^{13}C —SCS of C(4) carbon atom were calculated similarly. The values of substituent chemical shifts are presented in Table IV. Whereas the $^{15}\text{N}_1$ —SCS depend only very little on substitution, the ^{15}N —SCS for N_α , N_β , and N_2 exhibit very distinct dependences on the X substituent, the greatest effect being found — somewhat surprisingly — at the N_2 nitrogen atom. The substituent chemical shifts were correlated by means of Eq. (2) (ref. ¹⁵):

$$\text{SCS} = \varrho_I \sigma_I + \varrho_R \bar{\sigma}_R + \text{const.}, \quad (2)$$

where $\bar{\sigma}_R$ means one of the constants σ_R^0 , σ_R^{BA} , σ_R^- , or σ_R^+ (ref. ¹⁶). For the correlation of [$^{15}\text{N}_\alpha$]—SCS we took the values measured without addition of $\text{Cr}(\text{acac})_3$. The results of correlations by means of Eq. (2) are given in Table V for compounds *I* and (for comparison) also *trans*-4-X-azobenzenes (*II*)¹⁷ and some other model compounds. The differentiation between individual σ_R was carried out according to the lowest *f* value ($f = \text{SD}/\text{RMS}$; SD = standard deviation of the fit, RMS = root-mean-square size of the data¹⁸). The *f* values below 0.1 (N_α -*I* and N_β -*II*) indicate a very good fit, the *f* values from 0.1 to 0.2 (N_β -*I*, N_2 -*I*, N_α -*II*, C(4)-*I*) correspond to an acceptable correlation¹⁸. Positive values of the coefficients in Eq. (2) correspond to “normal” effects of the substituents, *i.e.* the electron-acceptor substituents will cause a downfield shift, whereas the negative values of the ϱ coefficients correspond to the “opposite” trend, *i.e.* the electron-acceptor substituents will induce an upfield shift¹⁸. The “opposite” effect was observed, *e.g.*, in the case of ^{15}N —SCS of 3- and 4-substituted nitrobenzenes¹⁸. The same paper¹⁸ also contains a detailed discussion of reasons and consequences of such a behaviour of substituents. For N_2 -*II* the constant ϱ_I is negative and ϱ_R is positive. Such behaviour of substituents, where the λ ($\lambda = \varrho_R/\varrho_I$) value is negative, is very rare with kinetic data¹⁹, whereas it is relatively frequent²⁰ with the substituent chemical shifts obtained from NMR data. From the data of Table V it is obvious, that the “opposite” trend was observed with nitro derivatives^{18,22} (NO_2 group is a strong electron acceptor) and also with both nitrogen atoms of the $-\text{N}_\alpha\text{H}-\text{N}_\beta=$ group in compounds *I*, the “normal” dependence, on the other hand, being found with anilines²¹ (NH_2 group is a strong electron donor) and also with N_β of azobenzenes¹⁷ and N_2 of compounds *I*. From the correlation results it is obvious that the ^{15}N substituent chemical shifts correlate well with dual substituent constants, but the mechanism of this effect is not known yet. For elucidation of the above-mentioned dependences it will be necessary to measure the ^{15}N —SCS in further suitably chosen compound series.

REFERENCES

1. Venkataraman K.: *The Chemistry of Synthetic Dyes*, Vol. 1, Chap. XVIII. Academic Press, New York 1952.

2. Lyčka A., Šnobl D., Macháček V., Večeřa M.: *Org. Magn. Reson.* *15*, 390 (1981).
3. Lyčka A., Šnobl D., Macháček V., Večeřa M.: *Org. Magn. Reson.* *16*, 17 (1981).
4. Hinsche G., Uhlemann E., Zeigan D., Engelhardt G.: *Z. Chem.* *21*, 414 (1981).
5. Zeigan D., Kleinpeter E., Wilde H., Mann G.: *J. Prakt. Chem.* *323*, 188 (1981).
6. Lyčka A., Hansen P. E.: *Org. Magn. Reson.* *22*, 569 (1984).
7. Michaelis A., Schäfer A.: *Justus Liebigs Ann. Chem.* *407*, 259 (1915).
8. Bülow C.: *Chem. Ber.* *33*, 187 (1900).
9. Hawkes G. E., Randall E. W., Elguero J., Marzin C. J.: *J. Chem. Soc., Perkin Trans. 2*, *1977*, 1024.
10. Bax A., Freeman R., Kempell S. P.: *J. Am. Chem. Soc.* *102*, 4849 (1980).
11. Hansen P. E., Lyčka A.: *Magn. Reson. Chem.* *24*, 772 (1986).
12. Ewing D. F.: *Org. Magn. Reson.* *12*, 499 (1979).
13. Lyčka A., Šnobl D.: *This Journal* *46*, 892 (1981).
14. Witanowski M., Stefaniak L., Webb G. A.: *Ann. Rep. NMR Spectrosc.* *11B*, 74 (1981).
15. Ehrenson S., Brownlee R. T. C., Taft R. W.: *Prog. Phys. Org. Chem.* *10*, 1 (1973).
16. Ref.¹⁵, p. 13.
17. Lyčka A.: *This Journal* *47*, 1112 (1982).
18. Craik D. J., Levy G. C., Brownlee R. T. C.: *J. Org. Chem.* *48*, 1601 (1983).
19. Ref.¹⁵, p. 48.
20. Bromilow J., Brownlee R. T. C., Craik D. J., Fiske P. R., Rowe J. E., Sadek M.: *J. Chem. Soc., Perkin Trans. 2*, *1981*, 753.
21. Martin G. J., Martin M. L., Gouesnard J. P. in the book: *NMR Basic Principles and Progress* (P. Diehl, E. Fluck and R. Kosfeld, Eds), Vol. 18, p. 99. Springer, Berlin 1981.
22. Lopyrev V. A., Larina L. I., Vakul'skaya T. I., Larin M. F., Shibanova E. F., Titova I. A., Voronkov M. G., Liepinsh E. E.: *Magn. Reson. Chem.* *23*, 301 (1985).
23. Lyčka A., Kaválek J.: *This Journal* *49*, 58 (1984).

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