^{13}C AND ^{15}N NMR STUDY OF AZO-HYDRAZONE TAUTOMERISM IN AZO DYES CONTAINING AMINO OR ACETAMIDO GROUPS

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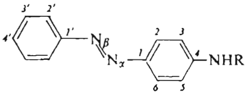
^{13}C and ^{15}N NMR spectra of ten model azo dyes containing NH_2 or $NHCOCH_3$ group in *ortho*- or *para*-position to the phenylazo group on benzene, naphthalene and anthracene skeleton were measured. A negligible content of the hydrazone form in these compounds follows from the ^{13}C and ^{15}N chemical shifts and from a slight temperature dependence of the ^{15}N chemical shifts and $^{1}J(^{15}N^{15}N)$ coupling constants. The ^{15}N isotope effect $\Delta\delta\ (^{15}N) = 0{\cdot}1$ ppm was observed and the values of $^{1}J(^{15}N^{15}N) = 15{\cdot}6 \pm 0{\cdot}3$ Hz were found with compounds double labelled by ^{15}N.

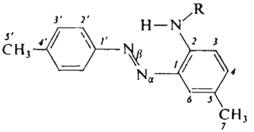
Since its discovery[1], the phenomenon of azo-hydrazone tautomerism has been studied by various methods (refs[2-5] and the literature cited therein). Considerable attention is given to this subject nowadays[5-9]. Presumably are studied the compounds containing hydroxyl groups[2-9], those containing amino groups in small extent only[2-5,8]. This proportion reflects roughly the division of monoazo dyes according to the passive components[8]: about 15% of dyes is prepared from anilines and naphthylamines as the passive components. Whereas the azo structure is commonly accepted in compounds of the 1-phenylazo-4-naphthylamine type[3], there is a controversy regarding the azo dyes derived from 2-naphthylamine. Martynoff[10] states that they exist in the azo-form but Skulski[11] considers the hydrazone-form as the prevailing one. Furthermore, it is assumed that the content of hydrazone-form should increase upon acetylation of the amino groups[3]. Analogous derivatives in anthracene series have not been studied in detail[3].

EXPERIMENTAL

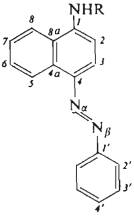
Compounds *Ia* and *IIa* were prepared from the corresponding triazenes by a rearrangement in acidic medium[12]. Compound *IIIa* was obtained by coupling of benzenediazonium chloride with 1-naphthylamine[13]. Analogously were prepared hydrochlorides of compounds *IVa* and *Va*. Compounds *Ib*—*Vb* were prepared by acetylation using acetanhydride[14]. All compound were purified by crystallization or column chromatography. ^{15}N-Labelled compounds were prepared using $Na^{15}NO_2$ (96·3% ^{15}N) and ^{15}N aniline (95·0% ^{15}N) (Isocomerz Berlin). The ^{15}N isotopic content was following: *Ia,b*, *IIa,b*: 96·3 $^{15}N_\alpha$; *IIIa,b*: 15% $^{15}N_\alpha$, 95% $^{15}N_\beta$; *IVa,b*: 15 and 50% $^{15}N_\alpha$, 95% $^{15}N_\beta$; *Va,b*: 50% $^{15}N_\alpha$, 95% $^{15}N_\beta$.



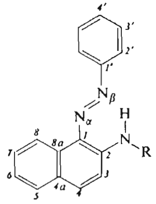
Ia, b



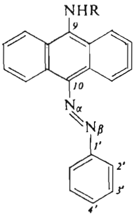
IIa, b



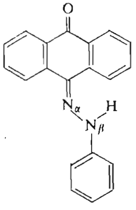
IIIa, b



IVa, b



Va, b



VI

In formulas *a*: R = H, b: R = $COCH_3$

^{13}C and ^{15}N NMR spectra were measured at 25·047 and 10·095 MHz, respectively, on a Jeol JNM-FX 100 spectrometer equipped by a tunable multinuclear probe, quadrature detection, and operating in the FT mode. Measurements were made in 10 mm NMR sample tubes. ^{13}C NMR spectra were run with 10—15% (w/v) solutions in deuteriochloroform or hexadeuteriodimethyl sulfoxide at 300 K. Deuterated solvents were used as internal lock substances. Following parameters were used to measure the ^{13}C chemical shifts: spectral width 5 000 Hz, pulse width 9 μs (23 μs corresponds to 90°), pulse repetition 3 s, proton noise decoupling. Chemical shifts are expressed with respect to internal tetramethylsilane. To measure the ^{15}N chemical shifts at the natural abundance level, we used 20—25% solutions containing 25 mg $Cr(acac)_3$ per 1 ml of deuteriochloroform and 10 mg Cr(acac)$_3$ per 1 ml of hexadeuteriodimethyl sulfoxide (saturated solution). Other parameters were: spectral width 5 000 Hz, pulse width 14 μs (30 μs (corresponds to 90°), pulse repetition 5 s, proton noise decoupling. ^{15}N Labelled compounds were studied as 2–6% (w/v) solutions; spectral width 4 000 or 1 000 Hz (for measurement of coupling constants $^1J(^{15}N^{15}N)$, 8 K memory, pulse width 11 μs, pulse repetition 20 s, inverse gated decoupling (proton noise decoupling on during acquisition). The methods used for ^{15}N measurement of individual compounds are given in Table III. ^{15}N Chemical shifts are related to external neat (25% ^{15}N) nitromethane (ref.[15]).; their positive values denote a downfield shift. With compound *IVa*, measured in hexadeuterioacetone at 200 K, the ^{15}N chemical shift was calculated using the resonance frequencies in Hz and the resonance frequency of nitromethane at 300 K (this standard melts at 244K). During the measurements in deuteriochloroform, nitromethane was kept in a capillary at 230 K as an undercooled liquid.

RESULTS AND DISCUSSION

^{13}C Chemical shifts of compounds *Ia,b – Va,b* are given in Table I. The ^{13}C chemical shifts in compounds *Ia* and *Ib* were assigned using the ^{13}C substitution chemical shifts[16] and ^{13}C chemical shifts of *trans* azobenzene[17]. The assignment was checked by the signal pattern of the proton-coupled spectrum. The chemical shifts of the

TABLE I

^{13}C Chemical shifts (δ scale, $\pm$0·10 ppm) in compounds *Ia,b– Va,b* measured in deuteriochloroform or hexadeuteriodimethyl sulfoxide, respectively

Atom	*Ia*[a]	*Ia*[b]	*Ib*[b,c]	*IIa*[a,d]	*IIb*[a]	*IIIa*[a]	*IIIb*[b]	*IVa*[a]	*IVb*[a]	*Va*[b]	*Vb*[b]
C(1′)	152·8	152·7	152·2	150·9	150·2	153·4	152·6	153·3	151·8	154·6	152·9
C(2′)	122·2	122·1	122·4	122·0	122·4	122·6	122·5	121·5	122·0	121·3	122·8
C(3′)	128·9	129·4	129·4	129·5	129·7	130·0	129·2	128·8	129·0	129·2	129·8
C(4′)	129·7	129·6	131·0	140·2	141·7	129·6	131·0	128·5	130·6	127·9	132·0
C(1)	145·3	143·3	147·0	137·0	138·4	146·2	137·4	134·5	129·8	[i]	[i]
C(2)	125·0	125·5	123·8	141·0	133·4	109·0	119·9	138·5	129·8	—	—
C(3)	114·5	113·8	119·3	116·9	119·8	113·8	111·8	119·3	119·0	—	—
C(4)	149·5	152·9	142·5	133·0	132·9	140·1	143·4	127·7	127·5	—	—
C(5)	114·5	113·8	119·3	126·6	132·7	123·9	123·0	133·3	133·6	—	—
C(6)	125·0	125·5	123·8	125·5	120·5	[e]	[f]	122·8	124·9	—	—
C(7)	—	—	—	20·2	20·7	[e]	[f]	127·3	127·2	—	—
C(8)	—	—	—	—	—	120·5	122·7	121·6	123·0	—	—
C(4a)	—	—	—	—	—	133·0	131·3	[g]	[h]	—	—
C(8a)	—	—	—	—	—	122·3	127·1	[g]	[h]	—	—
CO	—	—	169·0	—	168·2	—	169·0	—	169·8	—	169·9
CH$_3$	—	—	24·2	—	25·1	—	23·7	—	25·6	—	23·1

[a] Deuteriochloroform; [b] hexadeuteriodimethyl sulfoxide; [c] $\delta(C(5'))$ = 21·30; [d] $\delta(C(5'))$ = 21·40; [e] 127·0 or 125·2; [f] 127·1 or 126·1; [g] 126·9 or 126·4; [h] 132·9 or 129·8; [i] see text.

phenyl group carbons in *IIa,b–IVa,b* can be unambiguously assigned owing to the double relative intensity of the C(2′) and (C(3′) signals and the expected multiplicity of C(1′) and C(4′) in the protoncoupled spectra – (taking $^1J(^{13}CH)$ and $^3J(^{13}CH)$ into account) – triplet and doublet of triplets, respectively. The signals of carbons C(3), C(4), and C(6) in compounds *IIa* and *IIb* were assigned by selective decoupling. *IIa*: δ(C(3)) = 116·9 (δ(^{1}H) = 6·53; d, 8·3 Hz); δ(C(4)) = 133·0 (δ(^{1}H) = 6·90; q, 8·3 and 2·0 Hz); δ(C(6)) = 125·5 (δ(^{1}H) = 7·51; d, 2·0 Hz). *IIb*: δ(C(3)) = 119·8 (δ(^{1}H) = 8·46; d, 8·8 Hz); δ(C(4)) = 132·9 (δ(^{1}H) = 7·20; *q*, 8·8 and 2·0 Hz); δ(C(6) = 120·5 (δ(^{1}H) = 7·56; d, 2·0 Hz). Simultaneously can be assigned the signals of carbon C(5) that exhibit in these spectra quartets due to the off-resonance effect of the CH_3 group. The assignment of carbons C(5′) was achieved by comparison with the ^{13}C chemical shift of the methyl group in 4-methylazobenzene[17]. By selective decoupling were also assigned ^{13}C chemical shifts of carbons C(2) (δ(^{1}H) = 6·71) and C(5) (δ(^{1}H) = 9·00) in compound *IIIa*. The signal of C(3) has a coupling constant $^3J(^{13}CH) = 0$ and the value of δ(C(8)) is close to the corresponding one in 1-aminonaphthalene[18]. In compound *IIIb*, the chemical shifts of δ(C(5)) = 123·0 (δ(^{1}H) = 9·03) and δ(C(8)) = 122·7 (δ(^{1}H)8·34) were assigned by selective decoupling. The signals of C(1)–C(4) in *IIIa* and *IIIb* were located by comparison with model compounds (1-aminonaphthalene and 1-acetamidonaphthalene. respectively). The coupling constant $^3J(^{13}CH)$ is zero for carbons C(2) and C(3). In compound *IVa*, the chemical shifts of C(1) and C(2) were distinguished using the fine splittings in the proton-coupled spectra (doublet and quartet, respectively); δ(C(3)) and δ(C(8)) by selective decoupling (δ(^{1}H) = 6·64 and 8·79, respectively). The signal at δ = 127·7 exhibits $^3J(^{13}CH) = 5$ Hz and therefore represents C(4). The values δ(C(6)) and δ(C(7)) were compared with corresponding chemical shifts in 2-aminonaphthalene. The chemical shifts of C(3) and C(8) in compound *IVb* were assigned by selective decoupling (δ(^{1}H) = 8·72 and 8·62, respectively). Signal at 129·8 ppm belongs to C(1) since upon deuteration of the NH group the coupling $^3J(^{13}CNH)$ is reduced to 1/6·5 of its original value and also the corresponding multiplet in the proton-coupled spectrum is simplified. The deuteration also narrows the signal of C(2) in the protoncoupled spectrum. ^{13}C NMR spectrum of compound *Va* consists of 12 signals what means that there is a free rotation around the $—C_{(10)}—N_\alpha =$ bond, on the contrary to compound *VI* that exists in hydrazone-form[19,20], and its spectrum contains 18 carbon signals[20] up to 400 K. With the exception of signals of C(9), C(10), C(1′), and C(4′), the intensities of all signals are roughly equal. An unambiguous assignment of signals C(1′)—C(4)′ was achieved by measuring the ^{13}C NMR spectrum of the compound *Va* prepared from perdeuterated aniline. Signals of carbons C(2′)—C(4′) disappeared from the spectrum (the C—D triplets were not discernible) and the relative intensity of the C(1′) signal decreased to 1/5 of its original value as the results of the change in the relaxation mechanism. The signal δ = 149·4 was assigned to C(9). Other ^{13}C NMR signals: 129·6 128·2 125·2 123·5; 123·3;

116·3. The similar procedure was adopted for compound *Vb*. Other ^{13}C NMR signals: 169·9 (CO); 142·1 (C(9)); 132·5; 138·3; 127·7; 126·4; 124·4; 124·0; 123·9; 23·1 (CH_3).

The values of ^{15}N chemical shifts in compounds *Ia,b – Va,b* are given in Table II. To obtain an unambiguous assignment of the ^{15}N NMR signals of the azo bond nitrogen atoms, it is advantageous to use ^{15}N selective labelled compounds[17]. Two different contents of the ^{15}N isotope at N_β were used with compound *IIIb* to confirm the assignment of two close chemical shifts. Following coupling constants were measured in ^{15}N double labelled compounds: $|^1J(^{15}N^{15}N)|$: *IIIa*, 15·4 Hz; *IVa*, 15·4 Hz; *IVb*, 15·6 Hz; *Vb*, 15·9 Hz. Their changes with temperature were within the experimental error. The ^{15}N NMR signals in the compound *Va* were broad that rendered the determination of $^1J(^{15}N^{15}N)$ impossible. The magnitudes of $^1J(^{15}N^{15}N)$ in the above mentioned compounds agree with the published value $^1J(^{15}N^{15}N) = 15{\cdot}0 \pm 0{\cdot}5$ Hz for 4-hydroxyazobenzene[21]. The ^{15}N isotope effect on ^{15}N chemical shifts[22] was observed with ^{15}N double labelled compounds. The use of these compounds allows simultaneous measurement of $^{15}N_\beta$ chemical shifts in systems $^{14}N_\alpha = {}^{15}N_\beta$— and $^{15}N_\alpha = {}^{15}N_\beta$. The $^{15}N_\beta$ resonance in the system $—^{14}N_\alpha = {}^{15}N_\beta$ is shifted downfield $1{\cdot}0 \pm 0{\cdot}2$ Hz ($0{\cdot}1 \pm 0{\cdot}02$ ppm) with respect to that in the system $—^{15}N_\alpha = {}^{15}N_\beta$ (solved as an AB-system) (compounds *IIIa*; *IVa,b*; *Vb*). The published values are in the range 0·03 – 0·4 ppm (ref.[22]).

The situation of azo-hydrazone tautomerism in substances that differ from compounds *I – V* by replacement of NH_2 or $NHCOCH_3$ group by a hydroxyl one is following: the analogue of compounds *I* and *II* exist in azo-form[6,7,23]; compound similar to compound *IV* prefers hydrazone-form[6,7,23]; compound *VI* exists in chloroform in hydrazone-form only[19,20,23]. From the comparison of ^{13}C chemical shifts in studied compounds *Ia,b – Va,b* (with compound *IIa,b* after subtraction of ^{13}C substitution chemical shifts for the methyl group 10·5; 0·8; 0·0; −1·8 obtained through comparison of chemical shifts in *trans*-4-methylazobenzene and *trans*-azobenzene[17]), both mutual and with the ^{13}C chemical shifts of the phenyl group carbons in substituted *trans*-azobenzenes[17], it follows that compounds *Ia,b – Va,b* exist in the azo-form. With compound *IVa*, this fact is further supported by observation of practically unchanged[5] ^{13}C chemical shifts of C(2) ($\delta(C(2)) \sim 139$ in cases, where hydrogen at C(4′) is replaced by OCH_3, CN, and NO_2, respectively. On the contrary, the value of $\delta(C(2))$ varies from 160·8 to 180·0 ppm in products of coupling 4-substituted benzenediazonium salt (OCH_3; H; CN or NO_2, respectively) with 2-naphthol[5,6]. That corresponds to an increase in the hydrazone-form content with increasing positive values σ of the substituent at the position 4′. ^{13}C Chemical shifts of the acetamido group carbons in compounds *Ia,b – Va,b* are all alike.

^{15}N Chemical shifts of nitrogen atoms N_α, N_β in model azo-compounds have values greater than 65 ppm[7,17] whereas in hydrazo-compounds $\delta(N_\alpha)$ is close to zero[7,24] and $\delta(N_\beta)$ is about −200 ppm (ref.[7,24]). The comparison of these chemical shifts with the observed ^{15}N chemical shifts in compounds *Ia,b – Va,b* allows a conclusion that these compounds exist in azo-form in broad temperature range, in agreement with the ^{13}C NMR results. The differences in chemical shifts of $\delta(N_\alpha)$ and

TABLE II

^{15}N Chemical shifts (related to external neat nitromethane (25% ^{15}N); ±0·2 ppm) in compounds *Ia,b— Va,b*. Positive value denotes a downfield shift

Compound	Solvent[a–c]	Temperature, K	$\delta(N_\alpha)$	$\delta(N_\beta)$
Ia[d,e]	*a*	300	118·0	101·7
Ia[f]	*a*	300	121·2	—
Ia[d]	*a*	300	118·2	91·4
Ib[d,g]	*b*	300	124·3	118·1
Ib[f]	*b*	300	125·2	—
IIa[d,h]	*a*	300	115·0	97·3
IIa[f]	*a*	300	117·1	—
IIb[d,i]	*a*	300	106·4	110·9
IIb[f]	*a*	300	107·4	—
IIIa[j]	*a*	300	117·8	101·3
IIIa[j]	*b*	300	112·8	86·4
IIIa[j]	*b*	370	—	92·5
IIIa[j]	*c*	230	114·2	95·5
IIIa[j]	*c*	300	114·5	93·1
IIIb[j]	*b*	300	123·2	123·4
IIIb[j]	*b*	370	126·4	126·6
IVa[j]	*a*	230	115·8	69·0
IVa[j,k]	*a*	300	118·9	72·9
IVa[j]	*b*	300	114·8	65·9
IVa[j]	*b*	370	—	70·8
IVa[j]	*c*	200	112·8	63·9
IVa[j]	*c*	300	116·1	67·6
IVb[j]	*a*	230	125·8	89·1
IVb[j]	*a*	300	129·3	94·1
IVb[j]	*a*	330	130·3	95·9
Va[j]	*b*	300	117·4	77·2
Va[j]	*b*	370	122·9	87·2
Vb[j]	*b*	300	144·0	151·9
Vb[j]	*b*	370	146·6	153·8

[a] Deuteriochloroform; [b] hexadeuteriodimethyl sulfoxide; [c] hexadeuterioacetone; [d] measured at natural abundance of ^{15}N with $Cr(acac)_3$ added; [e] $\delta(NH_2) = -318·4$; [f] ^{15}N-labelled compound; [g] $\delta(NHCOCH_3) = -235·3$[d]; [h] $\delta(NH_2) = -322·7$; [i] $\delta(NHCOCH_3) = -255·8$; [j] ^{15}N double labelled compounds; [k] $\delta(NH_2) = -301·9$.

$\delta(N_\beta)$ between the compounds containing amino and acetamido groups are comparable for *I*, *III* and *IV* from the ^{15}N NMR spectroscopy point of view. In compounds of type *II* is the ^{15}N chemical shift $\delta(N_\alpha)$ smaller for *IIb* than that for *IIa*. The largest chemical shift difference exists between compounds *Va* and *Vb*. However, ^{15}N chemical shifts can be affected by the association of the molecules of dye[26] (broadened ^{15}N NMR signals in compound *Va*) what can provide their explanation. More important than the sole values of ^{15}N chemical shifts is their temperature dependence[7]. The largest temperature change (10 ppm/70 K) was observed for $\delta(N_\beta)$ in compound *Va*. Some temperature changes of the chemical shift have been already observed in azo dyes[7]. Nevertheless, the 10 ppm change in chemical shift corresponds to a 3% change in the hydrazone-form content since the chemical shift difference for N_α in azo and hydrazo-form is about 300 ppm[7]. Among all compounds studied, the probability of a small content of the hydrazone-form is the largest just with compounds *Va*. On the other side, it is assumed that the content of this form should increase in acetamido compounds[3] but there is a little temperature dependence of ^{15}N chemical shifts in compound *Vb*. The values of coupling constants $^1J(^{15}N^{15}N) = 15{\cdot}6 \pm 0{\cdot}3$ Hz correspond to azo- compounds since with hydrazone derivatives the value found is $|^1J(^{15}N^{15}N)| \sim 11$ Hz[25] and the experimental value of $^1J(^{15}N^{15}N)$ for the product of coupling benzenediazonium salt with 2-naphthol increases with the increasing portion of the azo-form[25]. $^1J(^{15}N^{15}N)$ in 4-hydroxyazobenzene is $15{\cdot}0 \pm 0{\cdot}5$ Hz[21]. The ^{15}N chemical shifts of $—NH_2$ and $—NHCOCH_3$ group (Table II) were measured where the solubility was sufficient. The observed values are in good agreement with ^{15}N chemical shifts of amino group nitrogens in monosubstituted anilines (-300 to -336 ppm[27]). The ^{15}N chemical shift of acetanilide is $-247{\cdot}0$ ppm[28]. Also these results confirm that compounds *Ia,b – Va,b* exist in the azo-form.

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