^{13}C, ^{15}N, AND ^{19}F NMR SPECTRA OF 2-PHENYLHYDRAZONOPROPANEDINITRILES AND METHYL 2-PHENYL HYDRAZONOCYANOACETATES

Antonín Lyčka

Research Institute of Organic Syntheses, 532 18 Pardubice - Rybitví

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^{13}C, ^{15}N, and ^{19}F NMR spectra of the azo coupling products obtained from 4-X-benzenediazonium salts (X = H, F, NO_2) and propanedinitrile (*I*) or methyl cyanoacetate (*II*) and of their ^{15}N isotopomers have been measured. The ^{13}C chemical shifts of cyano groups have been assigned unambiguously on the basis of the $^2J(^{15}N_\beta{}^{13}C)$ coupling constants, and mutual comparison of the ^{15}N chemical shifts in compounds *I* and *II* enabled also the assignment of the ^{15}N chemical shifts of these groups. The ^{13}C chemical shifts of cyano groups in *cis* position with respect to free electron pair at N_β nitrogen atom are shifted downfield, whereas $\delta(^{15}N)$ of the same groups exhibit upfield shifts as compared with the cyano groups in *trans* position. The azo coupling products of benzenediazonium salts and methyl cyanoacetate contain predominantly the *E* isomer even after long-term standing in hexadeuteriodimethyl sulphoxide.

Structure of azo coupling products formed from diazonium salts and compounds possessing an activated methylene group was studied in solid state by diffractography[1-4]. The structure of such compounds in solutions was investigated mostly by nuclear magnetic resonance spectroscopy: published are the ^1H (refs[2-7]), ^{13}C (refs[4,7,8]), and ^{15}N NMR spectra[7,8] of these compounds.

Little attention has been paid so far to the coupling products of methylene group with activating CN group(s). During preparation of manuscript of the present communication there appeared a multinuclear study[7] on the coupling product of benzenediazonium salt and propanedinitrile.

The aim of the present paper is to measure the ^{13}C, ^{15}N, and ^{19}F NMR characteristics of azo coupling products of substituted benzenediazonium chlorides and propanedinitrile or methyl cyanoacetate as well as of the respective ^{15}N isotopomers, to use mutual comparison *a*) for estimation of *E*/*Z* isomer ratio of compounds *II*, and *b*) to assign both the ^{13}C and ^{15}N chemical shifts of cyano groups which cannot be assigned on the basis of multiplicity, because they give singlets in both the proton-coupled and proton-decoupled spectra.

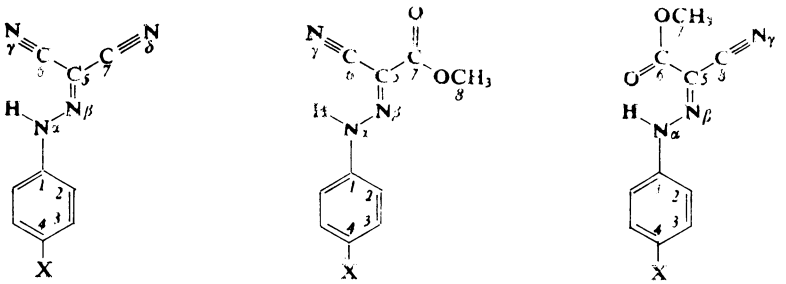
EXPERIMENTAL

The compounds *I* and *II* were prepared by azo coupling of substituted diazonium chlorides with propanedinitrile and methyl cyanoacetate, respectively, in acetate buffer[9]. The ^{15}N isotopomers were prepared from $Na^{15}NO_2$ (95% ^{15}N) and ^{15}N-aniline (95% ^{15}N) (Isocommerz, Berlin).

The ^{13}C and ^{15}N NMR spectra were measured at 25·047 and 10·095 MHz, resp., using a JNM-FX 100 (JEOL) apparatus equipped with multinuclear tunable probe and operating in FT mode. The parameters of the measurements were the same as in ref.[8]. The ^{19}F chemical shifts were measured at 93·709 MHz. The compounds were measured in hexadeuteriodimethyl sulphoxide in 10 mm NMR test tubes, and the solvent served as an internal lock substance. The ^{13}C chemical shifts are related to internal tetramethylsilane, the ^{15}N chemical shifts to external neat nitromethane (25% ^{15}N) (ref.[10]), and the ^{19}F chemical shifts to external neat trifluoroacetic acid. For the measurements of the ^{15}N chemical shifts of the cyano groups, the solutions in hexadeuteriodimethyl sulphoxide were treated with chromium tris(acetylacetonate) (about 10 mg $Cr(acac)_3$ per 1 ml).

RESULTS AND DISCUSSION

The values of ^{13}C and ^{15}N chemical shifts and absolute values of the coupling constants $^1J(^{15}N^{15}N)$, $^nJ(^{15}N_\beta{}^{13}C)$, and $^nJ(^{19}F^{13}C)$ of the compounds *I* and *II* (Scheme 1) are given in Tables I and II, respectively.



I (*E*)-*II* (*Z*)-*II*

a: X = H
b: X = F
c: X = NO_2

SCHEME 1

The ^{13}C chemical shifts of compound *Ia* agree with those given in ref.[7](According to a private communication[11], the ^{13}C chemical shifts of cyano groups given in ref.[7] were misprinted and should be mutually exchanged). The assignment of the ^{13}C chemical shifts of compounds *Ib* and *Ic* was made possible by application of the ^{13}C substituent chemical shifts[12]. The coupling constants $^2J(^{15}N^{13}C)$ are known

to be stereospecific[13,14]. The carbon atom at *cis* position with respect to free electron pair at nitrogen atom has the coupling constant markedly greater (~10 Hz) than that in *trans* position (~1 Hz). On this basis it was possible to assign the ^{13}C chemical shifts of cyano groups.

The ^{15}N chemical shifts were measured with ^{15}N doubly labelled compounds *Ia* and *Ic* (N_α: 15% ^{15}N; N_β: 95% ^{15}N) and with ^{15}N monolabelled compound *Ib* (N_β: 95% ^{15}N). The same ^{15}N labelling was also used with compounds *II*. Different values of the ^{15}N enrichment in compounds *Ia* and *Ic* makes it possible to measure $^1J(^{15}N^{15}N)$ coupling constant and, if necessary, to assign unambiguously the ^{15}N chemical shifts and determine the $^nJ(^{15}N_\beta{}^{13}C)$ values, all in one sample. The values of ^{15}N chemical shifts of N_α and N_β atoms in compounds *I* correspond to the shifts

TABLE I

^{13}C Chemical shifts (δ scale; ±0·1 ppm) and absolute values of the $^nJ(^{15}N_\beta{}^{13}C)$ coupling constants (Hz; ±0·2 Hz; the values given in brackets) in compounds *I* and *II* in hexadeuteriodimethyl sulphoxide

Compound	C—1	C—2	C—3	C—4	C—5	C—6	C—7	C—8
Ia	141·7 (6·6)	116·7 (2·5)	129·7 [a]	126·1 [a]	84·5 (7·5)	110·2 (1·0)	114·7 (12·0)	—
Ib[b]	138·1 (6·7)	118·6 (2·4)	116·5 [a]	160·3 [a]	84·5 (7·9)	110·1 (1·2)	114·5 (12·0)	—
Ic	147·1 (6·9)	116·9 (2·6)	125·6 [a]	144·1 [a]	88·4 (8·6)	109·7 (1·2)	114·1 (11·8)	—
(*E*)-*IIa*	142·0 (6·6)	116·4 (2·2)	129·5 [a]	125·1 [a]	103·6 (6·2)	111·6 (1·8)	161·7 (10·6)	52·8 [a]
(*E*)-*IIb*[c]	138·6 (6·8)	118·0 (2·2)	116·2 [a]	159·6 [a]	103·4 (6·1)	111·6 (2·2)	161·7 (11·0)	52·8 [a]
(*E*)-*IIc*	147·0 (6·9)	116·0 (2·6)	125·1 [a]	143·3 [a]	107·3 (6·6)	110·4 (2·6)	160·5 (11·1)	52·8 [a]
(*Z*)-*IIa*	141·1 (6·6)	116·3 (2·2)	129·7 [a]	125·9 [a]	104·2 (7·9)	161·3 (0·8)	53·0 [a]	116·0 (12·4)
(*Z*)-*IIb*[d]	137·8 (6·8)	118·2 (2·2)	116·4 [a]	160·1 [a]	104·1 (7·3)	161·3 (1·0)	53·0 [a]	115·9 (11·6)
(*Z*)-*IIc*	145·8	116·2	125·1	143·9	107·5	160·0	53·0	11·8

[a] ~0·5 Hz; [b] $|^nJ(^{19}F^{13}C)| = 243·5$ ($n = 1$), 22·9(2), 8·5(3), 3·1(4) and 1·2(7) Hz; [c] $|^nJ(^{19}F^{13}C)| = 242·0$ ($n = 1$), 22·8(2), 8·1(3), 2·5(4), 1·2(7) Hz; [d] $|^nJ(^{19}F^{13}C)| = 242·8$ ($n = 1$), 22·8(2), 8·3(3), 2·9(4), 1·2(7) Hz.

in phenylhydrazones[7,8]. The ^{15}N chemical shifts of the cyano groups were measured after addition of $Cr(acac)_3$ and were assigned on the basis of comparison with the ^{15}N chemical shifts of nitrogen atoms of cyano groups in 2-phenyl hydrazonocyanoacetates. The ^{19}F chemical shift (−37·8) was measured for compound *Ib*.

In case of the azo coupling products from substituted diazonium salts and methyl cyanoacetate, the ^{13}C NMR spectra exhibit two sets of signals whose proportion is slowly changed. The ^{13}C chemical shifts were assigned in the same way as those of compounds *I*. The precise value of the chemical shifts of the cyano group in the derivatives (*Z*)-*IIa* and (*Z*)-*IIb* had to be determined from the proton-decoupled spectrum with respect to the overlap of the ^{13}C NMR signals in spectra with noise decoupling. The ^{13}C chemical shifts of the cyano groups also were assigned with the help of $^2J(^{15}N_\beta{}^{13}C)$. From these measurements it follows that the *E* derivatives clearly predominate at the beginning of the measurements, and the amount of *Z* isomers gradually increases. After several weeks standing of the sample solutions in hexadeuteriodimethyl sulphoxide at room temperature, the ^{13}C NMR signal intensities allowed an estimate of the *E* : *Z* equilibrium ratio of the isomers: *IIa* 2 : 1; *IIb* 2 : 1; *IIc* 7 : 1.

The ^{15}N chemical shifts of the cyano groups were measured with the addition of $Cr(acac)_3$. After dissolution of compounds *II* in hexadeuteriodimethyl sulphoxide,

TABLE II

^{15}N Chemical shifts (±0·2 ppm) and absolute values of the $^1J(^{15}N^{15}N)$ coupling constants (Hz; ±0·2Hz) in compounds *I* and *II* in hexadeuteriodimethyl sulphoxide

Compound	$\delta(N_\alpha)$	$\delta(N_\beta)$	$\delta(N_\gamma)$	$\delta(N_\delta)$	$^1J(^{15}N^{15}N)$
Ia	−192·2[a]	− 2·2[a]	− 98·2[b]	−118·9[b]	10·2[a]
Ib	−194·3[c]	− 2·6[d]			—
	−194·4[b]	− 2·8[b]	− 98·2[b]	−119·0[b]	
Ic	−194·5[a]	− 3·6[a]	− 99·0[b]	−118·5[b]	10·3[a]
(*E*)-*IIa*	−203·0[a]	− 3·6[a]			10·5[a]
	−204·5[b]	− 4·5[b]	− 99·8[b]	—	
(*E*)-*IIb*	−205·1[c]	− 4·5[a]			—
	−205·0[b]		−100·1[b]	—	
(*E*)-*IIc*	−206·4[a]	− 7·4[a]	− 98·4[b]	—	10·3[a]
(*Z*)-*IIa*	−200·6[a]	− 8·1[a]	−122·6[b]	—	10·0[a]
(*Z*)-*IIb*	−202·4[c]	− 8·0[d]	−122·9[b]	—	—
(*Z*)-*IIc*	−203·0[a]	−11·0[a]	[e]	—	10·3[a]

[a] The ^{15}N doubly labelled compound; [b] with addition of about 10 mg $Cr(acac)_3$ per 1 ml; [c] at the natural abundance level; [d] the ^{15}N-mono labelled compound; [e] not found.

the signals of cyano groups with the chemical shift of about −100 (the *E* isomers) had a far greater integral intensity; thereafter the intensity of the signals at about −120 ppm (corresponding to the *Z* isomers) gradually increased. On the basis of these results it is possible to assign the ^{15}N chemical shifts in the compounds *Ia–Ic*, too, *viz* the signal shifted down field as belonging to the cyano group at *cis* position with respect to the proton of hydrazo group. The $^{1}J(^{15}N^{15}N)$ and $^{n}J(^{15}N^{13}C)$ coupling constants agree with those measured earlier in hydrazo compounds[8,15,16]. The values of ^{19}F chemical shifts were measured in compounds (*E*)-*IIb* (−39·4) and (*Z*)-*IIb* (−38·4).

As compared with the chemical shifts in propanedinitrile (hexadeuteriodimethyl sulphoxide; ^{13}C NMR: $\delta(CH_2) = 9{\cdot}0$, $\delta(CN) = 112{\cdot}2$; ^{15}N NMR: $\delta(CN) = -128{\cdot}0$ (with addition of $Cr(acac)_3$)), the ^{13}C chemical shifts of the cyano group at the *cis* position to the proton of hydrazo group are shifted upfield, those in the *trans* position downfield, whereas the both ^{15}N chemical shifts of the cyano groups in compounds *I* and *II* are shifted down field when compared with those of propanedinitrile.

The ^{13}C and ^{15}N NMR spectra present a very advantageous way of analysis of compounds *I* and *II*, because ^{1}H NMR does not give unambiguous results. The proton NMR signals of hydrogen atoms at hydrazo groups of compounds *I* are very broad (*Ia* $\delta(N_jH) = 13{\cdot}1$; *Ib* $\delta(NH) = 12{\cdot}9$; *Ic* not found). Broad signals were observed with compound *Ia* in hexadeuterioacetone at 295 K (ref.[7]). Narrow signals were obtained in this solvent at 198 K. Similarly broad signals (only one for the *E* isomer and for the *Z* isomer) were also found with compounds *II* (δ(NH) about 12·5). It is only the results of the ^{13}C NMR analysis of *Z*/*E* isomer proportion which allow the following assignment of the ^{1}H NMR signals of methoxyl groups: $\delta(OCH_3) = 3{\cdot}86$ and 3·90 in the *E* and *Z* isomers, resp.

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