STRUCTURE OF 1(5)-ARYL-3-PHENYL-5(1)-(2-BENZOTHIAZOLYL)FORMAZANES

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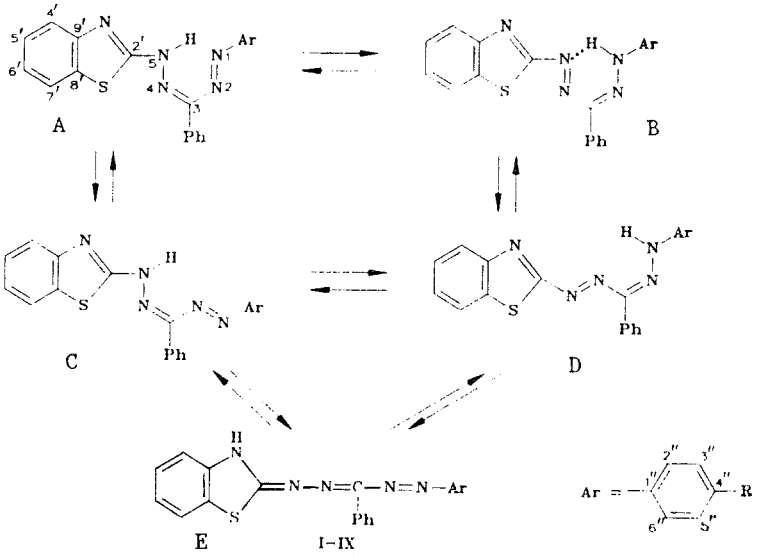
1,3-Diphenyl-5-(2-benzothiazolyl)formazane exists in its crystalline state (based on x-ray crystal structure data) in the $E^{1,2}Z^{2,3}Z^{3,4}$-conformation, which is stabilized by intramolecular hydrogen bonding (IMHB); the proton is localized on the nitrogen atom which is bound to the heterocycle. In chloroform solutions 1(5)-aryl-3-phenyl-5(1)-(2-benzothiazolyl)formazanes exist in the form of equilibrium mixtures of their chelate and open $E^{1,2}Z^{2,3}Z^{3,4}$-forms, in which the first of these forms predominates. Based on their ^{13}C-NMR spectral data the tautomeric equilibrium involving these forms is shifted in favor of the benzothiazolylhydrazone form. The amount of tautomer containing the benzothiazolidene fragment structure increases in DMSO solution.

The structure of 1(5)-aryl-3-phenyl-5(1)-(2-benzothiazolyl)formazanes in the gas phase and in the crystalline state has been considered previously in the literature [1]. However, x-ray structural analysis of 1-(4-methoxyphenyl)-3-phenyl-5-(2-benzothiazolyl)formazane was not sufficient to establish the site of localization of the NH proton; the authors predicted, therefore, that both the $N_{(1)}$- and $N_{(5)}$-amino tautomeric forms existed in the crystalline state. It was also found that the ratio of these forms in the gas phase was unaffected by the presence of a substituent in the p-position of the aryl fragment. On the other hand, it has also been demonstrated, using triarylformazanes as an example, that the ratio of $N_{(1)}$ and $N_{(5)}$ tautomers differs in the gas phase and in solution [2], while in the case of 1(5)-aryl-3-phenyl-5(1)-(2-quinazolinyl)formazanes the ratio is practically identical (in the gas phase and in solution)



I R=$N(CH_3)_2$, II R=OCH_3, III R=CH_3, IV R=1-methyl, V R=H, VI R=Cl, VII R=Br, VIII R=$COOCH_3$, IX R=NO_2

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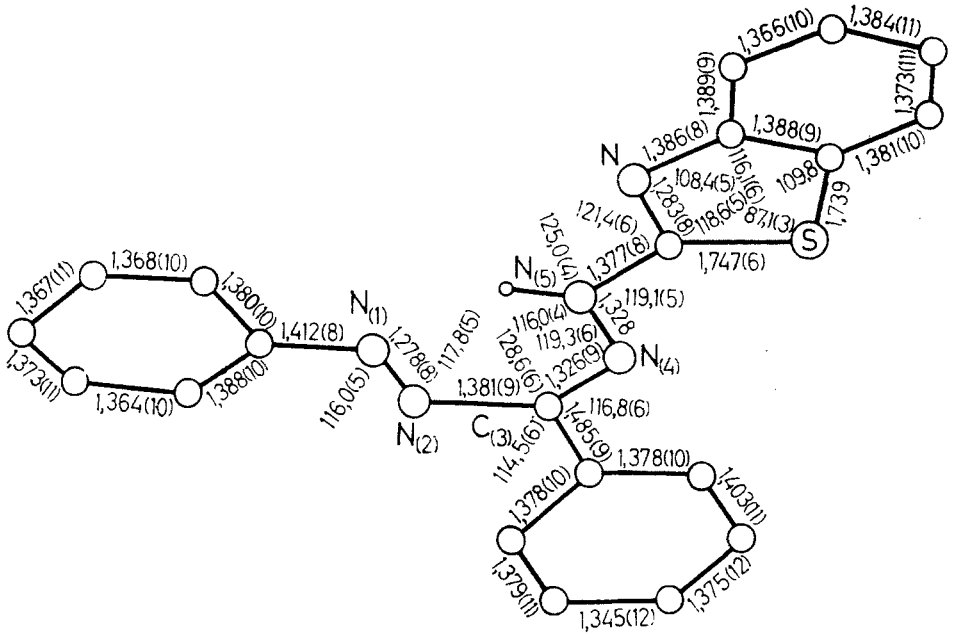

Fig. 1. Bond lengths (Å) and internal angles (deg) in the molecular structure of 1,3-diphenyl-5-(2-benzothiazolyl)formazane V. $R_{NH\cdots N} = 2.576(7)$ Å.

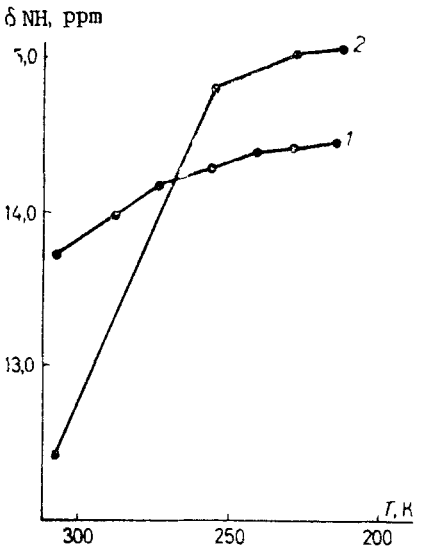

Fig. 2. Variation in δNH as a function of temperature: 1) II; 2) IX.

[3]. Based on these results, it was of interest to us to examine the effect of both solvent and p-substitution in the aryl fragment on the ratio of $N_{(1)}$- and $N_{(5)}$-tautomers for compounds I-IX in solution (see scheme above), and also to verify and refine the structure of formazanes in the crystalline state. We have therefore studied the IR and NMR spectra of formazanes I-IX, and have carried out an x-ray crystal structure investigation of compound V.

In the crystalline state 1,3-diphenyl-5-(2-benzothiazolyl)formazane V adopts a chelate $E^{1,2}Z^{2,3}Z^{3,4}$-conformation with asymmetric IMHB (Fig. 1), which is in contrast to the hydrogen bonding found in compound II [1]. The site of NH proton localization was established unequivocally in the crystal structure of formazane V, confirming that in the crystalline state this compound exists in the form of structure A. The fact that the bond lengths in the formazane chain are intermediate in value between those expected for single and double bonds (Fig. 1), as in compound II [1], indicates further that the degree of bond conjugation in the azohydrazone fragment is sufficiently great that bond length may not be used as a criterion to indicate the tautomeric structural form.

TABLE 1. PMR Spectra of the NH Protons in Compounds I-IX in Different Solvents

Compound	Solvent	Chemical shift, δ, ppm, at		
		214 K	307 K	344 K
I	$CDCl_3$	—	13,92	—
	DMSO-D_6	—	13,05	—
II	CCl_4	—	14,60	14,08
	$CDCl_3$	14,45	13,80	—
	DMSO-D_6	—	12,82	—
III	CCl_4	—	14,83	14,36
	$CDCl_3$	—	14,23	—
	DMSO-D_6	—	12,63	—
IV	CCl_4	—	15,14	14,71
	$CDCl_3$	—	14,15	—
	DMSO-D_6	—	13,00	—
V	CCl_4	—	14,24	12,94
	$CDCl_3$	—	—*	—
	DMSO-D_6	—	12,74	—
VI	CCl_4	—	14,81	14,51
	$CDCl_3$	14,59	14,30	—
	DMSO-D_6	—	12,93	—
VII	CCl_4	—	—*	—*
	$CDCl_3$	14,60	—*	—
	DMSO-D_6	—	12,85	—
VIII	CCl_4	—	15,25	—*
	$CDCl_3$	15,10	14,80	—
	DMSO-D_6	—	12,97	—
IX**	CCl_4	—	—***	—*
	$CDCl_3$	15,07	12,50	—

*Not observed due to broadening.
**Decomposes in DMSO.
***Poorly soluble in CCl_4.

TABLE 2. ^{13}C-NMR Spectra of Compounds II-XII ($CDCl_3$, 307 K)

Compound	Chemical shifts, δ, ppm*1													Δδ, ppm*2		
	$C_{(2')}$	$C_{(4')}$	$C_{(5')}$	$C_{(6')}$	$C_{(7')}$	$C_{(8')}$	$C_{(9')}$	$C_{(3'')}$	$C_{(1'')}$	$C_{(2'',6'')}$	$C_{(3'',5'')}$	$C_{(4'')}$	C(R)	$C_{(1'')}$	$C_{(2'',6'')}$	$C_{(4'')}$
II	167,9	120,6	126,2	123,2	121,4	131,8	152,2	143,8	146,8	125,4	114,8	163,9	55,7	26,0	−4,1	4,0
III	168,2	120,9	126,1	123,4	121,3	131,9	152,1	143,5	150,0	122,9	130,1	143,6	21,6	24,5	−5,5	5,9
IV	168,2	121,4	126,2	123,7	121,4	132,2	152,3	145,6	146,8	112,6	125,6	132,9	—*3	—	—	—
V	168,7	121,2	126,2	123,8	121,4	132,0	152,0	143,6	151,4	122,6	129,5	132,2	—	22,9	−5,9	3,7
VI	168,3	121,2	126,2	123,7	121,4	132,0	152,0	143,4	149,8	123,7	129,8	138,3	—	23,2	−6,2	3,5
VII	168,6	121,2	126,3	123,8	121,5	132,0	152,0	143,5	150,0	123,8	132,8	126,7	—	23,1	−6,3	4,0
VIII	166,2	122,4	126,5	125,1	121,7	132,8	152,5	143,4	151,2	120,2	131,0	130,8	171,0; 52,3	18,4	−8,2	0,3
X*4														14,5	−14,8	−5,3
X*5														24,6	−6,0	3,8
IX	168,5	123,7	126,7	126,1	121,5	133,6	152,9	143,9	150,3	118,6	125,5	146,2	—	15,7	−10,3	−2,2
XI	170,8	120,9	125,9	123,4	120,9	131,8	152,3	157,6	147,5	112,0	125,6	132,0	—*6	—	—	—
XII	168,0	109,3	126,1	121,9	122,5	124,8	141,1	159,1	152,7	123,0	129,1	132,1	—	24,2	−5,5	2,7

*1 ^{13}C-CS values for the 3rd phenyl substituent in formazanes II-IX: $C_{(1)}$ 134.7-135.2, $C_{(2,6)}$ 126-127.5, $C_{(3,5)}$ 128.4-128.8, $C_{(4)}$ 128.9-129.2; compound XI: $C_{(1)}$ 132.9, $C_{(2,6)}$ 127.5, $C_{(3,5)}$ 128.9, $C_{(4)}$ 129.6.
*2 CS changes (Δδ, ppm) for the N-aryl fragment atoms relative to the corresponding R-benzenes [11].
*3 ^{13}C-CS values for the 1-naphthyl substituent: $C_{(5'')}$ 128.2, $C_{(6'')}$ 126.9, $C_{(7'')}$ 128.5, $C_{(8'')}$ 122.6, $C_{(9'')}$ 130.2, $C_{(10'')}$ 134.4.
*4 Arylhydrazone tautomer.
*5 Azophenyl tautomer.
*6 ^{13}C-CS values for the 1-naphthyl substituent $C_{(5'')}$ 126.9, $C_{(6'')}$ 126.4, $C_{(7'')}$ 127.8, $C_{(8'')}$ 122.9, $C_{(9'')}$ 128.7, $C_{(10'')}$ 133.7.

The $E^{1,2}Z^{2,3}Z^{3,4}$-configuration of 1(5)-aryl-3-phenyl-5(1)-(2-benzothiazolyl)formazanes with intramolecular hydrogen bonding is retained in solution as well. This is supported by the position of the long-wavelength absorption maximum (λ_{max} 470-580 nm) for these compounds [4, 5], as well as by the results of Pariser—Parr—Pople quantum mechanical calculations [6, 7]. The chemical shifts (CS) values of the NH protons at δ 13.4-14.8 ppm in the PMR spectra of formazanes I-IX (Table 1) are also in accord with this conclusion. However, the experimental data relating to the effect of solvent polarity on the value of δNH and the substantial temperature gradient observed for the variation in δNH (cf. Table 1) are uncharacteristic of molecules featuring strong IMHB which is not cleaved in solution [8]. The temperature dependence observed for δNH in formazanes II and IX in $CDCl_3$ solution (Fig. 2) gives rise to curves which asymptotically approach a maximum, analogous to that observed previously for the temperature dependence in a series of quinoxalylformazanes [9].

The observed behavior can be explained starting from the assumption that the intramolecular hydrogen bonds in formazanes are cleaved reversibly by solvent action. Bond cleavage is accompanied by rotation of the arylazo fragment about the formal C—N single bond, resulting in the formation of short-lived (on the NMR time scale) "open-chain" $E^{1,2}Z^{2,3}Z^{3,4}$-isomers [3, 9]; a single set of signals is observed in the NMR spectrum, corresponding to nonequivalent, resonating nuclei.

Within the framework of this approach it is also possible to rationalize the presence of medium intensity* ν_{NH} bands at 3300-3330 cm^{-1} in the IR spectra of solutions of I-IX, and their absence in the spectra of crystalline samples due to the formation of unstable, "open-chain" $E^{1,2}Z^{2,3}Z^{3,4}$-isomers with a free NH group (structures C and D). It was not possible to estimate the amount of these isomers in solution, as had been done previously [3, 9], because of the difficulty in obtaining an accurate estimate or measure of the intensity of the free NH group band. The problem arises in that the IR spectra of formazanes I-IX exhibit NH group stretching vibration bands for intermolecularly associated amino groups (ν_{NH} 3160-3180 cm^{-1}, A = 1000-2000 liters/mole·cm^2) down to a concentration of 10^{-2} liter/mole in $CDCl_3$ and 10^{-3} mole/liter in CCl_4 solution. NH group absorption bands due to intermolecular association have also been observed in the IR spectra of 2-benzothiazolylhydrazone derivatives of benzaldehyde, which have been used as model compounds to estimate the limiting intensity of free NH group absorption bands.

We were able to establish the tautomeric composition for formazans II-IX based on their ^{13}C-NMR spectroscopic data. Two approaches have been proposed for this purpose [3, 9]. The first approach, involving determination of the $^2J_{^{13}CNH_2}$ geminal spin—spin coupling constants (SSCC) between the NH protons and $C_{(2')}$ benzothiazole and $C_{(1'')}$ aryl substituent carbon atoms, could not be applied in this case, due to interference arising from intermolecular NH proton transfer, which meant that the SSCC values could not be observed for both of the carbon atoms in question. We therefore turned our attention to the second approach, which is based on the premise that the carbon atom CS changes ($\Delta\delta$ ^{13}C) for the N-aryl fragment in these formazanes, relative to the corresponding CS values in R-benzenes [11], can be used to determine whether the N-aryl fragment is bound to a hydrazone or azo functional group. The observed CS changes (Table 2) were compared against the $\Delta\delta$ ^{13}C values for the $N_{(1)}$- and $N_{(5)}$-aryl groups in 1,3-diphenyl-5-(4-nitrophenyl)formazane X, which serves as a model for $\Delta\delta$ ^{13}C in individual azophenyl and arylhydrazone tautomers, in accord with an earlier study [12].

In the formazane series II-VII the root-mean-square deviations for $\Delta\delta$ ^{13}C for the ipso-, ortho-, and para-atoms in the N-aryl group relative to $\Delta\delta$ ^{13}C for the azophenyl tautomer were as follows: $\pm$1.5, $\pm$1.0, and $\pm$1.1 ppm, respectively; in contrast, the root-mean-square deviations relative to $\Delta\delta$ ^{13}C in the arylhydrazone tautomer were 10.6, 10.3, and 10.7 ppm, respectively. The confidence range for these calculated $\Delta\delta$ ^{13}C values in the individual tautomers is $\pm$0.9 ppm. We conclude that the differences between $\Delta\delta$ ^{13}C for the N-aryl group in formazanes II-VII and $\Delta\delta$ ^{13}C in the model arylhydrazone tautomer are both significant and statistically reliable, whereas the differences relative to $\Delta\delta$ ^{13}C in the model azophenyl tautomer are insignificant and essentially meaningless from a statistical viewpoint. Thus, formazanes II-VII exist in $CDCl_3$ solution primarily in the form of their azoaryl tautomers (A and C); we cannot obtain, however, an accurate quantitative estimate of the tautomer concentration. Formazane I would also be expected to exist in the form of its azoaryl tautomer, since the electron-withdrawing properties of the p-dimethylaminophenyl fragment are even less strong than for the aryl fragments in formazanes II-VII.

*Here and elsewhere band intensity determinations (1000-3000 liters/mole·cm^2) were made using the Ramsay method [10].

Only in the case of formazanes VIII and IX, containing strong electron-withdrawing substituents, were comparably large values observed for the $\Delta\delta$ ^{13}C deviations relative to the corresponding values in both pure tautomer models (cf. Table 2); this fact made it possible to estimate the fraction or amount of the arylhydrazone tautomer in these compounds, using the following equation:

$$R_{B,D} = [(\Delta\delta_f - \Delta\delta_a)/(\Delta\delta_h - \Delta\delta_a)] \cdot 100\% \quad [12],$$

where $R_{B,D}$ is the amount of arylhydrazone tautomer; $\Delta\delta_f$ is the δ ^{13}C change observed for the N-aryl fragment in the formazane derivative; $\Delta\delta_a$ is the δ ^{13}C change observed in the azophenyl tautomer model; and $\Delta\delta_h$ is the δ ^{13}C change measured in the arylhydrazone tautomer model.

The concentration of arylhydrazone tautomer (B, D) in $CDCl_3$ solution was found to be 25 and 55% for formazanes VIII and IX, respectively. Based on the roughly equal ratio of $N_{(1)}$ and $N_{(5)}$ tautomers observed for compound IX, we conclude that the benzothiazole and p-nitrophenyl substituents are very similar in terms of their electron-withdrawing characteristics. On the other hand, comparison of the concentrations of arylhydrazone tautomers in the series of N-(p-nitrophenyl)-substituted formazanes (100% in N-phenylformazane [13], 70% in N-(2-thiazolyl)formazane [12], 55% in N-(2-benzothiazolyl)formazane IX, and 17% in N-(2-quinazolinyl)formazane [3]), leads us to conclude that the benzothiazole substituent occupies a position intermediate between a thiazole and quinazoline ring in terms of its electron-withdrawing properties. The greater electron-withdrawing ability of benzothiazole relative to thiazole is consistent with data concerning the effect of a condensed benzene ring [14].

Studies of 1(5-aryl-3-phenyl-5(1)-(2-benzothiazolyl) formazanes have revealed that their IR spectra (in $CDCl_3$ solution) exhibit, in addition to a free NH group band (ν_{NH} 3300-3330 cm^{-1}), an additional weak-intensity ν_{NH} band at 3420-3440 cm^{-1} [15]. According to the authors of these studies [4, 15], this band provided evidence for the presence of an imino-tautomeric form E in solution, where the proton is localized on the nitrogen atom in the heterocycle. We have also attempted to deduce the presence of form E in solution for formazanes II-IX, based on ^{13}C-NMR spectral data for compounds with fixed amino- and imino-tautomeric structures [16]. In $CDCl_3$ solution the root-mean-square deviations in δ ^{13}C for the atoms in the benzothiazole fragment, which should be most sensitive to amino—imino conversion ($C_{(4')}$, $C_{(6')}$, $C_{(8')}$, and $C_{(9')}$), in formazanes II-VII, relative to or against the δ ^{13}C values for the same atoms in the spectrum of 1-(1-naphthyl)-3-phenyl-5-(2-benzothiazolyl)-5-methylformazane XI (the amino form), were $\pm$0.3, $\pm$0.3, $\pm$0.2, and $\pm$0.2 ppm, respectively (cf. Table 2), i.e., the δ ^{13}C deviations are within the confidence range of error limits for the determination of δ ^{13}C ($\pm$0.6 ppm), and are thus statistically insignificant. Comparison against the ^{13}C CS values for the corresponding atoms in 1,3-diphenyl-5-(3-methyl-2,3-dihydro-2-benzothiazolidene)formazane XII (the imino form [16]; cf. Table 2), in contrast, reveals very large root-mean-square deviations in δ ^{13}C for formazanes II-VII, on the order of 11.8, 1.7, 7.2, and 11.0 ppm. Although we cannot obtain a precise estimate of the amount of imino tautomer form E based on this ^{13}C-NMR data, we can assert that the amount does not exceed 5% [according to the error limit range for δ ^{13}C ($\pm$0.6 ppm)] and the observed differences in the CS values for the $C_{(4')}$, $C_{(8')}$, and $C_{(9')}$ atoms (11.6, 7.0, and 11.2 ppm) versus the amino- and imino-tautomeric forms). This lower limit is also in agreement with the low intensity (A ~ 500 liters/mole·cm^2) of the ν_{NH} 3440-3420 cm^{-1} band. In the case of formazanes VIII and IX, containing comparable concentrations of $N_{(1)}$- and $N_{(5)}$-amino tautomeric forms, their δ ^{13}C values for the $C_{(4')}$, $C_{(6')}$, $C_{(8')}$, and $C_{(9')}$ atoms exceed by a large amount the CS values for the amino tautomer (compound XI), and even more so the values for the imino tautomer (compound XII). It is not possible, therefore, to quantify the concentration of imino tautomer in these compounds based solely on interconversion of the amino- and imino-tautomers, as was done for compounds II-VII.

In DMSO solution, which is a strong proton-acceptor solvent, the amount of imino tautomer present in formazanes I-VIII increases relative to the amount present in $CDCl_3$ solution. This is suggested by the large degree of signal broadening observed for the $C_{(3')}$, $C_{(4')}$, $C_{(8')}$, and $C_{(9')}$ atoms (half-width $\geq$40 Hz). This degree of signal broadening may result both from interconversion among tautomer species, as well as from isomeric interconversion among formazanes, if the δ ^{13}C differences are greater than 2 ppm (corresponding to 50 Hz at an operating frequency for the NMR spectrometer for ^{13}C nuclei of 25.16 MHz).

It has been shown previously [3], however, that δ ^{13}C values do not differ among isomeric formazanes by more than 2 ppm, with the exception of δ ^{13}C for the $C_{(3)}$ atom [16]; in contrast, the CS values for the $C_{(4')}$, $C_{(8')}$, and $C_{(9')}$ atoms in amino- and imino-tautomers (compounds XI and XII) differ by more than 7 ppm (175 Hz) (cf. Table 2). The observed signal broadening in the ^{13}C-NMR spectra of these compounds in DMSO solution must be due exclusively to interconversion among the tautomer species noted above, i.e., significant concentrations of the imino-tautomers of formazanes I-VIII must be formed in DMSO solution. The observed signal broadening for the

$C_{(3)}$ atom is also indicative, however, of the formation of different configurational isomers for formazanes I-VIII in DMSO solution.

Formazane IX undergoes virtually quantitative decomposition in DMSO solution at room temperature to give the (2-benzothiazolyl)hydrazone of benzaldehyde (XIII), not benzaldehyde (4-nitrophenyl)hydrazone, which has been noted upon acidic hydrolysis or cleavage [17]. Formazane V is converted to hydrazone XIII to the extent of 50% in DMSO solution upon being stored for 1 h at 383 K. Hydrazone XIII formed in this manner was identified based on its ^{13}C-NMR spectrum upon addition of authentic hydrazone XIII prepared by an independent route.

EXPERIMENTAL

IR spectra of compounds I-IX in CCl_4 and $CDCl_3$ were obtained on a Perkin—Elmer 983G spectrophotometer in the LiF (frequency) range, with path lengths of 0.1 and 1.0 cm. Solution concentrations were in the 10^{-1} to 10^{-3} mole/liter range. PMR spectra (at 100 MHz) were recorded on a Varian XL-100-12 spectrometer using solutions in CCl_4, $CDCl_3$, and DMSO-D_6 at concentrations of 10^{-2} to 10^{-3} mole/liter. TMS was used as internal standard. CS values were determined at 307 K. ^{13}C-NMR spectra were measured on the Varian XL-100-12 spectrometer (operating at 25.16 MHz) in $CDCl_3$ or DMSO-D_6 solution under pulse Fourier transform conditions. Solution concentrations were 0.1 to 0.2 mole/liter. Signal assignments in their ^{13}C-NMR spectra were made based on analysis of spectra recorded using both complete and selective (off-resonance) proton decoupling. Spectra obtained without any spin—spin proton decoupling were also used to carry out the signal assignments. The accuracy of CS measurements is ±0.01 ppm for PMR spectra, ±0.05 ppm for ^{13}C-NMR spectra.

The CS values for the ^{13}C-NMR spectra of hydrazone XIII and the principal product formed upon decomposition of formazanes IX and V are as follows, in ppm: $C_{(2')}$ 167.1, 167.1, 167.0; $C_{(4')}$ 117.6, 117.6, 117.6; $C_{(5')}$ 125.8, 125.8, overlapped; $C_{(6')}$ 121.5, 121.5, overlapped; $C_{(7')}$ 121.4, 121.4, overlapped; $C_{(8')}$ 129.2, 129.3, 129.3; $C_{(9')}$ 149.8, 149.8, 149.8; CH=N 144.1, 144.0, 144.0; C-aryl fragment $C_{(1)}$ 134.4, 134.4, 134.4; $C_{(2,6)}$ 126.5, 126.5, overlapped; $C_{(3,5)}$ 128.7, 128.7, overlapped; $C_{(4)}$ 129.5, 129.4, overlapped.

The synthesis of formazanes I-IX has been reported previously [1]; their N-methyl derivatives XI and XII [16] and hydrazone XIII [15] have also been described in the literature.

LITERATURE CITED

1. N. A. Klyuev, V. G. Zhil'nikov, G. G. Aleksandrev, I. I. Grandberg, and G. N. Lipunova, *Zh. Org. Khim.*, **19**, 2615 (1983).
2. N. A. Klyuev, E. S. Karavaeva, V. G. Zhil'nikov, and N. P. Bednyagina, *Zh. Org. Khim.*, **17**, 1757 (1981).
3. L. V. Shmelev, G. N. Lipunova, E. S. Karavaeva, G. M. Adamova, and Yu. S. Ryabokobylko, *Zh. Org. Khim.*, **23**, 2458 (1987).
4. N. P. Bednyagina, I. Ya. Postovskii, A. D. Garnovskii, and O. A. Oispov, *Usp. Khim.*, **44**, 1052 (1975).
5. N. V. Serebryakova, G. N. Lipunova, N. P. Bednyagina, and L. F. Lipatova, *Khim. Geterotsikl. Soedin.*, No. 10, 1403 (1970).
6. G. N. Lipunova, N. N. Gulemina, A. P. Zeif, and N. P. Bednyagina, *Khim. Geterotsikl. Soedin.*, No. 4, 493 (1974).
7. A. P. Zeif, G. N. Lipunova, N. P. Bednyagina, L. N. Shchegoleva, and L. I. Chernyavskii, *Zh. Org. Khim.*, **6**, 2590 (1970).
8. B. Brzezinsky and G. Zundel, *J. Magn. Reson.*, **48**, 364 (1982).
9. L. V. Shmelev, M. N. Stopnikova, Yu. S. Ryabokobylko, A. V. Kessenikh, G. N. Adamova, and V. M. Ostrovskaya, *Khim. Geterotsikl. Soedin.*, No. 3, 404 (1985).
10. D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
11. D. F. Ewing, *Org. Magn. Reson.*, **12**, 499 (1979).
12. L. V. Shmelev, G. N. Lipunova, O. P. Sulim, and N. P. Bednyagina, *Zh. Obshch. Khim.*, **56**, 2393 (1986).
13. P. B. Fischer, B. L. Kaul, and H. Zollinger, *Helv. Chim. Acta*, **51**, 1449 (1968).
14. A. F. Pozharskii, *Theoretical Principles in Heterocyclic Chemistry* [in Russian], Khimiya, Moscow (1985).
15. I. I. Mudretsova and S. L. Mertsalov, *Khim. Geterotsikl. Soedin.*, No. 12, 1666 (1975).
16. N. B. Ol'khovikova, L. I. Rusinova, L. V. Shmelev, G. N. Lipunova, N. A. Klyuev, and A. V. El'tsov, *Zh. Obshch. Khim.*, **58**, 1626 (1988).

17. N. P. Bednyagina, E. S. Karavaeva, G. N. Lipunova, L. I. Medvedeva, and B. I. Buzykin, *Khim. Geterotsikl. Soedin.*, No. 9, 1268 (1977).