

STRUCTURE OF 1-ARYL-3-ALKYL-5-(2-BENZOTHAZOLYL)FORMAZANS

N. B. Ol'khovikova, G. N. Lipunova, L. V. Shmelev,
L. I. Rusinova, and I. G. Pervova

The isomeric and tautomeric structures of 1-aryl-3-alkyl-5-(2-benzothiazolyl)formazans in solutions were investigated by means of NMR, IR, and electronic spectroscopy. It is shown that the nature of the solvent and the alkyl substituent in the 3 position affects the ratio of the Z and E isomers relative to the C=N bond of the azohydrazone chain. An increase in the length of the alkyl substituent in the 3 position leads to preponderance of the Z isomer in solution, while branching stabilizes the Z configuration with an N²...HN⁵ intramolecular hydrogen bond (IMHB), regardless of the solvent. The nature of the solvent has a significant effect on the ratio of the amino and imino tautomeric forms of the E isomers. The benzothiazolylhydrazone form predominates in CHCl₃, while the tautomer with a benzothiazolidene fragment is the major form in DMSO.

In our preceding report [1] we examined the structure of 1-aryl-3-phenyl-5-(2-benzothiazolyl)formazans and showed that in nonpolar solvents they exist in the form of an equilibrium mixture of the "chelate" and open forms with a significant preponderance of the former. The spectral characteristics of these compounds differ significantly from those observed for formazans with an alkyl substituted meso carbon atom; this constitutes evidence that they have different structures.

The literature concepts with respect the structure of 1-aryl-3-alkyl-5-(2-benzothiazolyl)formazans, which are based only the result of electronic and IR spectroscopy [2-4], as well as the results of quantum-chemical calculations for 1-phenyl-3-methyl-5-(2-benzothiazolyl)formazan, have discrepancies and are contradictory [5]. In [3] an E^{1,2}Z^{2,3}Z^{3,4} configuration of the azohydrazone chain with the formation of an N⁵H...N¹ intramolecular hydrogen bond (IMHB) was assigned to this formazan, whereas in a review [6] it was concluded that 3-alkylbenzothiazolylformazans have an E^{1,2}E^{2,3}E^{3,4} configuration.

In the opinion of Lipunova and coworkers [7], the introduction of a branched substituent at the meso carbon atom leads to the development of, in addition to an "open" isomer, a "chelate" form in solutions.

The tautomeric equilibria in solution of 3-alkylbenzothiazolylformazans was previous examined only within the framework of the formation of amino and imino tautomers, evidence for the existence of which was provided by the ν_{NH} bands at 3440 cm⁻¹ (the imino tautomer) or at 3330-3350 cm⁻¹ (the amino tautomer) observed in the IR spectra [4]. N¹,N⁵-Tautomerism was not discussed at all.

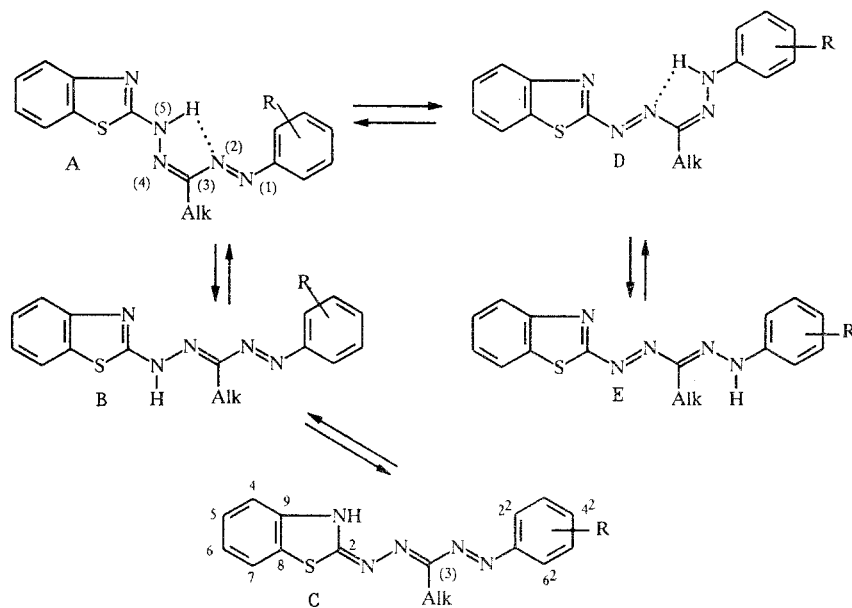
The aim of our research was to investigate the isomeric and tautomeric compositions of 1-aryl-3-alkyl-5-(2-benzothiazolyl)formazans in solutions. For this, we obtained the spectral characteristics of I-VIII, which differ with respect to the substituents attached to the meso-carbon atom and in the N-aryl fragment (Table 1).

First and foremost, one should note the absence of a strong IMHB in the molecules of these compounds. Evidence for this is provided by the ν_{NH} bands at 3330-3440 cm⁻¹ in the IR spectra of their solutions, as well as the intense, in contrast to "chelate" formazans [1], long-wave absorption in the electronic spectra (Table 1), the maximum of which is shifted hypsochromically.

The δ_{NH} chemical shifts of 10.8-12.1 ppm observed in the PMR spectra of I-VIII (Table 1, CDCl₃) are characteristic for E^{1,2}E^{2,3}Z^{3,4} isomers (amino tautomers A and D in the diagram) [8, 9]; however, one cannot exclude the close δ_{NH} values also in the case of imino tautomeric forms.

TABLE 1. Spectral Characteristics of 1-Aryl-3-alkyl-5-(2-benzothiazolyl)formazans I-VIII

Compound	Alk	R	ν_{NH} , cm^{-1} (CHCl_3)	δ_{NH} , ppm		λ_{max} , nm (lg ϵ) (CHCl_3)
				CDCl_3	$\text{DMSO}-d_6$	
I	CH_3	<i>p</i> - CH_3	3435, 3340	10,80	—	328 (4,06), 417 (4,20)
II	CH_3	<i>o</i> - CH_3	3440, 3355	10,90	12,46	318 (4,09), 420 (4,28)
III	CH_3	H	3413, 3333	11,07	12,48	309 (4,12), 422 (4,25)
IV	CH_3	<i>p</i> -Br	3419, 3333	12,11	12,53	327 (4,10), 420 (4,25)
V	C_2H_5	<i>p</i> - CH_3	3360	10,94	12,46	328 (4,11), 435 (4,21)
VI	C_4H_9	H	3464, 3328	10,97	11,62	313 (4,07), 434 (4,14)
VII	C_4H_9	<i>p</i> - C_4H_9	3466, 3342, 3331	10,94	—	330 (4,09), 435 (4,14)
VIII	<i>i</i> - C_3H_7	<i>p</i> - CH_3	3464, 3341, 3329	11,45	12,62	370 (4,15), 473 (4,19)



I - VIII

An x-ray diffraction study of formazan II [10] showed that in the crystalline form it exists in the N^5 -amino tautomeric form as a mixture of E and Z isomers relative to the $\text{C}=\text{N}$ bond (forms A and B). It is evident that the same isomeric forms are also retained in slightly polar solvents. Thus, in the ^{13}C NMR spectrum of formazan II in CDCl_3 one observed a doubled set of signals for the nonequivalent carbon nuclei (Table 2). The same pattern is characteristic for all formazans I-IV with a CH_3 group attached to the meso-carbon atom; the greatest differences in the chemical shifts for the various isomeric forms are noted for the $\text{C}_{(3)}$ and $\text{C}_{(1')}$ atoms (Table 2). In [11] it was shown that the magnitude of the chemical shift of the $\text{C}_{(3)}$ atom may serve as an indicative sign of the configuration of the azohydrazone chain within the confines of a series of formazans with identical substituents in the 3 position. For 3-methyl-substituted formazans I-IV the $\text{Z}^{3,4}$ configuration of the molecules is characterized by a strong-field chemical shift (CS) for the $\text{C}_{(3)}$ atom (150 ppm) and a weak-field CS for the $\text{C}_{(1')}$ (15 ppm) atom as compared with the $\text{E}^{3,4}$ configuration (160 and 9 ppm, respectively). In the ^{13}C NMR spectra of compounds that contain alkyl substituents other than CH_3 attached to the $\text{C}_{(3)}$ atom the number of signals either corresponds to the number of nonequivalent carbon atoms (VIII) or slightly increases it (V and VI, Table 2). For formazan VIII, which has significant solubility in CDCl_3 (~ 1 mole/liter), this attests to the absence in solution of even slight amounts of the $\text{E}^{3,4}$ isomer [or to fast (on the NMR time scale) $\text{E} \rightleftharpoons \text{Z}$ isomeric transformations].

In the case of formazans V and VI the percentage of the E isomer, which we were able to calculate from the intensities of the signals of the individual carbon atoms, does not exceed 5%. This, however, does not make it possible to draw a reliable conclusion regarding the absence of significant amounts of the E isomer in solutions of the indicated compounds because of the low (~ 0.3 mole/liter) solubility of the latter. In the ^{13}C NMR spectrum of specially synthesized formazan VII, which has

TABLE 2. ¹³C NMR Chemical Shifts of 1-Aryl-3-alkyl-5-(2-benzothiazolyl)formazans I-VIII (δ Scale, ppm Relative to TMS, 307 K)

Com- pound	Isomer, %	C(2)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(3)	C(1)'	C(2)'	C(3)'	C(4)'	C(1'')	C(2'')	C(3'')	C(4'')	C(R)
Deuterchloroform																		
I	Z	166,4	120,1	126,1	122,6	121,2	131,3	151,9	150,7	15,4	—	—	—	150,9	123,9	131,1	144,1	21,7
	E	167,8	118,7	126,2	122,9	121,6	**	**	159,9	8,4	—	—	—	150,5	123,5	129,8	142,4	21,6
II	Z	166,4	120,1	126,0	121,2	121,2	131,2	151,8	150,6	15,5	—	—	—	150,9	140,6	131,6	133,0	17,4
	E	168,1	118,4	126,5	122,9	121,6	**	148,7	159,8	8,7	—	—	—	150,3	138,7	**	**	17,4
III	Z	166,7	120,1	126,1	122,7	121,3	131,4	151,6	150,6	15,4	—	—	—	152,5	123,7	129,2	132,8	—
	E (31...34)	168,7***	118,1***	126,2	122,9	121,6	130,0***	148,5	159,9***	8,8***	—	—	—	152,3	123,4	129,1	131,5	—
IV	Z	166,8	120,1	126,1	122,8	121,2	131,1	151,5	150,6	15,4	—	—	—	151,1	124,9	132,5	131,5	—
	E (26...33)	168,8***	117,9***	126,3***	123,0***	121,7***	129,9	147,6	160,0***	8,8***	—	—	—	**	124,8	132,2	**	—
V	Z	166,8	120,2	126,0	122,6	121,4	131,4	152,0	153,6	22,1	10,4	—	—	150,9	123,8	130,0	143,9	21,7
	E (4)	**	118,6	**	**	**	**	**	**	17,2***	**	—	—	**	123,3	129,6	**	**
VI	Z	167,2	119,9	125,9	122,5	121,0	131,1	151,6	152,6	28,1	28,1	22,5	13,9	152,3	123,5	129,0	132,5	—
	E (5)	168,5	**	126,1***	122,9	**	**	**	**	20,1***	27,3	**	**	**	**	**	**	—
VII	Z	167,0	120,1	125,9	122,5	121,1	131,3	151,9	152,8	28,2	28,3	22,5	13,9	150,9	123,8	129,2	148,7	35,7
	E (4...7)	168,0***	118,3***	126,5***	**	121,5	**	**	162,9***	22,8	28,8	22,5	13,9	150,8***	123,4	129,8	147,2***	35,7
VIII	Z	167,4	120,1	126,0	122,6	121,2	131,3	151,8	156,0	27,6	20,5	—	—	150,9	123,8	130,0	143,9	21,1
Perdeuterated dimethyl sulfoxide																		
III	Z (2...7)	**	119,4***	**	**	**	**	**	**	15,3***	—	—	—	**	124,4***	**	132,8***	—
	E	169,3	115,9	126,4	122,5	122,5	127,7	145,5	161,7	9,4	—	—	—	151,7	122,3	129,4	131,0	—
IV	E	169,6	116,0	126,4	122,6	122,1	127,6	145,0	161,6	9,3	—	—	—	150,4	124,0	132,4	**	—
V	Z (34)	167,3	119,4***	125,9	122,6	121,5	130,6	152,1	152,8	21,4	10,6	—	—	150,6	124,5	130,0	143,5***	21,7
	E	169,3	115,1	126,5	122,5	122,5	127,0	143,5	166,2	16,1	10,3	—	—	150,1	122,3	129,9	141,6	21,7
VI	Z (24...28)	167,3***	119,5***	125,9***	122,2	121,4	130,8	152,1	152,4	27,6	27,6	21,9	13,8	151,8	124,4	129,3	132,7***	—
	E	169,5	115,1	126,4	122,2	122,2	127,2	144,5	165,3	22,4	27,6	22,4	21,1	151,8	122,2	129,3	131,2	—
VIII	Z	167,5	119,4	125,9	122,1	121,5	130,7	152,1	155,5	26,2	20,3	—	—	150,6	124,4	129,8	143,5	21,1

*C(Alk)

**Chemical shift not determined because of the low concentration of the isomer.

***The carbon atoms with respect to which the percentage of the isomer was calculated.

a solubility of ~ 1 mole/liter, we were able to detect a double set of signals (Table 2), while for III and IV the percentages were 26-34%. Thus an increase in the length of the alkyl chain attached to the meso-carbon atom leads to a significant decrease in the percentages of the $E^{3,4}$ isomers in solution, while branching of the alkyl chain strictly stabilizes the $Z^{3,4}$ configuration in slightly polar solvents. It should be noted that in the case of 1-aryl-3-methyl-5-(2-benzothiazolyl)formazans the ratio of the $Z^{3,4}$ and $E^{3,4}$ isomers in solution depends to a considerable extent on the conditions used to obtain and purify the formazan. Thus a sample of III recrystallized twice from ethanol displays in its ^{13}C NMR spectrum only signals corresponding to the $Z^{3,4}$ isomer. In all of our experiments the percentage of the $E^{3,4}$ isomer is significantly lower than the percentage of the $Z^{3,4}$ isomer. This constitutes evidence for the higher stability of the latter, stabilized by an $\text{N}^5\text{H}\dots\text{N}^2$ intramolecular hydrogen bond (IMHB) in the five-membered ring (forms A and D in the diagram).

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