STRUCTURE OF 2-BENZOTHIAZOLYLHYDRAZONES OF AROMATIC AND ALIPHATIC ALDEHYDES

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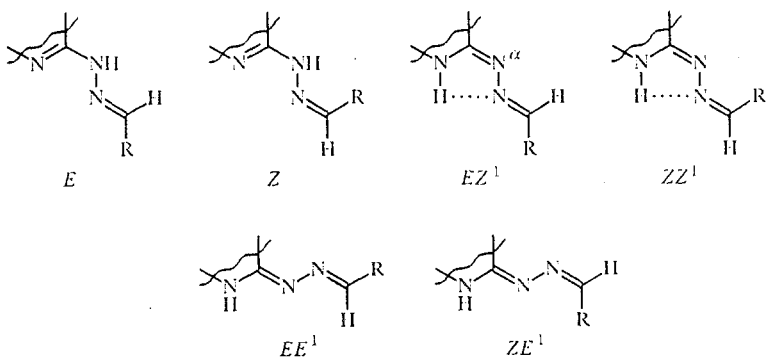
On the basis of data of ^{13}C and ^{1}H NMR and IR spectroscopy, it was shown that 2-benzothiazolylhydrazones of aliphatic aldehydes were in solution as a mixture of E and Z isomers, and hydrazones of aromatic aldehydes were in solution only as E isomers. All investigated compounds existed in solution mainly in an amino tautomeric form, and the content of the imino form did not depend on the nature of the aldehyde fragment.

Both stereoisomerism and structural isomerism are characteristic of hydrazones [1]. For alkyl- and arylhydrazones, the difference in the structure of the isomers is governed by the mutual arrangement of the molecular fragments with respect to the C=N bond [2]. When the hydrazone fragment contains an α-azaheterocycle, both stereoisomerism and isomerism related to the position of the NH proton can occur. Such isomerism of the type "hydrazone–mixed azine of a heterocyclic ketone and a carbonyl compound" [3] is often called amino–imino tautomerism [4] of hydrazones, by analogy with tautomeric transformations of α-azahetarylamines.

For amino tautomers of α-azahetarylhydrazones, both E and Z configurations with respect to the C=N bond are probable (Scheme 1). In the case of imino tautomers, in the opinion of Buzykin et al. [5], because of strong steric hindrances in the S-cis configurations, it is necessary to consider only EE′, EZ′, ZZ′, and ZE′ S-trans isomers (Z′ and E′ configurations with respect to the $C_{(2)}=N_{(\alpha)}$ bond).

Scheme 1



For hydrazones with different electron-deficient diazinyl heterocycles, examples are known of their existence both in the imino tautomeric form (1-phthalazinyl(1-pyridazinyl)hydrazones [3, 5, 6]) and in the amino tautomeric form (benzaldehyde 2-quinazolinylhydrazone [7] as E and Z isomers). 2-Quinoxalinylhydrazones exist as an equilibrium mixture of amino and imino tautomers [8].

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TABLE 1. Chemical Shifts of ^{13}C NMR of 2-Benzothiazolylhydrazones of Aliphatic Aldehydes (δ, ppm, from TMS)

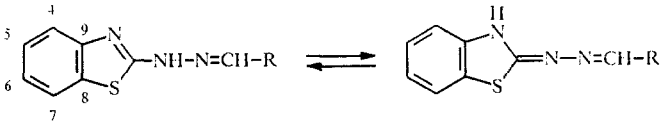
Compound	Isomer	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	N=C–H	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$
							$CDCl_3$						
I	*E*	168,7	117,8	126,0	121,8	121,4	130,1	150,1	144,0	18,4	–	–	–
	Z	168,9	118,8	126,0	122,3	121,2	130,8	152,2	141,9	13,7	–	–	–
II	*E*	169,2	117,6	125,9	121,7	121,3	130,2	150,2	149,0	25,8	10,6	–	–
	Z	*	118,6	125,9	122,2	121,3	*	*	148,7	21,0	10,4	–	–
III	*E*	169,4	117,4	125,8	121,5	121,3	130,1	150,3	148,2	32,0	28,4	22,2	13,8
	Z	169,7	118,3	125,8	122,1	121,3	130,4	*	147,9	27,6	28,2	22,2	13,5
IV	*E*	169,5	117,5	125,9	121,7	121,4	130,1	149,9	153,0	31,5	19,8	–	–
	Z	169,8	118,4	125,9	122,2	121,4	*	*	153,9	26,6	19,3	–	–
IX	*E*	169,4	119,8	125,6	121,9	120,8	132,2	152,2	136,1	18,6	31,8**		
							$DMSO-D_6$						
I	*E*	166,7	117,7	125,7	121,2	121,2	129,4	150,7	144,4	18,2	–	–	–
	Z	168,1	117,4	125,7	*	121,2	129,2	149,8	144,0	14,6	–	–	–
II	*E*	167,0	117,9	125,7	121,2	121,2	129,6	150,9	148,9	25,3	10,5	–	–
	Z	168,2	117,3	125,7	121,4	121,2	129,1	150,0	*	21,3	10,5	–	–
III	*E*	166,9	117,9	125,7	121,2	121,2	129,6	150,9	148,0	31,5	28,1	21,8	13,7
	Z	168,2	117,3	125,7	121,4	121,2	129,1	149,6	148,9	27,6	27,8	22,0	13,7
IV	*E*	167,1	117,9	125,6	121,2	121,2	129,6	150,9	152,4	30,8	19,6	–	–
	Z	168,0	*	125,6	121,5	121,2	*	*	(154,2)	26,3	19,6	–	–
IX	*E*	168,4	119,3	125,6	121,6	121,0	131,4	151,8	139,5	18,4	31,9**		

*Chemical shift of peaks was not determined because of low concentration of Z isomers.

**Chemical shift of $N-CH_3$ group.

For 2-benzothiazolylhydrazones, on the basis of IR-spectroscopic data, Mudretsova and Mertsalov [9] concluded that both amino and imino tautomers are present in solutions (CCl_4 and $CHCl_3$). In addition, the main feature of formation of imino tautomers is the appearance in IR spectra of the solutions of a ν_{NH} absorption band in the region 3400-3450 cm^{-1} [4]. However, we have shown [7] that this criterion is not absolute because such high-frequency absorption of the NH bond may be due to steric factors during formation of the Z isomer.

The purpose of the present paper was determination of the tautomeric and isomeric composition of 2-benzothiazolylhydrazones of aliphatic and aromatic aldehydes I-VIII on the basis of data of ^1H and ^{13}C NMR spectroscopy.



I) R = Me; II) R = Et; III) R = Bu, IV) R = i-Pr, V) R = $C_6H_4NMe_2$; VI) R = 4-$MeOC_6H_4$, VII) R = Ph, VIII) R = 4-$NO_2C_6H_4$

The NMR spectra of hydrazones I-IV (Table 1) contained two sets of peaks corresponding to resonating nuclei of the molecule. The ratio of the intensities of the peaks depended on the substituent R. The small difference in the values of the chemical shifts for atoms of the benzothiazolyl fragment $C_{(4)}$, $C_{(6)}$, $C_{(8)}$, $C_{(9)}$ ($\Delta\delta^{13}C$ 0.1-1.0 ppm) indicates that the double set of peaks is due to the presence of stereoisomers of hydrazones, but not their amino and imino tautomeric forms because in the latter case the differences in $\delta^{13}C$ should be 2-10 ppm [10].

On the basis of the greater value of the chemical shift of the methine proton (Table 2), according to data of [11], an E configuration should be assigned to the predominant isomer of hydrazones I-IV, and a Z configuration should be assigned to the other isomer. Such assignment of peaks also agrees with the value of the direct spin–spin coupling constant of iminyl carbon $^1J_{13CH}$ ~150 Hz for the E isomers and $^1J_{13CH}$ 175-180 Hz for the Z isomers. Such a relation of the direct spin–spin coupling constant to the molecular configuration was also noted previously for oximes of aliphatic aldehydes [12]. It should be noted that in the ^{13}C NMR spectra of hydrazones I-IV the peaks of the aliphatic-fragment carbon atoms closest to the C=N bond are in a stronger field for the Z isomers than for the E isomers ($\Delta\delta^{13}C$ 4-5 ppm). Such a relation can be used for identification of isomers. The amount of Z isomers was 36-38, 16-17, 10-11, and 5-6% for R = CH_3, C_2H_5, n-C_4H_9, and i-C_3H_7, respectively. For this, it is evident that the amount of Z isomers decreased with increasing length of the alkyl group and also during branching of the alkyl substituent (R = i-C_3H_7), which destabilized the Z configuration.

The NMR spectra of hydrazones V-VIII (Table 3) contained a single set of peaks of resonating nuclei of the molecules. Thus, it was impossible to determine the configuration of the molecule by direct comparison of δ^1H of methine protons. However, as is evident from the data of Table 4, the peaks of methine protons in benzene-D_6 were shifted to a strong field by 0.5-0.8 ppm with respect to their position in the nonaromatic solvent. According to Karabatsos et al. [11], such a change of δ^1H is characteristic only of the E isomers of hydrazones.

In the region of stretching vibrations of the NH bond, the IR spectra of hydrazones I-IV contained four absorption bands: 3425, 3362, 3340, and 3188 cm^{-1} ($CDCl_3$ and CCl_4). The latter of them was due to the presence of an intermolecularly bonded NH group because its intensity decreased during dilution of the solutions. According to the interpretation of Mudretsova and Mertsalov [9], the highest-frequency band belongs to the imino form, and two bands in the region of 3340-3365 cm^{-1} belong to the amino tautomeric form, which exists as two stereoisomers [7].

The IR spectra of hydrazones V-VIII contained only three absorption bands, i.e., 3425, 3330, and 3180-3190 cm^{-1}. From this, it is evident that in the solution of 2-benzothiazolylhydrazones we can expect the presence of the imino tautomeric form and one of the isomers of the amino tautomer, namely, the E isomer (ν_{NH} 3330 cm^{-1}). In the opinion of Buzykin et al. [5], the higher-frequency absorption of the hydrazone isomers is due to the steric effect of the alkyl group and a decrease of bonding of the amino fragment with the indene part of the molecule.

Thus, there are discrepancies between the results of interpretation of the data of IR and NMR spectroscopy as to the presence of the imino tautomeric form in solutions of hydrazones I-VIII. As was said previously, in the NMR spectra, the peaks of the imino tautomer were not observed separately. However, it is possible that fast (on the NMR time scale) interconversions of the amino and imino tautomers occurred in the solution, resulting in averaging of the chemical shifts of the observed peaks. For confirmation of this assumption and evaluation of the ratio of the tautomers in solutions of hydrazones I-VIII, we synthesized model compounds with rigidly fixed amino and imino tautomeric structures, i.e., N-alkyl derivatives of hydrazones I and V.

TABLE 2. Chemical Shifts of Peaks in PMR Spectra of 2-Benzothiazolylhydrazones (δ, ppm, from TMS) (br. denotes broadened)

Compound	NH(CH_3)	4-H	5-H	6-H	7-H	N=C—H		1'-H	(2',3',4')-H	2',6'-H	3',5'-H	4'-R	Note
						E	*Z*						
						CDCl₃							
I	6,22	7,45	7,26	7,08	7,61	7,33	6,83	2,02	–	–	–	–	δ(1'-H) 1,90 (*Z*)
II	10,35	7,45	7,29	7,09	7,62	7,35	6,61	2,31	1,13	–	–	–	
III	11,56	7,43	7,28	7,10	7,64	7,33	6,67	2,24	0,93	–	–	–	$\delta(CH_2)_2$ 1,2...1,7
IV	11,06	7,44	7,28	7,09	7,63	7,31	6,54	2,55	1,13	–	–	–	δ(7-H) 7,81 (*Z*)
IX	(3,55)	7,61	7,29	7,09	7,61	7,05	–	2,07	–	–	–	–	
V	10,20	7,53	7,32	7,10	7,65	7,94	–	–	–	7,54	6,70	3,02	δNH 13,7 (−60 °C)
VI	br.	7,53	7,33	7,13	7,66	7,95	–	–	–	7,60	6,93	3,74	δNH 14,35 (−60 °C) δNH 12,40 (14 °C)
VII	br.	7,55	7,34	7,14	7,68	7,97	–	–	–	7,66	7,37	–	
X	(3,67)	7,62	7,29	7,09	7,62	7,59	–	–	–	7,69	7,34	7,31	
						DMSO-D_6							
I	10,85	7,40	7,18	6,98	7,70	7,45	6,84	1,92	–	–	–	–	
II	11,68	7,39	7,24	7,04	7,70	7,46	6,70	2,26	1,05	–	–	–	
III	11,73	7,42	7,27	7,06	7,70	7,45	6,73	2,25	0,92	–	–	–	
IV	11,79	7,43	7,27	7,06	7,73	7,40	–	2,64	1,07	–	–	–	
IX	(3,50)	7,54	7,29	7,10	7,75	7,25	–	2,00	–	–	–	–	
V	11,85	7,39	7,25	7,04	7,70	7,94	–	–	–	7,49	6,74	2,94	
VI	12,06	7,43	7,28	7,06	7,73	8,10	–	–	–	7,65	7,00	3,79	
VII	12,00	7,45	7,30	7,10	7,75	8,16	–	–	–	7,71	7,42	7,36	
VIII	12,51	7,47	7,32	7,14	7,78	8,24	–	–	–	7,92	8,28	–	
X	(3,68)	7,65	7,36	7,17	7,83	7,98	8,42	–	–	7,83	7,44	–	

TABLE 3. Chemical Shifts of ^{13}C NMR of 2-Benzothiazolylhydrazones of Aromatic Aldehydes (δ, ppm, from TMS)

Compound	$C_{(2)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	N=C–H	$C_{(1')}$	$C_{(2',6')}$	$C_{(3',5')}$	$C_{(4)}$	$N(CH_3)_2$	OCH_3
							$CDCl_3$							
V	168,3	117,9	126,0	121,8	121,5	130,5	150,1	145,4	122,4	128,6	112,2	151,9	40,3	
VI	169,3	117,4	126,0	121,9	121,5	130,1	149,6	144,2	127,2	128,5	114,2	161,1		55,4
VII	168,4	118,4	126,2	122,3	121,6	132,0	–	144,3	134,2	127,1	128,8	130,0		
X	169,5	120,3	125,8	122,3	120,9	132,6	152,2	137,1	134,7	126,9	128,8	129,4	32,2	
XI	–	109,1	126,2	119,5	121,6	(126,0)	141,1	152,8	136,3	127,5	128,1	130,0	30,6	
							$DMSO-D_6$							
V	166,6	117,3	125,8	121,3	121,2	129,3	150,1	145,3	122,1	127,9	112,0	151,4	39,8	
VI	166,9	117,4	125,8	121,3	121,3	129,1	149,9	144,1	127,0	128,1	114,3	160,5		55,2
VII	167,1	117,6	125,8	121,5	121,4	129,2	149,8	144,1	134,4	126,5	128,7	129,5		
VIII	167,5	117,6	126,1	122,1	121,6	129,1	149,0	142,2	141,0	127,4	124,1	147,6		
X	168,6	119,7	125,9	122,1	121,2	131,8	151,9	138,9	134,5	126,7	128,8	129,4	32,3	
XI	166,6	110,0	125,9	(121,7)	121,1	123,5	140,8	152,2	135,1	127,1	128,8	129,4	30,8	

TABLE 4. Chemical Shifts of Peaks in PMR Spectra of 2-Benzothiazolylhydrazones of Aromatic Aldehydes (benzene-D_6, 30°C) (br. denotes broadened)

Compound	NH	4-H	5-H	6-H	7-H	CH=N*	2'-H, 6'-H	3'-H, 5'-H	4'-R
V	7,90	7,34	7,13	6,88	7,57	7,40	7,61	6,47	2,42
VI	8,50	7,31	7,10	6,87	7,53	7,41	7,50	6,70	3,24
VII	br.	7,32	7,16	6,90	7,55	7,35	7,62	7,07	—
VIII**	br.	7,45	7,18	6,95	7,65	8,04	7,38	7,86	—

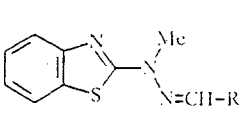
*Chemical shifts are given at 78°C because for hydrazones V and VII the peak of the methine proton is overlapped with the solvent peak at 30°C.
**For hydrazone VIII, the chemical shifts are given in a mixture containing ~10 vol. % DMSO-D_6.

TABLE 5. Evaluation of Amount of Amino Tautomer in Solutions of Hydrazones I-VIII According to Observed ^{13}C Chemical Shifts of $C_{(4)}$, $C_{(8)}$, and $C_{(9)}$ Carbon Atoms, %

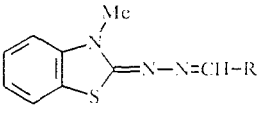
Compound	$C_{(4)}$	$C_{(8)}$	$C_{(9)}$	$C_{(4)}$	$C_{(8)}$	$C_{(9)}$
	$CDCl_3$			DMSO-D_6		
I	78	62	81	80	71	89
II	77	64	82	82	74	91
III	74	62	83	82	74	91
IV	75	62	79	82	74	91
V	78	68	81	76	70	84
VI	74	62	77	77	68	82
VII	83	91	*	79	69	81
VIII				79	68	74

*Peak of $C_{(9)}$ atom was not observed because of low solubility of hydrazone VII.

The structure of the model hydrazones was established on the basis of NMR-spectroscopic data according to the chemical shifts of peaks of carbon atoms of the heterocycle, as was done for N-alkylated formazans in [13]. The compounds with a rigidly fixed amino tautomeric structure were N-methyl-N-(2-benzothiazolyl)hydrazones of acetaldehyde IX and benzaldehyde X. The fixed imino tautomeric form was a mixed azine of 3-methyl-2-benzothiazoles and benzaldehyde XI.



IX, X



XI

IX) R = Me; X, XI) R = Ph

The chemical shifts of $C_{(4)}$, $C_{(6)}$, $C_{(8)}$, and $C_{(9)}$ atoms of isomers of hydrazones I-IV and V-VIII occupied an intermediate position between the chemical shifts of the same carbon atoms in compounds IX, X, and XI (Tables 1 and 3). That confirms the stated assumption concerning the fast interconversions of the tautomeric forms in solutions of hydrazones I-VIII. The chemical shifts of the peaks observed in their spectra had averaged values, the magnitude of which was determined from the fast-exchange correlation [14]

$$\delta = \delta_a P_a + \delta_i P_i.$$

TABLE 6. Characteristics of Hydrazones II, III, V, VI, and VIII-XI

Compound	Empirical formula	mp, °C	Yield, %
II	$C_{10}H_{11}N_3S$	171	82
III	$C_{12}H_{15}N_3S$	132	88
V	$C_{16}H_{16}N_4S$	225	80
VI	$C_{15}H_{13}N_3OS$	187	74
VIII	$C_{14}H_{10}N_4O_2S$	273	74
IX	$C_{10}H_{11}N_3S$	108	71
X, XI	$C_{15}H_{13}N_3S$	112...116	66

where δ_e is the observed value of $\delta^{13}C$, δ_a and δ_i are the values of $\delta^{13}C$ of the fixed amino and imino tautomeric forms, and P_a and P_i are the relative fractions of the amino and imino tautomers.

The content of the amino tautomer in the hydrazone solutions (Table 5) was calculated according to the equation

$$P_a = \frac{\delta_e - \delta_i}{\delta_a - \delta_i} \cdot 100\%.$$

The calculation was carried out according to the chemical shifts of the $C_{(4)}$, $C_{(8)}$, and $C_{(9)}$ atoms. The chemical shifts of the $C_{(6)}$ atoms of compounds X and XI differed insufficiently from each other to give a statistically significant evaluation of the tautomeric composition ($\Delta\delta C_{(6)}$ was ± 2.8 ppm, and the confidence interval for $\delta^{13}C$ was ± 0.5 ppm). As is evident from Table 5, the evaluation of the content of the amino tautomer in $CDCl_3$ according to the chemical shift of the $C_{(8)}$ atom gave understated results in comparison with the evaluation according to the chemical shifts of $C_{(4)}$ and $C_{(9)}$ atoms. Thus, transfer of the electronic effect from the reaction center (the $N_{(3)}$ atom of benzothiazole) to the ortho positions of the condensed benzene ring probably occurred in different ways. The para position with respect to the reaction center was found to have low sensitivity and was therefore not used for such an evaluation. We should note the absence of any significant relation of the amount of the amino tautomer both to the length and branching of the aliphatic substituent R and to the electronic effect of the substituent in the para position of the benzene ring in the ylidene fragment of the hydrazone molecule. Nevertheless, in our opinion, for all hydrazones I-VIII, regardless of the properties of the solvent, the amount of the imino tautomer was significant, ~15-25%, which agrees with the IR-spectral data, indicating a significant amount of the imino tautomer in solutions of hydrazones I-VIII.

EXPERIMENTAL

The IR spectra of compounds I-VIII in CCl_4 and $CDCl_3$ were obtained with a Perkin–Elmer 983G spectrometer (the concentration of the solutions was 10^{-1}-$5 \cdot 10^{-4}$ M, and l was 0.1-1.0 cm). The PMR spectra were obtained with a Varian XL-100-12 spectrometer for solutions in $CDCl_3$, DMSO-D_6, and C_6D_6 (concentration 10^{-2}-$5 \cdot 10^{-1}$ M), and the internal standard was TMS. The peaks in the PMR spectra were assigned using homonuclear internuclear double resonance (INDOR) [15]. It was assumed that the 6-H proton of the benzothiazole fragment was in the strongest field, as was established for aminobenzothiazoles [16]. The chemical shifts of the proton peaks were determined with respect to the centers of multiplets. The accuracy of the determination for the most strongly bonded protons of the 5- and 6-H benzothiazole fragment according to the calculation by the method of [15] was ± 0.03 ppm.

The ^{13}C NMR spectra (20.08 MHz) were recorded under pulsed conditions with a Fourier transform using a Tesla BS-587A NMR spectrometer. The peaks were assigned on the basis of analysis of the spectra obtained with both complete and selective decoupling from spin–spin coupling with protons and also by comparison with the spectra of benzothiazole derivatives [17]. In addition, proton-coupled spectra were used.

The accuracy of determination of the chemical shifts was ± 0.01 ppm in the PMR spectra and ± 0.05 ppm in the ^{13}C NMR spectra.

The synthesis of hydrazones I and VII is described in [18], and that of hydrazone IV is described in [19].

The elemental-analysis data correspond to the calculated values.

Valeraldehyde 2-Benzothiazolylhydrazone (III). To a suspension of 8 g (0.049 mole) of 2-benzothiazolylhydrazone in 50 ml of isopropyl alcohol was added 8 ml (0.075 mole) of valeraldehyde, and the whole was heated for 10 min. The reaction mixture was cooled, and the precipitate was filtered and dried. The yield was 10 g.

Hydrazones II, V, VI, and VIII were similarly synthesized, and 2-benzothiazolylhydrazine was dissolved in alcohol in the case of compounds VI and VIII. The characteristics of hydrazones II, III, V, VI, and VIII-XI are given in Table 6.

Acetaldehyde N-Methyl-N-(2-benzothiazolyl)hydrazone (IX). To a suspension of 0.95 g (0.005 mole) of acetaldehyde 2-benzothiazolylhydrazone in 20 ml of alcohol was added 0.4 ml of a 30% NaOH solution. The reaction material was heated, 1.5 ml (0.025 mole) of CH_3I was added, and the whole was boiled for 1 h. After completion of the reaction, the pH was 6. The solution was filtered and evaporated to dryness, and the precipitated crystals were recrystallized from heptane. The course of the reaction was monitored by thin-layer chromatography (the eluent was $CHCl_3$).

Benzaldehyde N-Methyl-N-(2-benzothiazolyl)hydrazone (X) and Mixed Azine of 3-Methyl-2-benzothiazolone and Benzaldehyde (XI). Benzaldehyde 2-benzothiazolylhydrazone was alkylated by the method described for compound IX. According to NMR spectral data, the obtained compound was a mixture of the two isomers X and XI, indistinguishable chromatographically.

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