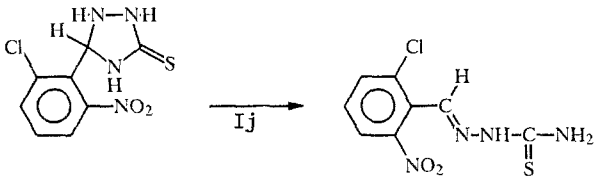
RING–CHAIN TAUTOMERISM OF THE THIOSEMICARBAZONES OF SUBSTITUTED BENZALDEHYDES AND ACETOPHENONES IN ACID MEDIA

K. N. Zelenin, O. B. Kuznetsova, P. B. Terent'ev, V. N. Torocheshnikov, V. V. Lashin, and V. V. Alekseev

Ring–chain tautomerism between the protonated form of the thiosemicarbazone and the 5–amino–2,3–dihydro–1,3,4–thiadiazolium cation is characteristic for thiosemicarbazones and 4–methylthiosemicarbazones of substituted benzaldehydes and acetophenones in CF_3COOH solutions.

The tendency of thiosemicarbazones to exist as the cyclic 5–amino–2,3–dihydro–1,3,4–thiadiazolium cations in acid solution is well known[1–3]. In principle this tendency may be suppressed through stabilization of the linear structure by conjugation. This should occur in particular for derivatives of benzaldehyde and acetophenone which are the subject of the present communication. To judge from the ^1H (Table 1) and ^{13}C NMR spectra (see experimental), compounds Ia–k and IIa–f exist in DMSO–d_6 solution in the "classical" thiosemicarbazone form and as the *cis*–isomer only.

The exception is the product from thiosemicarbazide and 2–chloro–6–nitrobenzaldehyde, Ij, which exist in freshly prepared DMSO–d_6 solution as a mixture of the thiosemicarbazone and the corresponding 1,2,4–triazolidin–3–thione. However the latter transforms into the linear hydrazone form on standing or heating.



The structures of both isomers were confirmed by the set of signals in the ^1H and ^{13}C NMR spectra, and the 1,2,4–triazolidin–3–*one* structure was demonstrated by the ^{15}N NMR spectrum (see experimental, 3 strong field signals of sp^3 hybridized nitrogen atoms, cf [3]). This stimulated us to carry out a detailed study of the behavior of the thiosemicarbazones under electron impact.

Analysis of the mass spectra (Table 2) of the benzaldehyde derivatives Ia–h, j, k, and the acetophenone derivatives IIa, c, e, f showed that the stability of their molecular ions (Table 3) depended to a considerable extent on the presence of the substituent R^1, for example, the $M^{+\cdot}$ ions for compounds with $R^1 = CH_3$ are considerably more stable than compounds with an unsubstituted terminal nitrogen atom. On the other hand, the substituent X in the aromatic ring does not affect the value of W_M to any great extent. This allows the suggestion that the positive charge in the molecular ions of these compounds resides on the thioamide unit.

Analysis of the fragmentation ions in the mass spectra (Table 3) permits the conclusion that most of the molecular ions of the compounds studied exist in the gas phase in the linear thiosemicarbazone form. For this form fission of the

Academy of Military Medicine, St. Petersburg 194175; M. V. Lomonosov State University, Moscow 119899.
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TABLE 1. Characteristics of the Thiosemicarbazones of Substituted Benzaldehydes and Acetophenones

Compound	Mp, °C		H NMR spectrum in DMSO-d_6, δ, ppm (coupling constant Hz)			
			R	H_{arom}	R^1, X	NH
Ia	161...162	[10]	8,00 (1H,s)	7,36...7,90 (5H, d)		6,68 (1H, br); 7,50 (1H, br.); 10,35 (1H,s)
Ib	161...163	[11]	7,93 (1H, s)	7,32...7,77 (6H, d)	3,23 (3H, d, 4,5)	*; 10,38 (1H,s)
Ic	172...174	[10]	8,01 (1H,s)	6,98 (2H, d, 9,0); 7,72 (2H, d, 9,0)	3,79 (3H, s, OCH_3)	7,92 (1H, br); 8,13 (1H, br); 11,34 (1H,s)
Id	207...209	[12]	8,00 (1H,s)	6,95 (2H, d, 9,0); 7,72 (2H, d, 9,0)	3,02 (3H, d, 4,5)	8,41 (1H,q, 4,5); 11,34 (1H,s)
Ie	234...235	[10, 13]	8,06 (1H,s)	8,05 8,10; A_2B_2 (J_{AB} = 9,0)	—	8,20 (1H,br); 8,37 (1H, br.); 11,76 (1H, s)
If	252...254 dec.		8,09 (1H,s)	8,06 8,18; A_2B_2 (J_{AB} = 9,0)	3,04 (3H, d, 4,0)	8,73 (1H, q, 4,0); 11,82 (1H,s)
Ig	202...203 dec.	[10]	7,95 (1H,s)	6,61 (2H, d, 8,0); 7,54 (2H, d, 8,0)	2,84 (6H, s, dimethylamino group)	7,72 (1H,br); 8,00 (1H, br); 11,18 (1H,s)
Ih	223...225 dec.	[10, 14]	7,97 (1H,s)	6,77 (2H, d, 8,0); 7,59 (2H, d, 8,0)	9,86 (1H,s, OH)	7,80 (1H, br); 8,00 (1H, br); 11,22 (1H, s)
Ii	239...241 dec.	[10]	8,52 (1H,s)	6,88...7,00 (2H, m); 7,10...7,34 (1H, m); 7,90 (1H,d, 7,0)	9,98 (1H,s, OH)	7,90 (1H, br); 8,16 (1H, br); 11,50 (1H,s)
Ij	199...201 dec.		8,42 (1H,s)**	7,60...7,97 (3H, m)	—	7,14 (1H, br); 8,56 (1H, br); 11,98 (1H,s)
			6,88 (1H,d) 4,0)***	7,60...7,97 (3H, m)	—	5,47 (1H, d, 9,0); 5,48 (1H, d.d, 4,0, 9,0); 11,98 (1H,s)
Ik	231...233 dec.		8,44 (1H,s)	7,14 (1H, d 9,0); 8,14 (1H, d, 3,0, 9,0); 8,87 (1H, d, 3,0)	—	8,27 (2H, br.); 11,58 (1H, s)
IIa	120...122	[10]	2,27 (3H,s)	7,20...7,53 (3H,m); 7,70...8,10 (3H,m)	—	8,20 (1H, br)*; 10,20 (1H,s)
IIb	249...250 dec.	[10]	2,34 (3H,s)	8,17 (4H,s)	—	8,46 (2H, br); 10,52 (1H, s)
IIc	201...202	[10]	2,28 (3H,s)	7,50 (2H, d, 9,0); 7,85 (2H, d, 9,0)	—	7,96 (1H, br); 8,28 (1H, br); 10,32 (1H,s)
IId	186...188	[10]	2,20 (3H,	6,64 (2H, d, 8,5); 7,63 (2H, d, 8,5)	5,28 (2H, br, NH_2)	7,76 (1H, br); 8,12 (1H, br); 9,96 (1H, s)
IIe	232...233 dec.	[10]	2,30 (3H,s)	7,59 (1H, t, 8,0); 8,09 (1H, d. d, 8,0, 3,5); 8,31 (1H, d. d, 8,0, 3,5); 8,48 (1H, t, 3,5)	—	8,16 (1H, br); 8,38 (1H, br); 10,42 (1H, s)
IIf	234...235 dec.		2,28 (3H,s)	7,28 (1H, d, 9,0); 8,10 (1H, d.d, 9,0, 3,0); 8,46 (1H, d.d, 3,0)	3,94 (3H,s, OCH_3)	8,10 (1H, br); 8,30 (1H, br); 10,23 (1H,s)

*Signal hidden by protons of the aromatic ring.

**Linear form, 60%.

*** Cyclic form.

TABLE 2. Mass Spectra* of Compounds Ia–h,j,k, IIa,c,e,f

Compound	m/z (I_{rel}, %)
Ia	179 (12) M, 145 (61), 105 (38), 104 (77), 103 (66), 90 (22), 78 (24), 77 (100), 76 (32), 51 (58), 50 (23)
Ib	193 (100) M, 120 (18), 119 (33), 106 (11), 104 (19), 93 (12), 90 (40), 77 (25), 74 (40), 57 (71), 51 (15)
Ic	209 (14) M, 150 (100), 135 (50), 134 (52), 133 (66), 108 (47), 90 (32), 77 (43), 64 (29), 63 (28), 51 (29)
Id	223 (96) M, 135 (52), 134 (86), 120 (42), 92 (34), 91 (45), 90 (69), 77 (59), 74 (79), 57 (100), 51 (42)
Ie	224 (44) M, 103 (48), 102 (40), 77 (40), 76 (100), 75 (44), 65 (55), 63 (41), 60 (52), 51 (47), 50 (57)
If	238 (86) M, 165 (12), 118 (10), 90 (28), 78 (38), 77 (13), 76 (14), 74 (75), 65 (11), 57 (100), 50 (12)
Ig	222 (31) M, 163 (82), 162 (34), 148 (79), 147 (94), 146 (92), 145 (100), 121 (37), 120 (42), 119 (31), 77 (40)
Ih	195 (18) M, 161 (41), 160 (42), 120 (59), 119 (100), 93 (23), 91 (85), 77 (22), 55 (52), 64 (29), 63 (27)
Ii	258** (27) M, 152** (52), 139** (27), 90 (76), 89 (28), 76 (80), 75 (100), 63 (61), 60 (88), 51 (24), 50 (28)
Ij	240 (85) M, 164 (56), 134 (52), 119 (56), 90 (52), 76 (80), 65 (56), 63 (100), 60 (83), 59 (54), 51 (60)
IIa	193 (23) M, 178 (22), 159 (17), 133 (14), 119 (40), 118 (31), 104 (75), 103 (23), 78 (20), 77 (100), 51 (42)
IIb	271** (37) M, 197** (62), 183** (63), 155** (91), 102 (75), 77 (78), 76 (98), 75 (100), 60 (63), 51 (63), 50 (83)
IIe	238 (24) M, 163 (33), 149 (31), 132 (30), 118 (29), 117 (87), 103 (93), 77 (48), 76 (100), 75 (33), 50 (44)
IIf	268 (12) M, 194 (76), 180 (66), 179 (100), 118 (70), 104 (72), 103 (75), 77 (72), 76 (81), 63 (67), 60 (92)

*The molecular and the 10 most intense ions are cited.

**Ions containing the lighter halogen isotope.

TABLE 3. Intensities of The Peaks of the Characteristic Ions in the Mass Spectra of Compounds Ia–h,j,l and IIa,c,e,f (% Σ_{50})

Compound	M	Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	$Z = \frac{I_{\Phi_2} + I_{\Phi_4}}{I_M}$
Ia	2,0	0,9	1,3	1,0	9,2	0,5	12,0	5,3
Ib	21,7	7,4	6,1	1,9	3,5	1,9	4,6	0,4
Ic	1,6	1,3	1,3	1,0	5,1	0,7	1,8	4,0
Id	8,0	5,4	2,3	0,9	5,9	0,5	1,0	1,0
Ie	3,5	3,8	0,3	3,3	1,6	3,0	0,2	0,6
If	15,7	11,8	0,5	1,6	0,6	1,1	—	0,1
Ig	2,5	1,2	2,3	1,0	6,2	2,0	2,8	3,4
Ih	2,3	1,0	0,8	0,8	5,8	0,5	2,4	2,9
Ij	2,5	5,3	—	6,0	1,2	1,5	0,1	0,5
Ik	4,8	3,7	0,3	0,8	1,5	0,8	0,1	0,4
IIa	4,2	2,2	2,2	0,9	5,0	0,8	15,8	1,7
IIc	3,5	2,6	1,6	4,1	4,7	0,7	7,4	1,7
IIe	2,5	2,1	0,4	3,0	3,0	1,3	0,1	1,4
IIf	0,6	3,7	0,1	1,2	0,9	0,4	0,1	1,7

=N–/–NH– and –NH–/–CS– bonds to give ions Φ_1–Φ_4 is characteristic (scheme 1). It is seen from Table 3 that the total intensity of these four ions alone amounts to 5.9 to 18.9% of the total ion current. However a peak for the ion Φ_5 is observed in the mass spectra (see scheme 1). This ion arises by elimination of the aryl residue Φ_6 from the sp^3 hybridised carbon of the cyclic tautomer.

TABLE 4. PMR Spectra of Salts I and II in CF_3COOD, ppm (coupling constant Hz)

Compound	Form A			Form B			Other signals
	R, c		R^1, X	R, c		R_1, X	
Ia	7,85 (1H)	7,20...7,45 (5H, m)		6,25 (1H)	7,20...7,45 (5H, m)		65
Ib	7,85 (1H)	7,20...7,50 (5H, m)	2,85 (3H, br., NCH_3)	6,16 (1H)	7,20...7,50 (5H, m)	2,45 (3H, br, NCH_3)	25
				6,82 (1H)	7,20...7,50 (5H, m)	2,73 (3H, br., NCH_3)	50
Ic	7,15 (1H)	6,75 (2H, d, 8,5); 7,85 (2H, d, 8,5)	3,58 (3H, s, OCH_3)	6,72 (1H)	6,72 (2H, d, 8,5); 7,15 (2H, d, 8,5)	3,59 (3H, s, OCH_3)	55
Id	7,14 (1H)	6,75 (2H, d, 9,0); 7,87 (2H, d, 9,0)	2,95 (3H, br., NCH_3); 3,58 (3H, s, OCH_3)	6,75 (1H)	6,74 (2H, d, 9,0); 7,15 (2H, d, 9,0)	2,95 (3H, br., NCH_3); 3,59 (3H, s, OCH_3)	45
				6,97 (1H)	6,71 (2H, d, 9,0); 7,05 (2H, d, 9,0)	2,88 (3H, br, NCH_3); 3,59 (3H, s, OCH_3)	10
Ie	7,73 (1H)	7,70 (2H, d, 8,5); 8,13 (2H, d, 8,5)	—	6,47 (1H)	7,50 (2H, d 8,5); 8,15 (2H, d, 8,5)	—	45
If	*	*	*	6,27 (1H)	7,45 (2H, d, 8,5); 7,93 (2H, d, 8,5)	2,75 (3H, br, NCH_3)	40
				6,32 (1H)	7,46 (2H, d, 8,5); 7,94 (2H, d, 8,5)	2,80 (3H, br, NCH_3)	50
Ig	7,98 (1H)	7,33 (2H, d 8,0); 7,70 (2H, d, 8,0)	3,05 (6H, s, dimethylamino group)	6,35 (1H)	7,30 7,40; A_2B_2 (J_{AB} = 8,0)	3,05 (6H, dimethylamino group)	65
Ih	7,15 (1H)	6,75 (2H, d, 8,5); 7,90 (2H, d, 8,5)	—	6,40 (1H)	6,70 (2H, d, 8,5); 7,25 (2H, d, 8,5)	—	50
Ii	*	6,65...7,25 (4H, m)	—	6,75 (1H)	6,65...7,25 (4H, m)	—	50
Ij	8,25 (1H)	7,15...7,65 (3H, m)	—	—	—	—	0
Ik	*	6,74...8,09 (3H, s)	—	6,50 (1H)	6,74...8,09 (3H, m)	—	30
IIa	1,97 (3H)	6,90...7,35 (5H, m)	—	1,65 (3H)	6,90...7,35 (5H, m)	—	73
IIb	2,17 (3H)	7,62 (2H, d, 8,5); 7,92 (2H, d, 8,5)	—	1,81 (3H)	7,50 (2H, , 8,5); 7,90 (2H, d, 8,5)	—	75
IIc	2,01 (3H)	7,10 (4H, br.s)	—	1,67 (3H)	7,10 (4H, br.s)	—	70
IId	2,10 (3H)	7,20 (2H, d, 8,0); 7,60 (2H, d, 8,0)	—	1,85 (3H)	7,20 (2H, d, 8,0); 7,60 (2H, d, 8,0)	—	75
IIe	2,16 (3H)	7,20...8,30 (4H, m)	—	1,76 (3H)	7,20...8,30 (4H, m)	—	75
IIf	2,10 (3H)	6,90 (1H, d, 8,5); 7,50...8,00 (2H, m)	3,64 (3H, s, OCH_3)	1,79 (3H)	6,90 (1H, d, 8,5); 7,50...8,0 (2H, m)	3,64 (3H, s, OCH_3)	55

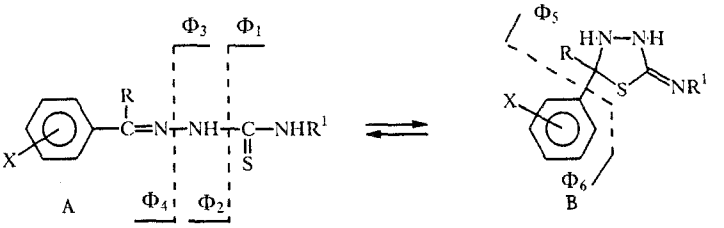
*Signal basically formed, correlation which estimates approximately from ^{13}C NMR spectra.

**At −15°C.

TABLE 5. ^{15}N NMR Spectra of Salts I and II in CF_3COOH, ppm (NH_3 scale)

Compound	Form A			Form B		Other signals
	C=N	C=NH$^+$	N-4	N-4	N-3	
If	309,7	164,5	110,1	136,4; 138,1	96,0; 96,4	370,9; nitro group
Ig	307,9	167,0	106,3	143,8	91,2	50,7 и 51,1; dimethylamino group
Ik	294,4	165,7	106,6	148,8	91,4	371,3; nitro group
IIb	302,2	161,5	108,0	174,4	93,8	371,1; nitro group
IIc	294,8	161,1	106,0	150,0	95,0	—

Scheme 1



The qualitative correlation between the amount of the linear form in the gas phase, the electronic properties of the substituent X and the presence or absence of the substituent R^1 should be especially noted. This is seen from the absolute value of the parameter Z (see Table 3), the ratio of the sum of the intensities of ions Φ_2 and Φ_4 to the intensity of the molecular ion. A large value of Z (> 1) characterizes a relatively high concentration of the linear form. In fact Z > 1 for X = H, OCH_3, $N(CH_3)_2$, and OH, whereas with an electron withdrawing substituent (X = NO_2, Hal) and R^1 = CH_3, Z < 1. Note that compound If contains a considerable amount of the cyclic form in both DMSO–d_6 solution and the gas phase.

When thiosemicarbazones I and II are dissolved in trifluoroacetic acid a complex spectrum is observed at first (an abundance of overlapping, broadened lines) which changes with time and becomes uninterpretable. After several days the final change occurs and it becomes possible to draw conclusions about the establishment of the ring–chain equilibrium A ⇄ B. We successfully used solutions in CF_3COOD to separate the NH signals of the two forms A ⇄ B with a sufficiently complex configuration and overlapping with the rest of the signals.

The signals of the azomethine proton in the 7.14–8.25 ppm range for compounds I and the weak field methyl signal at 1.97–2.17 ppm for compounds II are indicators of the linear tautomer A in the ^1H NMR spectrum (Table 1), together with the signal for the carbon atom of the C=N bond at 141.1–162.8 ppm in the carbon spectrum (Table 4), and the signal of the nitrogen atom of the same bond in the range 294.8–309.7 ppm in the ^{15}N NMR spectrum (Table 5).

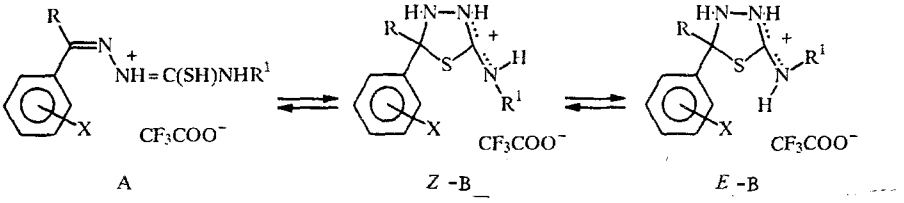
The cyclic form B may be detected in the ^1H NMR spectrum of compounds I by the weak field methyl signal at 6.16–6.97 ppm and of compounds II by the methyl group at 1.65–1,85 ppm. In the carbon spectra of tautomers B the $C_{(2)}$ signal at 74.0–82.7 ppm is indicative.

A characteristic spectroscopic phenomenon of the equilibrium solutions is the broadening of the signals for atoms and groups in the cyclic tautomer which are directly involved in the A ⇄ B equilibrium, particularly atom $C_{(2)}$ in the ^{13}C NMR spectra. As a result it is not observed at all in some cases (Table 6). Consequently it is necessary to observe the signals of the exocyclic nitrogen atom of this form which occurs in the 128–135 ppm range. This signal in the nitrogen spectrum of the 2,2–dimethyl–2,3–dihydro–5–amino–1,3,4–thiadiazolium cation occurs at 129.2 ppm but is much broadened [3]. The same situation occurs with the methyl group signals for the acetophenone thiosemicarbazones IIa,c,f. However satisfactory ^1H NMR spectra were obtained at low temperature (–15 to –30°C). It is characteristic that changing the temperature from –30 to 80°C can cause coalescence of the methyl group signals for tautomers A and B of all salts II, but there is no strict connection between the coalescence temperature and the nature of the substituent in the aromatic ring.

The structure of the linear cation A deserves separate discussion. The question of the center of protonation of the thiosemicarbazones has already been settled [4–6], however sceptics have reached the opposite conclusion, particularly since the possibility that the cyclic tautomer exists was not taken into account. The lack of major changes in the nature and position

of the azomethine proton signals in the ^1H NMR spectra and of the C=N carbon atom in the carbon spectra on going from the free bases to the salts (see data in Tables 1 and 4 and in the experimental part of Table 6) on the one hand and the strong field shift of the thioamide carbon atom under the same conditions on the other hand indicates the formation of the azinethiol ion A. In addition, the positions of the carbon signals in the C=N and C=NH^+ bonds (Table 6) agree with values for the same signals in the spectrum of benzaldehyde S−methylisothiosemicarbazone hydrogen iodide (151.9 and 166.1 ppm [7]) which can be considered a model for the azinethiol cation A. The ^{15}N NMR spectra do not contradict this conclusion.

Scheme 2



A Z-B E-B

I R = H; a X = H, R^1 = H; b X = H, R^1 = Me; c X = 4-OMe, R^1 = H; d X = 4-OMe, R^1 = Me; e X = = 4-NO_2, R^1 = H; f X = 4-NO_2, R^1 = Me; g X = 4-NMe_2, R^1 = H; h X = 4-OH, R^1 = H; i X = 2-OH, R^1 = Me; j X = 2-Cl-6-NO_2, R^1 = H; k X = 2-OH-5-NO_2, R^1 = H

II R = Me, R^1 = H; a X = H; b X = 4-NO_2; c X = 4-Br; d X = 4-NH_2; e X = 3-NO_2; f X = 3-NO_2-4-OMe

A distinguishing characteristic of the cyclic tautomeric cations B of the N−methyl−substituted thiosemicarbazones Ib,d,f is the existence of two rotamers as a result of hindered rotation around the partial double bond $C_{(5)}-N_{exo}$ which appears as a doubling of all the signals in the carbon spectrum, and in the ^{15}N NMR spectrum for salt If. Confirmation of the existence of the *E,Z* isomers is the reversible coalescence of the methine signals (and only those signals) in the ^1H NMR spectrum of compound If on heating to 70°C. The absence of suitable criteria or close analogies makes it impossible to assign the signals to one or other of the stereoisomers.

The ratio of the tautomeric forms A ⇄ B is not very sensitive to changes in X. The fraction of the cyclic form B increases somewhat from derivatives of benzaldehyde I to the acetophenone thiosemicarbazones II. The exception is 2−chloro−6−nitrobenzaldehyde thiosemicarbazone, Ij, the cation of which is exclusively in the linear form A. This anomaly, and the behavior of the compound in neutral media, is apparently linked with steric factors.

So we have observed ring−chain tautomerism in protonated thiosemicarbazones for the first time.

Attention is now turned to the specific behavior of thiosemicarbazones in comparison with some hydrazones at the C=S bond. While thiocarbohydrazones tend to exist in the 1,2,4,5−hexahydrotetrazine form [8] and thiobenzohydrazones are inclined to cyclize into 1,3,4−thiadiazolines [9], thiosemicarbazones have a tendency to prefer the linear form which probably results from an extension of π,p,π conjugation in that form.

EXPERIMENTAL

^1H (100 MHz) and ^{13}C (20.41 MHz) NMR spectra of 5−15% solutions with HMDS as internal standard were recorded on a Tesla BS−497 instrument. ^{15}N (30.4 MHz) NMR spectra were obtained with a Varian VXR−300 machine. Chemical shifts were measured relative to nitromethane as internal standard and converted to the NH_3 scale. To avoid hydrolysis all spectroscopic measurements should be carried out so as to avoid contact with aerial moisture and with completely anhydrous solvents.

Mass spectra of compounds Ia, c-e, g, j, k and IIa, c, e, f were measured with a Kratos MS 25RFA machine and of compounds Ia, b, d, f and IIa with an MX 1321A instrument with direct inlet, an ionizing energy of 70 eV, and ionizing chamber temperatures of 250 and 200°C respectively. We noted no major differences in the mass spectra of the same compound obtained on the two different machines.

Thiosemicarbazones I and II were prepared by a standard method. Methanolic solutions of equivalent amounts of thiosemicarbazide and the carbonyl compound were mixed and 2 or 3 drops of CF_3COOH added. For the benzaldehydes the mixture was kept over might, while for the acetophenones it was boiled for 3 h. The residue was filtered off and recrystallized.

TABLE 6. ^{13}C NMR Spectra of Salts I and II in CF_3COOH, ppm

Compound	Form A				Form B			
	C=N	C=NH$^+$	D_{arom}	other signals	C_2	C=NH$^+$	Darom	other signals
Ia	148,5	169,5	128,8; 129,3; 131,1; 135,2	–	82,7	171,8	127,5; 129,6; 131,5; 131,3	–
Ib	147,3	168,0	126,3...133,0 (3 singl.); 135,6	30,8 (CH_3N)	78,4	174,1	126,3...133,0 (3 singl.); 133,6	31,0 (CH_3N)
					81,9	177,8	126,3...133,0 (3 singl.); 134,5	34,7 (CH_3N)
Ic	147,9	168,3	115,8; 126,0; 130,8; 166,7	55,3 (CH_3O)	82,0	172,1	115,3; 120,0; 137,5; 161,8	55,4 (CH_3O)
Id	146,9	166,3	115,8; 126,0; 130,1; 167,3	31,5 (CH_3N); 55,4 (CH_3O)	81,4	173,5	115,3; 130,1; 137,0; 161,5	31,5 (CH_3N); 55,4 (CH_3O)
					82,5	179,0	115,1; 120,0; 137,0; 160,8	33,7 (CH_3N); 55,4 (CH_3O)
Ie	148,8	166,2	124,6; 128,3; 138,1; 150,2	–		175,2	124,2; 128,3; 142,3; 150,2	–
If	149,5	168,3	125,2; 129,1; 139,5; 150,4	32,8 (CH_3N)	74,2	174,6	125,2; 129,1; 143,8; 150,3	32,8 (CH_3N)
					77,2	178,3	125,2; 129,1; 144,1; 150,3	36,5 (CH_3N)
Ig	151,9	168,1	121,9; 130,0; 139,6; 145,5	48,5 (CH_3O)	76,6	176,1	121,5; 130,8; 136,0; 144,1	48,5 (CH_3O)
Ih	148,1	163,1	117,1; 123,5; 137,7; 157,6	–	82,2	168,9	117,5; 126,5; 130,5; 161,6	–
Ii	146,3	169,7	117,8; 122,0; 133,5; 134,6; 139,2; 158,8	–	77,2	172,1	116,3; 123,2; 128,4; 133,5; 134,6; 154,2	–
Ij	144,6	172,5	123,5; 125,1; 132,8; 135,1; 136,8; 150,1	–	–	–	–	–
Ik	141,1	170,8	121,0...133,0 (4 singl.); 142,2; 164,6	–	77,6	174,4	121,0...133,0 (4 singl.); 141,6; 163,1	–
IIb	158,9	167,9	125,1; 129,5; 143,6; 149,5	15,2 (CH_3)	74,0**	176,9	125,3; 128,5; 148,2; 150,3	23,9 (CH_3)
IIc	160,8	165,4	127,3; 130,6; 132,1; 134,3	13,8 (CH_3)	*	175,4	128,0; 132,1; 132,5; 134,5	22,0 (CH_3)
IId	162,8	166,6	123,4; 128,0; 131,4; 138,2	14,2 (CH_3)	79,0**	175,1	123,4; 128,0; 130,8; 141,8	22,5 (CH_3)
IIe	161,5	166,7	122,0; 125,9; 130,4; 133,5; 137,6; 148,5	13,9 (CH_3)	*	175,3	121,2; 125,1; 130,4; 132,7; 141,5; 148,5	21,9 (CH_3)
IIf	157,3	165,8	114,2; 123,9; 127,0; 133,2; 138,6; 157,8	13,3 (CH_3O); 56,2 (CH_3O)	*	174,5	114,2; 123,7; 127,0; 133,5; 138,6; 157,8	20,7 (CH_3); 56,2 (CH_3O)

*Signal not observed.

**Low intensity signal.

Product purity was monitored by TLC. Most of the thiosemicarbazones had been prepared previously. The elemental analyses for the new compounds If,j,k and IIf agreed with calculated values.

^{13}C NMR spectra:

Benzaldehyde Thiosemicarbazone Ia ($CDCl_3$): 178.5 (C=S), 144.1 (C=N), 133.0, 130.7, 128.8, 127.5 ppm (C_{arom}).

4-Methoxybenzaldeyde Thiosemicarbazone Ic (DMSO-d_6): 177.9 (C=S), 142.5 (C=N), 160.7, 128.9, 126.7, 114.2 (C_{arom}), 55.3 ppm (OCH_3).

4-Methoxybenzaldeyde 4-methylthiosemicarbazone Id (DMSO-d_6): 177.8 (C=S), 141.8 (C=N), 160.7, 128.8, 126.9, 114.2 (C_{arom}), 55.3 (OCH_3), 30.8 ppm (NCH_3).

2-Chloro-6-nitrobenzaldehyde Thiosemicarbazone Ij (DMSO-D_6): 179.0 (C=S), 149.3 (C=N) -- linear form; 182.0 (C=S), 81.9 ($C_{(5)}$) — cyclic form. The aromatic carbon atoms of the two forms gave 12 signals in the 122-155 ppm range. ^{15}N NMR spectrum (DMSO-d_6): 328.8 (C=N), 174.1 (NH), 105.3 (NH_2) — linear form; 132.2 ($N_{(1)}$), 104.0 ($N_{(4)}$), 96.3 ppm $N_{(2)}$) — cyclic form. The nitro group of both forms gave a signal at 373.9 ppm.

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