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RING-CHAIN TAUTOMERISM OF THIOCARBOHYDRAZONES

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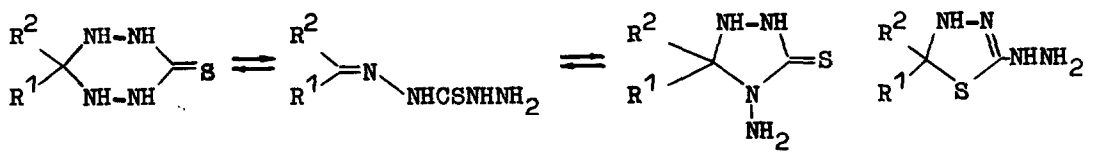
Abstract: Thiocarbohydrazones undergo intramolecular ring-closure in solutions into both 1,2,4,5-hexahydrotetrazine-3-thiones and 4-amino-1,2,4-triazolidine-3-thiones.

According to PMR spectroscopic data, thiocarbohydrazones A in solution have a tendency to reversible cyclization into derivatives of 1,2,4,5-hexahydrotetrazine-3-thione B[1,2]. However, from the given spectra it is impossible to reach the conclusion about the formation of this particular ring rather than of derivatives of 4-amino-1,2,4-triazolidine-3-thione C or 2-hydrazino-4,5-dihydro-1,3,4-thiadiazole D. The existence of any of the four forms (A, B, C, D) should really be taken into account, because thioacylhydrazones cyclize to 4,5-dihydro-1,3,4-thiadiazoles[3], thiosemicarbazones cyclize to 4,5-dihydro-1,3,4-thiadiazoles and 1,2,4-triazoline-3-thiones[4,5,6], and 2-aminoacylhydrazones to corresponding derivatives of 1,2,4-triazine[7]. Accordingly we have examined the structure of thiocarbonydrazones 1-4 [8] using the methods of ^{1}H, ^{13}C and ^{15}N NMR spectroscopy.



B A C D

1: R^1 = H, R^2 = 4-$CH_3OC_6H_4$; 2: R^1 = R^2 = CH_3;
3: R^1 = CH_3, R^2 = C_6H_5; 4: R^1 = CH_3, R^2 = $CH_2C_6H_5$

The NMR ^{15}N spectrum in DMSO of 1 (table 1) show four signals of the A form (C=N bond, 2 thioamide and amine atoms). With substance 3 there ap-

Table 1. NMR ^{15}N (50.63 MHz) spectra of substances 1-4 in DMSO-d_6, chemical shift, p.p.m. (J, Hz) on the NH_3-scale.

Substance, form	C=N, s	$N_{thioamide}$	N_{amine}
1, A	310.3	131.3 d (103), 165.5 d (102)	70.5 [a]
2, A	319.3	- [b]	70.6 [a]
2, B	-	130.0 d (107)	107.9 d (75)
2, C	-	134.2 d (102) 155.0 s	64.4 [a], 100.4 d (75)
3, A	308.1	134.1 d (102), 161.4 d (98)	72.0 [a]
3, B	-	131.1 d (107)	102.0 d (77)
4, A	307.7	132.9 d (102), 159.3 d (98)	70.7 [a]
4, B	-	129.7 d (107)	104.9 d (74)
4, C	-	132.4 [a], 154.3 s	64.7 [a], 96.6 [a]

[a] J_{NH} does not appear because of the exchange processes. [b] Not found because of the small content of the form.

pear two more doublet signals of the amine and thioamide atoms of nitrogen which indicate the appearance of the B tautomer in the solution. In the thiocarbohydrazone 4 spectrum besides the 6 signals of the A and B forms there are 4 more signals of the two thioamide and two amine nitrogen atoms of the C tautomer. C form signals of the same type are present in the spectrum of substance 2. The thiadiazoline isomer D should be excluded because of the absence of the downfield signal of the nitrogen atom of the C=N bond for this structure. A small content of the A isomer in substancs 2 doesn't allow to find out, for sure, all the signals of this form in nitrogen spectra, however, its existence is proved by the data of NMR ^1H and ^{13}C spectra (table 2). The position and splitting of the signals in NMR ^1H and ^{13}C spectra of the other substances at equilibrium, set up over several days at 26°C, completely correspond to the data from the nitrogen spectra.

This A $\rightleftharpoons$ B $\rightleftharpoons$ C equilibrium is the first example of the tautomerism of nitrogen heterocycles involving 5- and 6-membered rings at the same time, similar to the carbohydrates forming pyranoses and furanoses. Ring-ring equili-

Table 2. NMR ^{1}H (100 MHz) and ^{13}C (20.41 MHz) spectra of thiocarbohydrazones 1-4 in DMSO-d_6.

Substance	Form, %	NMR ^{1}H spectrum			NMR ^{13}C spectrum		
		R^1, s	R^2	NH	C=S	C=N or $C^5(C^6)$	Other signals
1	A, 100	8.01 (1H, CH)	3.90 s (3H, OCH_3), 7.05 and 7.82 (4H, C_6H_4)	4.80 s (2H), 9.65 s (1H), 11.20 s (1H)	176.3	142.5	55.3 (CH_3), 114.1, 126.8, 128.9, 160.8 ($C_{arom.}$)
2	A, 5	1.91 (3H, CH_3)	1.96 s (3H, CH_3)	4.73 s (2H), 9.90 s (1H), a	177.7	151.6	17.4 (CH_3), 24.9 (CH_3)
	B, 70	1.11 s (6H, CH_3)		4.53 s (2H), 9.17 s (2H)	172.0	63.1	22.6 (CH_3)
	C, 25	1.18 s (6H, CH_3)		4.59 s (2H), 5.47 s (1H), 9.66 s (1H)	182.1	81.8	21.8 (CH_3)
3	A, 65	2.32 (3H, CH_3)	7.2-7.3, 7.8-8.0 m (5H, C_6H_5)	4.63 s (2H), 9.25 s (1H), 10.21 s (1H)	176.4	148.0	13.8 (CH_3), 126.5, 128.1, 129.0, 137.4 ($C_{arom.}$)
	B, 35	1.30 (3H, CH_3)	7.2-7.5 m m (5H, C_6H_5)	4.57 s (2H), 9.16 s (2H)	172.5	68.1	26.4 (CH_3), 126.5, 127.2, 128.0, 141.9 ($C_{arom.}$)
4	A, 17	1.78 (3H, CH_3)	3.53 s (2H, CH_2), 7.26 s (5H, C_6H_5)	a, 9.55 s (1H), 9.98 s (1H)	177.2	152.6	15.4 (CH_3), 44.2 (CH_2)
	B, 70	0.84 (3H, CH_3)	2.62 s (2H, CH_2), 7.26 s (5H, C_6H_5)	4.85 s (2H), 9.25 s (2H)	172.4	65.8	19.7 (CH_3), 40.1 (CH_2)
	C, 13	1.06 (3H, CH_3)	2.74 s (2H, CH_2), 7.26 s (5H, C_6H_5)	a	182.3	84.0	19.0 (CH_3), 38.7 (CH_2)

[a] Signals are not found.

bria of the nitrogen heterocycles were observed only for 5-member rings and included tautomeric pairs of pyrazoline - thiadiazoline, pyrazoline - isoxazoline or thiadiazoline - isoxazoline[3,9,10].

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8. The compounds 1-3 were described elsewhere[1,2]. Thiocarbohydrazone 4 was obtained for the first time by us and gave satisfactory elemental analyses. Mp 180-181 °C (CH_3CN), yield 80%.

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