

The electronic spectra of the crystals were photographed with an ISP-28 spectrograph in polarized light at 4.2°K by the method described in [3].

The lattice parameters and the space group of the IIIa crystal were determined from the rotational x-ray diffraction patterns and reciprocal lattice patterns and were refined with a DARM-2.0 diffractometer. The set of integral intensities was generated with a DARM-2.0 diffractometer. A total of 1240 independent reflections was measured. No correction for absorption was introduced. The structure was decoded by direct methods [12]. The bond lengths and valence angles are presented for R-0.114.

LITERATURE CITED

1. T. É. Bezmenova, S. M. Lukashov, V. P. Tantsyura, T. S. Lutsii, A. F. Rekasheva, and T. D. Zaika, *Khim. Geterotsikl. Soedin.*, No. 8, 1072 (1975).
2. C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).
3. V. L. Broude, G. V. Klimusheva, A. L. Liberman, M. I. Onoprienko, A. F. Prikhod'ko, and A. I. Shatenstein, *Absorption Spectra of Molecular Crystals* [in Russian], Vol. 1, Naukova Dumka, Kiev (1965), p. 11.
4. J. Petruska, *J. Chem. Phys.*, **34**, 1111 (1961).
5. E. N. Prilezhaeva, L. V. Tsymbal, O. N. Domanina, T. N. Shkurina, and M. F. Shostakovskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 3, 724 (1960).
7. E. C. Muller and A. Schweig, *Tetrahedron*, **29**, 3973 (1973).
8. R. I. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).
9. Yu. A. Kolesnik and V. V. Kozlov, *Usp. Khim.*, **37**, 1192 (1968).
10. N. Kharasch (editor) [no title given], Vol. 2, Pergamon Press, New York (1966), p. 1.
11. Yu. N. Usenko, S. M. Lukashov, and T. É. Bezmenova, *Khim. Geterotsikl. Soedin.*, No. 11, 1489 (1972).
12. V. N. Andrianov, Z. Sh. Safina, and B. L. Tarnopol'skaya, *Rentgen-70. Automated System of Programs for X-Ray Diffraction Calculations* [in Russian], Izd. Akad. Nauk SSSR, Chernogolovka (1970), p. 3.

SOME TRANSFORMATIONS OF

α, ω -BIS(1,3-THIAZAN-2-THION-4-ON-3-YL)ALKANES

B. S. Zimenkovskii and N. M. Turkevich

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The reaction of α, ω -bis(1,3-thiazan-2-thion-4-on-3-yl)alkanes with hydrazine gives the corresponding α, ω -di(4-thiosemicarbazido)alkanes, which are readily acylated. Subsequent dehydration of the acylation products gives the corresponding 5,5'-dialkyl- α, ω -bis(2,3-dihydro-1,2,4-triazole-3-thion-4-yl)alkanes, which are converted to 5,5'-dialkyl- α, ω -bis(1,2,4-triazol-4-yl)alkanes by known methods. The UV and IR spectral data are presented.

Compounds having bactericidal, chemotherapeutic, and cytostatic activity have recently been observed among 1,2,4-triazole derivatives [1-3]. Some triazoles have found technical application [4, 5]. In view of the practical significance of this class of compounds, we set out to synthesize some bistriazolinethiones.

One of the well-known methods for the preparation of 3-mercapto-1,2,4-triazoles consists in acylation of thiosemicarbazide [6] and subsequent dehydration of the product. We carried out the hydrazinolysis in n-butyl alcohol or in an aqueous alkali solution of α, ω -bis(1,3-thiazan-2-thion-4-on-3-yl)alkanes (I) synthesized via a simplified method [7, 8] to give the corresponding α, ω -di(4-thiosemicarbazido)alkanes (II) (Table 1), which are the starting compounds for the synthesis of bistriazole-3-thiones. Similar compounds have been described in the literature, but they were obtained by a fundamentally different method and in lower yields [9].

Compounds II are relatively easily acylated by glacial acetic acid and benzoyl chloride in dry pyridine. In the case of the first reagent α, ω -bis(1-acyl-4-thiosemicarbazido)alkanes (IIIa) are formed smoothly. The use of acetic anhydride as the acylating agent leads to oils that are difficult to purify.

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TABLE 1. α,ω -Di(4-thiosemicarbazido)alkanes and Their Derivatives

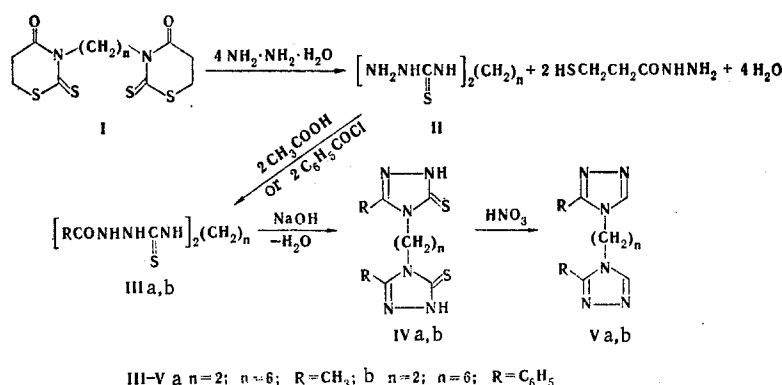
Compound	R	n	mp, °C	Found, %		Empirical formula	Calc., %		UV spec. in methanol		Yield, %
				N	S		N	S	λ_{max}, nm	$\lg \epsilon$	
II	—	2	221—222	40.2	30.8	$C_4H_{12}N_6S_2$	40.4	30.8	239	3.95	77
II	—	6	141—142	32.1	24.5	$C_8H_{20}N_6S_2$	31.8	24.2	238—239	4.34	54
III a	CH ₃	2	240 (dec.)	29.0	22.1	$C_8H_{16}N_6O_2S_2$	28.7	21.9	245	4.42	54
III b	C ₆ H ₅	2	184—186	19.7	15.5	$C_{18}H_{24}N_6O_2S_2$	20.2	15.4	245	4.47	61
III a	CH ₃	6	189—191	24.2	18.0	$C_{12}H_{24}N_6O_2S_2$	24.1	18.4	245	4.41	57
III b	C ₆ H ₅	6	130—132	18.1	13.3	$C_{22}H_{28}N_6O_2S_2$	17.8	13.6	246	4.42	49
IV a	CH ₃	2	320—321	32.6	25.3	$C_8H_{12}N_6S_2$	32.9	25.0	256	4.46	91
IV b	C ₆ H ₅	2	300 (dec.)	22.4	17.2	$C_{18}H_{16}N_6S_2$	22.1	16.8	257	4.35	28
IV a	CH ₃	6	212—213	26.6	20.4	$C_{12}H_{20}N_6S_2$	26.9	20.0	254	4.47	96
IV b	C ₆ H ₅	6	195—197	19.6	14.9	$C_{22}H_{24}N_6S_2$	19.2	14.7	257	4.44	75
V a	CH ₃	2	186—188	43.1	—	$C_8H_{12}N_6^*$	43.7	—	—	—	22
V b	CH ₃	6	117—120	33.5	—	$C_{12}H_{20}N_6^\dagger$	33.8	—	—	—	72

* Found: C 49.6; H 6.2%. Calculated: C 50.0; H 6.3%.

† Found: C 58.2; H 8.0%. Calculated: C 58.0; H 8.1%.

We obtained the corresponding 5,5'-disubstituted α,ω -bis(1,2,4-triazol-5-ine-3-thion-4-yl)alkanes (IV) by heating acyl derivatives III with aqueous alkali solution and subsequent neutralization with hydrochloric or acetic acid solutions.

5,5'-Disubstituted α,ω -bis(1,2,4-triazol-4-yl)alkanes (V) are formed by desulfuration of IV with a mixture of dilute nitric acid and sodium nitrite.



The UV spectra of methanol solutions of II-IV are characterized by one absorption maximum at 238-257 nm, which corresponds to the maxima of unsubstituted thiosemicarbazide (241 nm) and thiourea (239 nm).

A characteristic hypsochromic shift of the maximum, respectively, from 256 to 236-238 nm (i.e., a shift of 19 nm) and from 254 to 232-234 nm (i.e., a shift of 21 nm) is observed when IVa (R = CH₃) are dissolved in a 0.1 N NaOH solution; this is evidently associated with conversion of IV to the sodium thiolate form NH—

$C=S \xrightarrow{NaOH} N=C-S^-Na^+$ and with hindered electron transfer in the molecules, which requires a higher energy for ΔE of, respectively, 37.6560 and 41.840 kJ/mole (9 and 10 kcal/mole).

Solid IV exists in the thione form; this is confirmed by the IR spectra. Thus the spectra of IVa (R = CH₃) are characterized by strong and medium bands (successively for n = 2 and n = 6) at 1460 and 1456 (I NCS), 1352 and 1354 (II NCS), and 1045 and 1050 cm⁻¹ (III NCS). The presence of these bands is in good agreement with the data in [10] for a number of different thioamides. In addition, the spectra of IV do not contain deformation vibrations of a S—H bond at 2550-2600 cm⁻¹, and the presence in the spectra of both compounds of strong bands corresponding to N—H stretching vibrations at 3450 and 3334 cm⁻¹ confirms the presence of a hydrogen atom attached to the nitrogen atom rather than to the sulfur atom.

EXPERIMENTAL

The UV spectra of methanol solutions of the compounds were recorded with an SF-4A spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

α,ω -Di(4-thiosemicarbazido)alkanes (II). These compounds were obtained by reaction of 0.005 mole of I ($n = 2$) with 0.01 mole of a 48% solution of hydrazine hydrate in 250 ml of *n*-butyl alcohol by refluxing for 15-20 min. The reaction mixture was cooled, and the resulting precipitate was removed by filtration, washed with methanol, and dried. The product can be purified by chromatography on silica gel, but it is suitable for the subsequent syntheses without additional purification.

In the preparation of II ($n = 6$), I ($n = 6$) was treated with hydrazine hydrate in aqueous alkali solution, and the mixture was refluxed for 10 min, after which it was allowed to stand for 4-5 h until a precipitate formed. The precipitate was removed by filtration, washed with ether, and dried.

The synthesized II were obtained as white crystalline substances that were insoluble in most of the ordinary organic solvents even when the mixtures were heated.

α,ω -Bis(1-acyl-4-thiosemicarbazido)alkanes (IIIa). A 0.004-mole sample of II was refluxed in 15 ml of glacial acetic acid for 1-4 h, after which the mixture was cooled and allowed to stand for 24 h. The resulting precipitate was removed by filtration, washed with water, methanol, and ether, and dried to give white crystalline substances that were soluble in dilute alkali solutions and insoluble in most of the ordinary organic solvents even when the mixtures were heated.

α,ω -Bis(1-benzoyl-4-thiosemicarbazido)alkanes (IIIb). A 2.9-ml sample of benzoyl chloride was added dropwise with cooling (to 0°C) and continuous stirring in the course of 40 min to a solution of 0.01 mole of II in 6 ml of anhydrous pyridine, after which the mixture was stirred with cooling for 40 min and at 20°C for another 30 min. It was then allowed to stand for 12 h, after which it was stirred with 10 ml of water. The resulting oil was separated and dissolved in methanol. The colorless crystalline solid was removed by filtration, and the filtrate was treated with water to precipitate the reaction product as a colorless crystalline compound, which was removed by filtration, washed with ether, and dried. In the case of the preparation of III ($n = 6$) the methanol eluate was evaporated to dryness, and the residue was washed with ether. The synthesized compounds were soluble in DMF, acetone, and dioxane but insoluble in water and other organic solvents.

5,5'-Disubstituted α,ω -Bis(1,2,4-triazol-5-ine-3-thion-4-yl)alkanes (IV). A mixture of 0.01 mole of IIIa, 0.02 mole of NaOH, and 4 ml of water was refluxed for 1 h, and the mixture was cooled with ice and treated with 2 ml of concentrated HCl. After 2 h, the resulting colorless crystalline substance was removed by filtration, washed with water and ether, and dried.

In the preparation of IV from IIIb, the reaction mixture was filtered immediately at the end of the refluxing period. The filtrate was acidified with acetic acid to pH 4.5, and the resulting precipitate was removed by filtration, washed with water and ether, and dried to give white crystalline substances that were soluble in DMF but insoluble in most of the ordinary organic solvents and water.

5,5'-Dimethyl- α,ω -bis(1,2,4-triazol-4-yl)alkanes (V). A 0.005-mole sample of IVa ($R = CH_3$) and 0.1 ml of concentrated HNO_3 were added to a heated (to 45°C) mixture of 1.5 ml of concentrated HNO_3 , 0.01 g of sodium nitrite, and 3 ml of water, and mixture was stirred for 1 h, after which it was neutralized to pH 7.5-8.0 by the addition of 1.1 g of sodium carbonate and bicarbonate. The water was then removed by vacuum distillation, and the residue was extracted with four 15-ml portions of ethanol. The extract was evaporated to dryness, and the residue was extracted repeatedly with four 25-ml portions of methanol. The methanol extract was decolorized with activated charcoal and filtered, and 250 ml of benzene was added to the filtrate. After 24 h, the solution above the solid was decanted, and a new portion of benzene was added. Where necessary, the process was repeated until a crystalline substance was obtained; this substance was extracted with three 25-ml portions of ethyl acetate to obtain the product. The solvent was removed by vacuum distillation, and the residue was treated with 4 ml of ethanol. The ethanol mixture was filtered, and the filtrate was evaporated to dryness. The residue was washed with ether, and the purification process was repeated to give a colorless substance that was soluble in cold or hot water, methanol, and glacial acetic acid.

LITERATURE CITED

1. L. A. Vlasova, E. M. Shamaeva, G. B. Afanas'eva, and I. Ya. Postovskii, *Khim. Farm. Z.*, **8**, 25 (1971).
2. I. Mir, M. T. Siddiqui, and A. Comria, *Tetrahedron*, **26**, 5235 (1970).
3. H. L. Yale and J. J. Plata, *J. Med. Chem.*, **9**, 42 (1966).
4. C. Sueling, H. Logemann, and E. Roos, West German Patent No. 1494018 (1970); *Chem. Abstr.*, **74**, 13839 (1971).
5. I. Noboru, T. Senji, T. Hirokaro, and K. Norio, West German Patent No. 2040801 (1971); *Chem. Abstr.*, **74**, 149248 (1971).

6. R. Elderfield (editor), *Heterocyclic Compounds*, Vol. 7, Wiley (1965), p. 325.
7. N. M. Turkevich and B. S. Zimenkovskii, USSR Inventor's Certificate No. 180603 (1966); *Byul. Izobr.*, No. 8, 23 (1966).
8. B. S. Zimenkovskii, *Zh. Org. Khim. Collection: Problems in the Preparation of the Intermediates of the Organic Synthesis Industry* (1967), p. 24.
9. V. Ya. Kazakov and I. Ya. Postovskii, *Khim. Khim. Tekhnol.*, **4**, 238 (1961).
10. C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

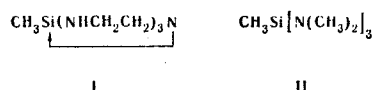
¹H, ¹³C, and ²⁹Si NMR SPECTRA OF 1-METHYLAZASILATRANE

S. N. Tandura, V. A. Pestunovich,
M. G. Voronkov, G. I. Zelchan,
I. I. Solomennikova, and É. Ya. Lukevits

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Considerable shielding of the ¹H and ²⁹Si nuclei due to transannular nitrogen-silicon coupling, which is expressed more clearly than in the case of silatranes, was established on the basis of ¹H, ¹³C, and ²⁹Si NMR data for the methylsilyl group in 1-methyl-2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0^{1,5}]undecane (1-methylazasilatrane) and a comparison of these data with the data for the methyl[tris(dimethylamino)]silane model. It is shown that the change in the hybridization of the silicon atom associated with the increase in its coordination number is not only reflected in the chemical shifts but also leads to an increase in ¹J_{CH} and ²J_{SiH}.

We have measured the chemical shifts of the ¹H, ¹³C, and ²⁹Si nuclei and the constants of spin-spin coupling between them for the methylsilyl group in the molecules of the recently synthesized 1-methyl-2,5,8,9-tetraaza-1-silatricyclo[3.3.3.0^{1,5}]undecane [1-methylazasilatrane (I)] [1] and the model compound methyl[tris(dimethylamino)]silane (II) (Table 1).



The existence of transannular nitrogen-silicon coupling in the I molecule ensures appreciably greater, as compared with II, shielding of the hydrogen and silicon-29 nuclei of the CH₃-Si fragment. The difference in the ²⁹Si chemical shifts in these compounds is also due to the paramagnetic contribution (+16 ppm) [2] of the three "additional" methyl groups attached to the nitrogen atom in model compound II. Thus the contribution of the N → Si coordinate bond to shielding of silicon-29 in 1-methylazasilatrane I is ~34 ppm. According to our data, the differences in the chemical shifts of silicon-29 between organylsilatranes RSi(OCH₂CH₂)₃N and the corresponding organyltriethoxysilanes RSi(OCH₂CH₃)₃ are 20-25 ppm. It may therefore be assumed that the transannular nitrogen-silicon coupling in the azasilatranes is expressed more clearly than in silatranes. The latter assumption is also in agreement with the results of a study of the dipole moments of these compounds [1].

The change in the hybridization of the silicon atom in the I molecule due to the increase in its coordination number leads to an appreciable decrease in its electronegativity. This is reflected not only in the ¹H and

TABLE 1. Parameters of the NMR Spectra of 1-Methylazasilatrane and Methyl[tris(dimethylamino)]silane

Compound	Chemical shifts, ppm			SSCC, Hz	
	δ(¹ H)	δ(¹³ C)	δ(²⁹ Si)	¹ J _{CH}	² J _{SiH}
I	-0.37	+2.46	-68.5	113.7	5.6
II	-0.01	-6.36	-16.3	117.2	6.3

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR, Riga 226006. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 8, pp. 1063-1064, August, 1977. Original article submitted November 11, 1976.