

SHORT
COMMUNICATIONSRing–Chain Tautomerism of the Condensation Product
of Acetone with 2-SulfanylbenzohydrazideA. Yu. Ershov^a, I. V. Lagoda^b, S. I. Yakimovich^c, V. V. Pakal'nis^c, and V. V. Shamanin^a^a Institute of High-Molecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31, St. Petersburg, 199004 Russia
e-mail: ershov@hq.macro.ru^b Research Test Center for Medicobiologic Protection, State Research Test Institute of Military Medicine,
Ministry of Defense of the Russian Federation, St. Petersburg, Russia^c St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia

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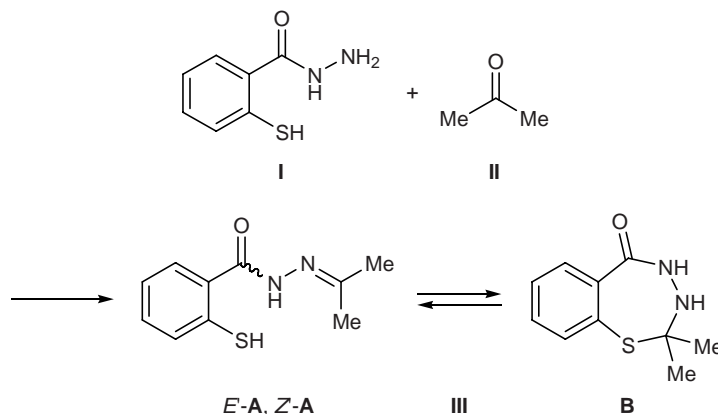
Condensation products of acetone with salicylic and anthranilic acid hydrazides are known to have linear hydrazone structure [1, 2]. By contrast, previously unknown condensation product **III** obtained by heating a mixture of 2-sulfanylbenzohydrazide (**I**) and acetone (**II**) in water for a short time at the boiling point was found to exist in DMSO-*d*₆ solution as a mixture of linear hydrazone **A** and cyclic 2,2-dimethyl-3,4-dihydro-1,3,4-benzothiadiazepin-5-one **B**, the latter appreciably prevailing.

The presence of thiadiazepine tautomer **B** followed from the ¹H NMR spectrum of compound **III**, which contained two doublets at δ 5.62 and 9.57 ppm from the NH protons. The methyl proton signal was displaced upfield (a singlet at δ 1.38 ppm) relative to the corresponding signal of linear hydrazone **A** (δ 2.00 ppm), and a signal at δ_C 77.6 ppm from *sp*³-hybridized carbon atom (C²) was observed in the ¹³C

NMR spectrum. Linear tautomer **A** is characterized by a downfield signal at δ 11.00 ppm, belonging to the NH proton. Apart from ring–chain tautomerism, some signals in the ¹H NMR spectrum of **III** were doubled due to the presence of two isomers of linear structure **A**; this is the result of restricted rotation of the *o*-sulfanylbenzoyl group about the C–N bond.

The observed pattern is a rare example of tautomeric equilibrium involving seven-membered thiadiazepine ring. Pihlaja et al. [3] were the only to report on analogous transformations in the series of 1,3,4-benzotriazepine derivatives [3].

2,2-Dimethyl-3,4-dihydro-1,3,4-benzothiadiazepin-5(2H)-one (III). Yield 85%, mp 118–120°C. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: *E'*-**A** (2%): 1.93 s (CH₃), 2.00 s (CH₃), 10.96 br.s (NH); *Z'*-**A** (1%): 1.96 s (CH₃), 2.06 s (CH₃); **B** (97%): 1.38 s



(CH₃), 5.62 d (NH, $J = 4.5$ Hz), 7.39–7.64 m (H_{arom}), 9.57 d (NHCO, $J = 4.5$ Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ_C, ppm: **B**: 27.6 (CH₃); 77.6 (C²); 128.5, 130.4, 130.8, 131.4, 133.5, 140.6 (C_{arom}); 173.2 (C⁵). Found, %: C 57.73; H 5.78; N 13.40. C₁₀H₁₂N₂OS. Calculated, %: C 57.67; H 5.81; N 13.45.

The ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 instrument at 400 and 100 MHz, respectively. 2-Sulfanylbenzohydrazide (**I**) was synthesized according to the procedure described in [4].

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