CYANOETHYLATION OF 4-AMINO-1,2,4-TRIAZOLIDINE-3,5-DITHIONE

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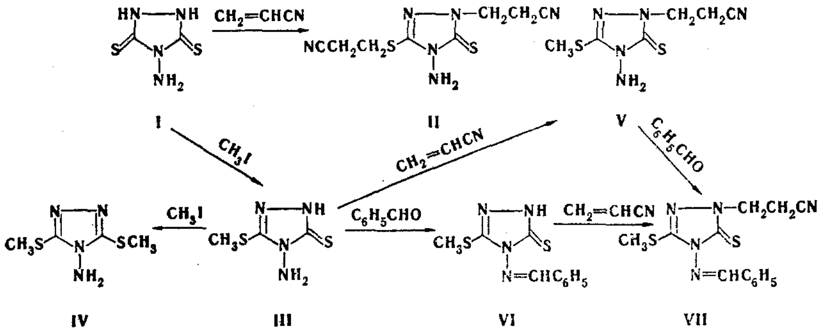
The cyanoethylation of 4-amino-1,2,4-triazolidine-3,5-dithione was studied. One cyanoethyl group adds to the nitrogen atom, while the other adds to the sulfur atom of the thioamide groupings. The mechanism of the reaction, which was confirmed by quantum-chemical calculations, was examined.

It has been shown [1] that only an N-cyanoethylation product is formed in the cyanoethylation of 4-phenyl-1,2,4-triazoline-3-thione. This was explained by destabilization of the S-cyanoethyl transition state because of the presence on the ring carbon atom of a positive charge. It might have been assumed that the introduction of a donor into the 4 position would create a negative charge on this atom and would thereby favor the formation and stabilization of the S-cyanoethylated isomer. With this end in mind, we turned to a study of the cyanoethylation of 4-amino-1,2,4-triazolidine-3,5-dithione (I), which has a donor amino group in the 4 position and contains two thioamide residues in the ring.

The spectroscopic investigation of I shows that this compound exists in the dithione form. Its IR spectrum does not contain bands that are associated with the vibrations of the thiol group (SH, at 2500-2600 cm^{-1}), but frequencies of the stretching vibrations of the C=S group (1333 cm^{-1}) and the thioamide fragment $\mathrm{NH{-}\overset{|}{C}{=}S}$ (1519 cm^{-1}) are observed. Both of these bands vanish in the IR spectrum of IV, which is obtained by alkylation of I with methyl iodide and has a fixed dithiol structure.



Cyanoethylation of I with acrylonitrile in alkaline media gave addition product II, in which one cyanoethyl grouping is found on the nitrogen atom and the other is found on the sulfur atom. The structure of II was confirmed by UV and IR spectroscopy. Compound II differs substantially with respect to the shape of its spectrum in the UV region both from I and from dimethylthio compound IV, and its IR spectrum contains a band affiliated with the vibrations of the C = S group.

To confirm this, we synthesized III, in which one thioamide grouping is fixed in the imidothiol form and the other is retained. The IR spectrum contains the corresponding bands (C–S at 670 cm^{-1} and NH–C = S at 1515 cm^{-1}). Compound V was obtained from III by cyanoethylation. The electronic spectrum of

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II in the UV region (see Fig. 1) proves to be quite similar to the spectra of III and V; this proves the "mixed" N,S-dicyanoethylated structure of II. The production of azomethine VI from III excludes the participation of the exocyclic amino group in cyanoethylation. Azomethine VI was cyanoethylated to VII, which was also obtained by reaction of V with benzaldehyde.

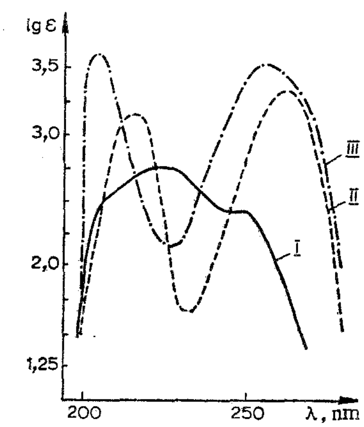
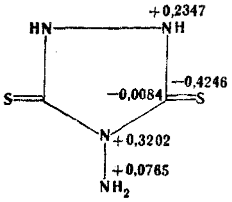
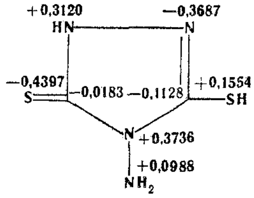


Fig. 1. UV spectra of I-III in ethanol (10^{-4} M).

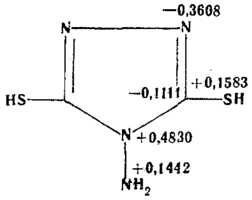
The explanation of the specific behavior of I in cyanoethylation can be given in conformity with a previously proposed mechanism [2]. Using the same parameters as in [2], we carried out the quantum-mechanical calculation of the electronic structure of I and structures IIIa and IVa, which are models of III and IV, by the Hückel MO method.



I



IIIa



IVa

It can be concluded from the molecular diagrams that primary attack in the presence of excess acrylonitrile proceeds at the sulfur atom of I to give a product with structure IIIa. This compound undergoes attack by a second molecule of acrylonitrile, also at the sulfur atom, with conversion to IVa. The next step is the attack of a third molecule at any of the pyridine nitrogen atoms of IVa with transcyanoethylation again to IIIa. As shown in [2], during transcyanoethylation the S-cyanoethyl grouping is stabilized more strongly when the charge on the sulfur atom bonded to it is less negative and the charge on the ring carbon adjacent to the sulfur atom is more negative. On passing from IVa to IIIa, one sees a tendency for an increase in the electron density on the carbon and sulfur atoms, and structure IIIa has the smallest positive charge on the sulfur atom and the largest negative charge on the carbon atom; this hinders transfer of electrons to the C−S bond and thereby fixes this structure.

EXPERIMENTAL

The UV spectra of 10^{-4} M solutions in alcohol were recorded with a Perkin-Elmer-402 spectrometer. The IR spectra of mineral oil suspensions were recorded with a UR-20 spectrometer.

4-Amino-1,2,4-triazolidine-3,5-dithione (I), 4-amino-3,5-dimethylthio-1,2,4-triazolidine (IV), and 4-amino-3-methylthio-1,2,4-triazolidine-5-thione (III) were obtained by the method in [3].

1-(β-Cyanoethyl)-3-(β-cyanoethylthio)-4-amino-1,2,4-triazoline-5-thione (II). A mixture of 0.5 g (3.8 mmole) of I, 1 ml (15 mmole) of acrylonitrile, 0.5 ml of triethylamine, and 9 ml of alcohol was refluxed for 2 h, during which a colorless precipitate formed. Workup of the mixture gave 0.45 g (52%) of a product with mp 160-161° (plates, from alcohol). Found: C 37.9; H 4.2; N 32.8%. $C_8H_{10}N_6S_2$. Calculated: C 37.8; H 4.0; N 33.0%.

1-(β-Cyanoethyl)-3-methylthio-4-amino-1,2,4-triazoline-5-thione (V). A mixture of 0.6 g (3 mmole) of III, 0.25 g (4.7 mmole) of acrylonitrile, a few drops of triethylamine, and 20 ml of ethanol was refluxed for 30 min, after which it was poured with stirring over ice to give a colorless precipitate. Workup of the mixture gave 0.62 g (82%) of a product with mp 108-109° (plates, from alcohol). Found: C 33.7; H 4.2; S 29.9%. $C_6H_9N_5S_2$. Calculated: C 33.5; H 4.2; S 29.8%.

3-Methylthio-4-benzylideneamino-1,2,4-triazoline-5-thione (VI). A 0.2-ml (1.9 mmole) sample of benzaldehyde and a few drops of 5 N hydrochloric acid were added to a solution of 0.3 g (1.8 mmole) of III in alcohol, and the mixture was heated for 15 min. It was then cooled to precipitate a colorless substance. Workup of the mixture gave 0.4 g (86%) of a product with mp 205-206° (plates, from alcohol). Found: C 48.3; H 4.2; S 25.7%. $C_{10}H_{10}N_4S_2$. Calculated: C 48.0; H 4.0; S 25.6%.

1-(β-Cyanoethyl)-3-methylthio-4-benzylideneamino-1,2,4-triazoline-5-thione (VII). A. A mixture of 0.3 g (1.2 mmole) of VI, 0.72 g (1.4 mmole) of acrylonitrile, a few drops of triethylamine, and 5 ml of alcohol was refluxed for 2 h, after which it was poured with stirring over ice to give a colorless precipitate.

Workup of the mixture gave 0.35 g (99%) of a product with mp 123-134° (needles, from ethanol). Found: C 51.4; H 4.4; S 21.3%. $C_{13}H_{13}N_5S_2$. Calculated: C 51.4; H 4.3; S 21.1%.

B. A 0.2-ml (1.9 mmole) sample of benzaldehyde and a few drops of concentrated hydrochloric acid were added to a solution of 0.3 g (1.5 mmole) of III in alcohol, and the mixture was heated for 40 min and cooled to precipitate a colorless substance, which on workup gave 0.3 g (54%) of a product with mp 123-124° (needles, from ethanol). Found: C 51.5; H 4.7; N 22.8%. $C_{13}H_{13}N_5S_2$. Calculated: C 51.4; H 4.4; N 23.1%.

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