LITERATURE CITED

1. G. G. Skvortsova, D. G. Kim, and M. V. Sigalov, Khim. Geterotsik. Soedin., No. 8, 1147 (1975).
2. V. I. Staninets and E. A. Shilov, Usp. Khim., 40, 491 (1971).
3. A. R. Katritzky (ed.), Physical Methods in the Chemistry of Heterocyclic Compounds [Russian translation], Khimiya, Moscow—Leningrad (1966), p. 576.
4. Yu. L. Frolov, V. K. Voronov, N. M. Deriglazov, L. V. Belousova, N. M. Vitkovskaya, S. M. Tyrina, and G. G. Skvortsova, Khim. Geterotsik. Soedin., No. 1, 95 (1972).
5. V. K. Voronov, M. A. Andriyanov, and G. G. Skvortsova, Khim. Geterotsik. Soedin., No. 5, 666 (1975).

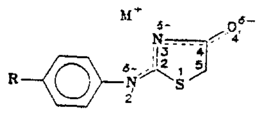
STRUCTURE OF THE ALKALINE SALTS OF 2-PHENYL- AND 2-p-METHOXYPHENYLIMINO-4-THIAZOLIDINONES

S. M. Ramsh and E. S. Khrabrova

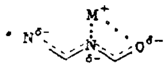
UDC 543.789.1.3

The structure of the undissociated molecule of the alkali salt of 2-arylimino-4-thiazolidinone conforms with the more stable tautomer of the NH acid: the iminotautomer. In the free anion formed by the dissociation of the salt the negative charge is concentrated mainly at the ring nitrogen atom; however, a negligible resonance delocalization of the charge to the exocyclic oxygen and nitrogen atoms takes place. Such a charge distribution of the anion is also retained in the crystalline state, thanks to the fact that the lattice structure allows the coordination of the cation with the heteroatoms of the mesomeric fragment of the anion.

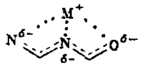
The alkaline salts of 2-phenylimino-4-thiazolidinone (Ia-d) and 2-p-methoxyphenylimino-4-thiazolidinone (II) are of interest as objects for the study of dual reactivity [1, 2]; nevertheless, their structure has not been studied so far. The objective of the present work was to obtain a qualitative picture of the distribution of the negative charge in mesomeric anions of the salts I and II, based on their spectrometric characteristics. Starting from the fact that O-alkylation takes place not only in the case of the above-mentioned salts, but also in the case of other 4-azolidinones [3], it is particularly important to establish whether exclusive N-alkylation is related to the exclusive localization of the negative charge of the anion at the nitrogen atoms.



Ia-dII



IV



V

I a–d R=H, a M=Li, b M=Na, c M=K, d M=Cs; II R=p-OCH$_3$, M=Na

Comparison of the UV spectra of the solutions of the salts Ia-d in acetonitrile shows a noticeable difference between the distribution of electrons in the anion and in the corresponding undissociated molecule. At concentrations of $3\cdot10^{-5}$ M the spectra of the potassium salt (Ic) and the cesium salt (Id) are very similar and represent two overlapping bands with

---

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1399-1404, October, 1986. Original article submitted June 25, 1985.

0009-3122/86/2210-1134$12.50

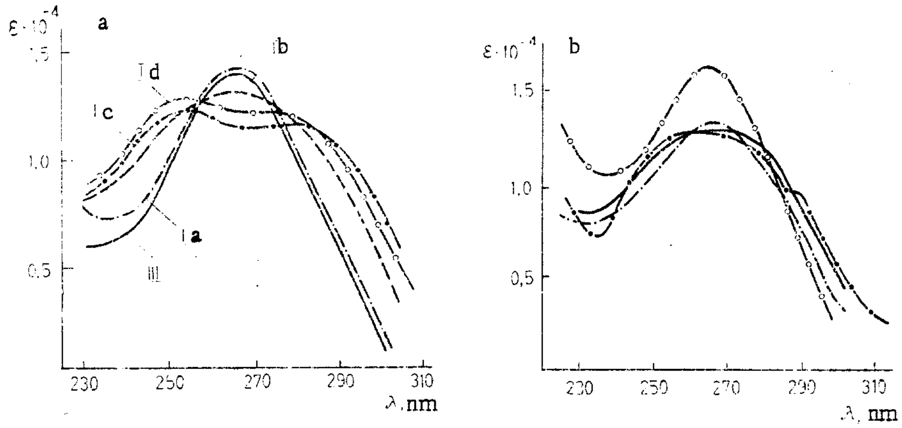


Fig. 1. UV spectra (in acetonitrile): a) 2-phenylamino-4-thiazolinone (III) and its salts Ia-d; b) sodium salt Ib at concentrations: $3.58 \cdot 10^{-5}$ (——), $0.88 \cdot 10^{-3}$ (-·-), $0.86 \cdot 10^{-3}$ M with the addition of sodium tetraphenylborate at a concentration of $4.2 \cdot 10^{-3}$ M (○), $3.58 \cdot 10^{-5}$ M with the addition of dibenzo-18-crown-6 at a concentration of $4.87 \cdot 10^{-5}$ M (●).

absorption maxima at 255 and 270 nm (Fig. 1a). At the given concentration these salts are dissociated by more than 99% [4], i.e., the observed spectra represent the spectra of the free anion. The addition of a 1.5-fold excess of dibenzo-18-crown-6 does not affect their shape. At the same concentration the lithium salt Ia is completely associated [4] and its UV spectrum coincides with the spectrum of 2-phenylimino-4-thiazolidinone (III) (Fig. 1a). This leads to the conclusion that the salt Ia exist in acetonitrile in the form of a contact ion pair, stabilized by the polarization of the negative charge of the anion on the heteroatom [5] (to which the proton is attached in compound III, in particular, on the atom $N_{(3)}$ [6]); or, no charge separation takes place in the undissociated molecule Ia and the Li—$N_{(3)}$ bond has a covalent character. The addition of a crown-polyether does not alter the shape of the spectrum; this is related to the weak tendency of the lithium cation to form complexes with dibenzo-18-crown-6 [7].

At the concentration $3 \cdot 10^{-5}$ M the sodium salt Ib is dissociated 92% [4]. At this concentration the UV spectrum of the salt Ib appears as a broad band with a "washed-out" maximum at 262-268 nm (Fig. 1b). As expected, the addition of the crown-polyether has only a negligible effect on the spectrum (Fig. 1b); however, when the salt concentration is increased to $0.9 \cdot 10^{-3}$ M, which corresponds to a reduction of the degree of dissociation to 0.49, the absorption band narrows (Fig. 1b). Finally, in the presence of sodium tetraphenylborate at a concentration of $4 \cdot 10^{-3}$ M, when the degree of dissociation is less than 0.08 [1], the UV spectrum of the undissociated salt Ib narrows even more and becomes practically identical to the spectra of salt Ia and compound III (Fig. 1b).* It must be pointed out that, although the nature of the cation has some effect on the UV spectrum of the free anion, this does not reflect itself on the relative reactivity of its nucleophilic centers $N_{(2')}$ and $N_{(3)}$ [1].

The IR spectra of the crystalline lithium (Ia), sodium (Ib), and potassium (Ic) salts are identical (Fig. 2a-c), except that the intensity of the band at 1715 cm^{-1} decreases with increasing radius of the cation; in the spectrum of salt Ic this band is not present at all. The IR spectrum of the cesium salt Id shows a very weak band at 1680 cm^{-1} (Fig. 2d) in the region of absorption of multiple bonds; the intensity of some bands changes in comparison with the spectra of salts Ia-c, however, the absorption frequencies remain practically the same. The absence of a frequency shift indicates that the mesomeric distribution of the negative charge in the anion I is independent of the nature of the cation, at least in the case of the salts Ia-c.

---

*We failed to obtain the UV spectrum corresponding to 100% dissociation of salt Ib, because at the required concentration of 10^{-6} M [1] the salt was either completely hydrolyzed by the moisture remaining in acetonitrile or neutalized by an acidic impurity present in the solvent; as a result of this, the spectrum was identical to the spectrum of the NH acid III.

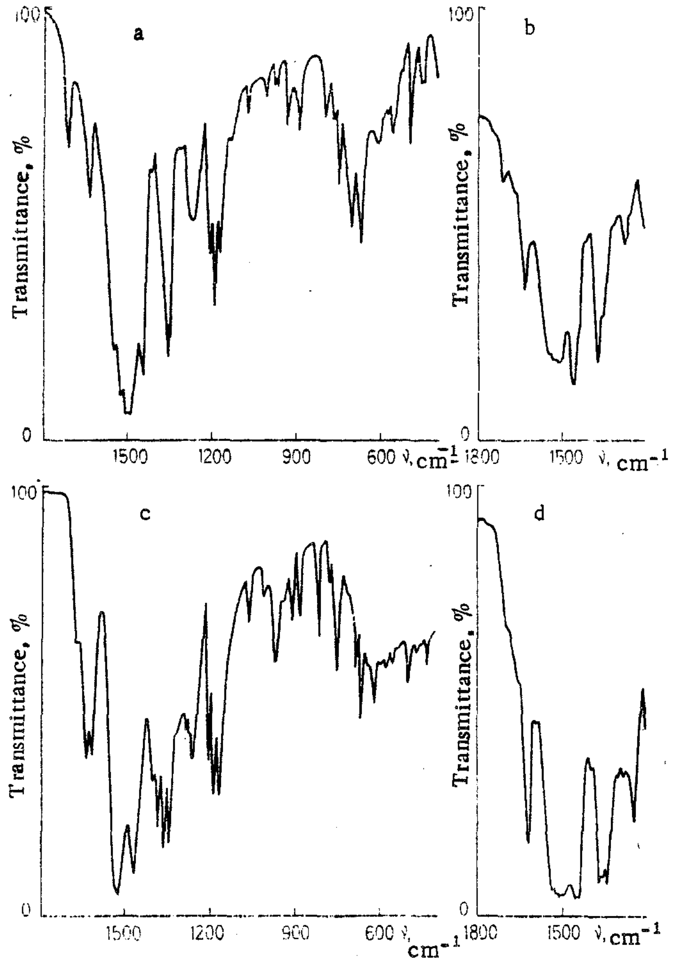


Fig. 2. IR spectra of the crystalline salts of compound III: a) lithium; b) sodium; c) potassium salt; d) cesium.

To assume that the charge of the anion is concentrated only at the $N_{(3)}$ atom and that the band at 1715 cm^{-1} is due to carbonyl absorption would be an unjustified simplification. The anion I represents a tridentate ligand which carries the nucleophilic centers $N_{(2')}$, $N_{(3)}$, and $O_{(4')}$. In analogy to the sodium salt of 5-phenyl-2,4-thiazolidinedione [4] we can assume that in the ionic crystal of the salts Ia-d the alkali metal cation is coordinated with six nucleophilic centers, belonging to four anions: $N_{(2')}$, $N_{(3)}$ (first anion); $O_{(4')}$ (second anion); $N_{(2')}$ (third anion); $N_{(3)}$, $O_{(4')}$ (fourth anion). Coordination with the rigid centers of the mesomeric anion must be preferable [10]. In the given case such atoms are $N_{(3)}$ [11] and $O_{(4')}$, whereby, judging from the structure of the undissociated molecule of salt Ia or Ib, coordination with the ring nitrogen atom $M^{+}\ldots N_{(3)}$ must predominate. This tendency must be particularly pronounced in the lithium salt Ia. As the radius increases, the cation, located in the "cavity" formed by the ligands, starts to "reach" for the center $N_{(2')}$, i.e., to coordinate with it. In the plane this can be presented by the transition from the bridge structure IV to the symmetrical structure V. Based on these concepts, we attribute the bands at 1715 and 1640 cm^{-1} to the symmetrical and asymmetrical complex vibrations of the anionic resonance system $[N_{(2')}\overline{---}C_{(2)}\overline{---}N_{(3)}\overline{---}C_{(4)}\overline{---}O_{(4')}]^{-}$, with strong contributions from the vibrations of the carbonyl group. The increase in the coordination of the mesomeric fragment with the cation in the order Li < Na < K leads to inactivation of the symmetrical vibration with the frequency 1715 cm^{-1}. Such an explanation of the decrease in the intensity of the band at 1715 cm^{-1} is in agreement with the data on the methylation of salts la-d in the solid phase [12].

The estimated value of the force constant of the bond $C_{(4)}\overline{---}O_{(4')}$ at a vibration frequency of 1640 cm^{-1}, calculated from the harmonic oscillator equation, is $17.0 \cdot 10^{6}$ cm^{2}; this corresponds to a π-order of ~0.92 and bond length of ~1.22 Å [13]. This is somewhat longer than the length of the C=O double bond 1.20 Å, but significantly shorter than the $C-O^{-}$ bond

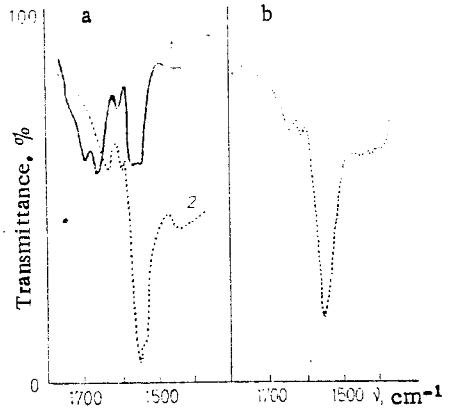


Fig. 3

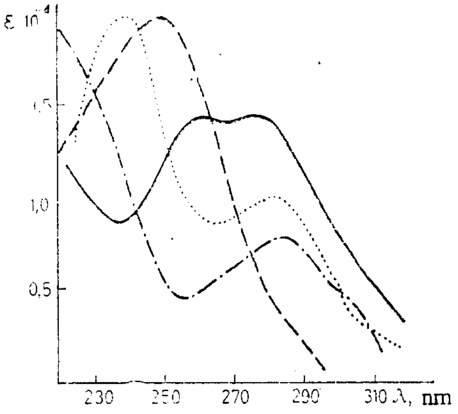


Fig. 4

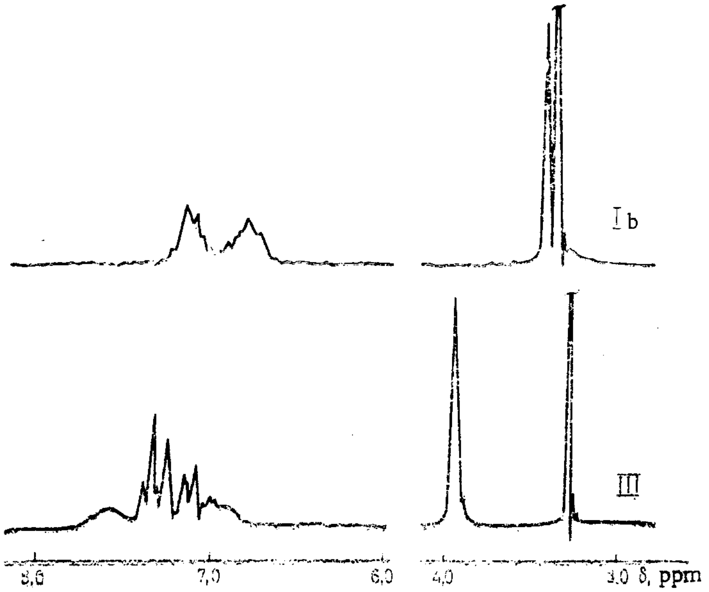


Fig. 5

Fig. 3. IR spectra (in methanol): a) compound III (curve 1) and its sodium salt Ib (curve 2) (c = 0.1 M; b) sodium salt of 2-p-methoxyphenylimino-4-thiazolidinone (II) (c = 0.05 M).

Fig. 4. UV spectra: 2-p-methoxyphenylimino-4-thiazolidinone in methanol (——), in 0.01 N sodium methylate (···), 2-methyl-p-methoxyphenylimino-4-thiazolinone (---) and 3-methyl-2-p-methoxyphenylimino-4-thiazolidinone (-·-) in methanol.

Fig. 5. PMR spectra (in DMSO-D$_6$) of the sodium salt Ib and compound III.

1.45 Å and approximately equal to one of the C---O bonds in the molecule of the sodium salt of 5-phenyl-2,4-thiazolidinedione (1.23 Å [9]). Consequently, the negative charge of the anion is delocalized partially, even to a small degree, to the carbonyl oxygen O$_{(4')}$.

The fact that the IR spectrum of the Cs salt Id differs from the IR spectra of the other salts Ia-c is attributed to small structural changes caused by the increase in the radius of the cation. The complex absorption in the region 1515-1545 cm^{-1}, observed in the IR spectra of all salts Ia-d, is due to the interacting vibrations of not-whole-number C---N bonds. The IR spectrum of the crystalline sodium salt of 2-p-methoxyphenylimino-4-thiazolidinone (II), the methylation of which we have thoroughly studied earlier [11], is analogous to the IR spectrum of salt Ib.

The distribution of the electron density in the free anion I must provide the maximum energy of delocalization of the negative charge with account of the solvation interactions.

Evidently, it differs only little from the distribution in the crystal. In fact, the vibrations corresponding to the frequency 1715 cm^{-1} do not appear in the IR spectrum of the methanol solution of salt Ib,* due to the symmetry of the mesomeric anion; however, a band at 1645 cm^{-1} is present and a strong absorption at ~1550 cm^{-1}, i.e., the spectrum (Fig. 3) is practically analogous to the spectrum of the solid salt.

The same picture is obtained in the transition from the crystals to the methanol solution of salt II. The delocalization of the negative charge in the anion I to the exocyclic nitrogen atom is confirmed by the inhibited rotation around the partial double bond $C_{(2)}\underline{===}N_{(2')}$, observed in the acetone solutions of salts Ia-c [15]. The similarity of the UV spectra of the anion II and 2-p-methoxyphenylimino-3-methyl-4-thiazolidinone in methanol (Fig. 4) leads to the conclusion that this delocalization is insignificant, i.e., that the atom $N_{(3)}$ carries the major portion of the negative charge of the anion and that the bond $C_{(2)}\underline{===}N_{(2')}$ is essentially a double bond. This does not contradict the conclusion, reached when studying the dual reactivity [2], that in the anions I and II the ring nitrogen atom $N_{(3)}$ is more rigid than the nitrogen atom $N_{(2')}$, i.e., that it is more basic and less polarizable; consequently, it carries a large negative charge.

The comparison of the NMR spectra of the sodium salt Ib and the NH acid III also confirms delocalization of the negative charge on the mesomeric fragment of anion I. In the NMR spectra of the salt Ib† the signal of the methylene protons $C_{(5)}H_2$ is shifted towards the strong field when compared with compound III (3.40 against 3.95 ppm); on the other hand, the signal of the $C_{(5)}$ carbon is shifted to the weak field (38.1 against 35.0 ppm). This can be attributed to hyperconjugation in the molecule III ($CH_2-C{=}O \rightleftarrows H^+\ {}^-CH-C{=}O \rightleftarrows H^+CH{=}C-O^-$) which is weaker in the anion I due to localization of a part of its charge at the carbonyl oxygen. Characteristic aromatic absorption in the PMR spectrum of anion I (Fig. 5a) suggests such an absorption for compound III (Fig. 5b), which possesses an imino structure in DMSO-D_6 [6]; this could be expected due to the strong double bond between the exocyclic nitrogen and the carbon in the anion. The increased density of the negative charge in the mesomeric fragment of anion I shifts the signals of the atoms $C_{(2)}$ and $C_{(4)}$ towards the strong field in comparison with the NH acid III (151.6 and 186.3 ppm against 160.8 and 188.3 ppm, respectively).

EXPERIMENTAL

The preparation of compounds Ia-d, II, and III has been described in [1, 6, 15]. Prior to taking the spectra, the salts Ia-d and II were kept in vacuum (1-2 mm) at T = 100° for 3 h. The UV spectra were taken on an SF-16 spectrophotometer. The concentration of the solutions was $0.8\cdot10^{-3}$-$4\cdot10^{-5}$ M, the thickness of the cells was 0.01, 0.05, and 1.00 cm. Acetonitrile and methanol were purified as described in [1, 6]. When taking the UV spectra in the presence of dibenzo-18-crown-6 and sodium tetraphenylborate, these compounds were also added to the reference solution. The IR spectra of the solid samples were taken on an IKS-29 spectrophotometer; the samples were prepared as suspensions in Vaseline or perfluorovaseline oil on KBr plates. The IR spectra of solutions in methanol were recorded on an UR-10 spectrophotometer using cells made of CaF_2. Methanol was purified in the same way as for UV spectrophotometry.

The PMR spectra were taken on a Tesla BS-497C spectrometer (100 MHz) with HMDS as the internal standard. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer, by using TMS as the reference for the determination of the chemical shifts.

LITERATURE CITED

1. S. M. Ramsh, Yu. G. Basova, and A. I. Ginak, Zh. Org. Khim., 18, 2200 (1982).

---

*At a concentration of 0.1 M the solvolysis of salts Ib and II is negligible [6] and the degree of dissociation is equal to 0.47 and 0.36, respectively [14]. The shape of the spectrum, in particular, the intensity ratio of the bands at 1645 and 1550 cm^{-1}, is independent of the concentration when it changes from 0.05 to 0.2 M. Evidently, the vibration frequencies of the undissociated molecule and the free anion are so similar, that the corresponding absorption bands are not resolved.

†Although the dissociation constant in DMSO is close to the value of K_{diss} in DMFA, at the concentration of ~0.1 M the salt Ib is almost completely dissociated [14] and the discussed PMR spectra belong to the free anion.

2. S. M. Ramsh, A. I. Ginak, Yu. G. Basova, and L. P. Shamina, Zh. Org. Khim., 17, 846 (1981).
3. Yu. G. Basova, S. M. Ramsh, and A. I. Ginak, Khim. Geterotsikl. Soedin., No. 8, 1046 (1981).
4. Yu. G. Basova, S. M. Ramsh, and A. I. Ginak, Zh. Org. Khim., 17, 663 (1981).
5. G. Gordon, Organic Chemistry of Electrolyte Solutions [Russian translation], Mir, Moscow (1979), p. 548.
6. S. M. Ramsh, N. A. Smorygo, A. I. Ginak, and E. G. Sochilin, Zh. Org. Khim., 15, 1506 (1979).
7. I. Smid, in: Ions and Ion Pairs in Organic Reactions [Russian translation], Mir, Moscow (1975), p. 98.
8. Yu. G. Basova, Candidate Dissertation [in Russian], Leningrad (1980).
9. B. W. Matthews, Acta Cryst., 17, 1413 (1964).
10. S. A. Shevelev, Usp. Khim., 39, 1773 (1970).
11. S. M. Ramsh, A. I. Ginak, Yu. G. Basova, and L. P. Shamina, Zh. Org. Khim., 17, 851 (1981).
12. Yu. G. Basova, S. M. Ramsh, and A. I. Ginak, Zh. Org. Khim., 17, 986 (1981).
13. E. M. Popov, G. A. Kogan, and V. N. Zheltova, Teor. Éksp. Khim., 6, 14 (1970).
14. S. M. Ramsh, Yu. G. Basova, A. I. Ginak, and E. G. Sochilin, Zh. Org. Khim., 16, 651 (1980).
15. S. M. Ramsh, Yu. G. Basova, and A. I. Ginak, Khim. Geterotsikl. Soedin., No. 7, 905 (1984).

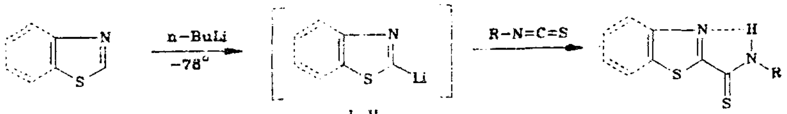
SYNTHESIS AND SPECTROMETRIC INVESTIGATION OF THE THIOAMIDES OF THIAZOLE- AND BENZOTHIAZOLE-2-CARBOXYLIC ACIDS

T. Yagodzinski, T. Dzembovska, É. Yagodzinskaya,
and Z. Yablonski

UDC 547.298.4'789.6.04:
543.422

The reaction of 2-lithiumthiazole and benzothiazole with isothiocyanates gave the corresponding thioamides. Based on the IR, UV, and PMR spectra it was established that an intramolecular hydrogen bond is formed in these thioamides between the NH fragment of the thioamide grouping and the nitrogen atom of the thiazole ring. The main routes of the mass-spectrometric decomposition of the obtained thioamides have been determined.

As reported earlier [1], the reaction of thiophene with isocyanates and isothiocyanates in a nitromethane solution of $AlCl_3$ leads to the formation of amides and thioamides of the thiophene-2-carboxylic acid. The IR and UV spectra, and quantum-mechanical calculations by the CNDO/2 method showed that the thioamides of the thiophene-2-carboxylic acid exist mainly in the trans-s-trans form [2]. The present work is devoted to the synthesis and spectrometric investigation of the thioamides of thiazole- and benzothiazole-2-carboxylic acids. The corresponding thioamides (IIIa-c, IVa-g) were obtained in the reactions of 2-lithiumthiazole (I) and 2-lithiumbenzothiazole (II) with isothiocyanates [3-7].



I, II

IIIa-c, IVa-g

III a $R = CH_3$, b $R = C_6H_5$, c $R = \alpha$-naphthyl; IV a $R = CH_3$, b $R = $-*cyclo*-$C_6H_{11}$, c $R = C_6H_5$,
d $R = 4\text{-}ClC_6H_4$, e $R = 4\text{-}BrC_6H_4$, f $R = 4\text{-}CH_3C_6H_4$, g $R = 4\text{-}CH_3OC_6H_4$

Institute of Fundamental Chemistry, Technical University, Szczecin, Poland 71-065. Agricultural Academy, Szczecin, Poland 71-065. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1405-1411, October, 1986. Original article submitted March 15, 1985.

0009-3122/86/2210-1139$12.50