LYSINE SALTS OF BENZOXAZOLINE-2-THIONES

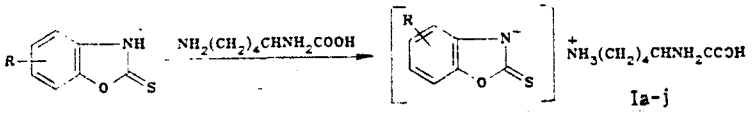
K. Davidkov

UDC 547.466.46'787.3

The synthesis of lysine salts of benzoxazoline-2-thiones is presented together with their spectral properties and electrical conductivity data.

Benzoxazoline-2-thiones (BT) are known to be weak acids ($K = 4.7 \cdot 10^{-7}$) [1] forming salts with heavy metal cations [2, 3] and with amines [4, 5]. The practical application of BT, in particular their pharmacological use [6, 7], is made much more difficult by their low water solubility and makes worthwhile a study of the reactions of freely soluble BT amine salts.

In this work we have studied lysine salts of BT having different substituents in the benzene ring (see Table 1). The salts were formed at 20°C.



Ia-j

For comparison the following lysine salts were also obtained: 3H-oxazolo[4,5-b]pyridine-2-thione (Ik), benzothiazoline-2-thione (II), and 5-methyl-3H-oxazolo[4,5-b]pyridine-2-thione (Im). All of these salts were readily water soluble and corresponded to a 1:1 ratio of starting materials according to elemental analytical data. The IR spectra of I (Vaseline oil) showed absorption bands at 2500-3200 cm^{-1} corresponding to NH vibrations in the NH_3^+ group. The UV spectrum of the lysine BT salt in aqueous ethanol solution did not significantly differ from that of the starting BT pointing to a thione structure for the anion in the salt. The UV spectra of the BT salts which contained a substituent at position 5 (Cl, NO_2, and NH_2) or 6 (Br, SO_2NH_2, SO_2CH_3) showed a bathochromic shift of the long-wave absorption when compared with the unsubstituted BT (see Fig. 1). The values of the electrical conductivity of aqueous ethanol solutions of I salts were two orders of magnitude greater than the starting benzoxazoline thione and depended on the benzene ring substituent (see Table 1). Moreover, this variation was in accord with overall organic chemistry concepts.

TABLE 1. Lysine Salts of Benzoxazoline-2-thiones (I)

Compound	R	T_{mp}, °C	N, % found	N, % calculated	Electrical conductivity,* $cm^2 \cdot ohm^{-1}$	Yield, %
Ia	H	188	14,0	14.1	106	87
Ib	5-Cl	204	12,3	12,7	110	89
Ic	5-NO_2	159	16,0	16,4	144	97
Id	5-SO_2NH_2	191	14.7	14.9	—	95
Ie	5-CH_3	199	13,5	13,5	—	96
If	5-NH_2	174	17,8	17,9	56	96
Ig	6-Cl	182	12,5	12,7	126	94
Ih	6-Br	183	10,9	11,2	112	86
Ii	6-SO_2NH_2	203	14.6	14,9	—	97
Ij	6-SO_2CH_3	184	11,2	11,2	136	88
Ik		184	18,8	18.8	—	96
Il		216	13,6	13.4	—	97
Im		214	17,7	17,9	—	97

*Electrical conductivity of benzoxazoline-2-thione measures 1.3 and lysine 16 $cm^2 \cdot \Omega^{-1}$.

Kl. Okhridskii University, Sofia, Bulgaria, 1126. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1127-1128, August, 1987. Original article submitted April 14, 1986.

0009-3122/87/2308-0903$12.50

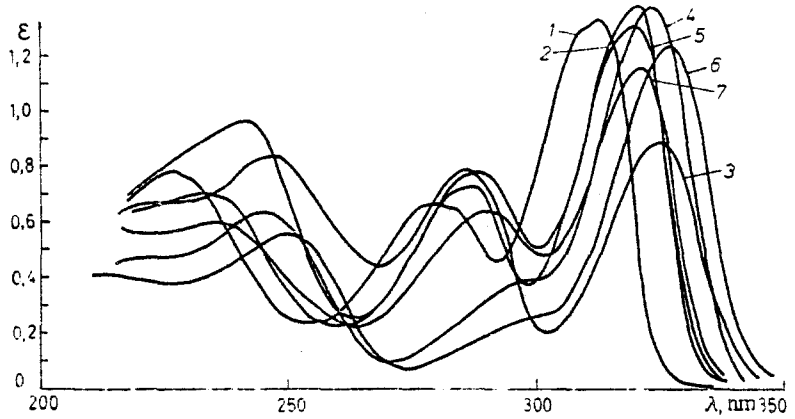


Fig. 1. UV spectra of lysine salts. Curve 1) Ia; 2) Ib; 3) If; 4) Ii; 5) Ig; 6) Ij; 7) Ih.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument for Vaseline oil mulls and UV spectra on a Specord UV-vis for aqueous ethanol solutions. Electrical conductivities were determined at 23.5°C for 0.01 molar aqueous ethanol solutions of the salts.

Lysine Salts of Benzoxazoline-2-thiones. Lysine (0.5 g, 3 mmole) was dissolved in hot ethanol (96%, 150 ml), cooled, and the corresponding benzoxazoline-2-thione (3 mmole) added. The solution was filtered and petroleum ether (200 ml) was added to the filtrate. The crystalline precipitate was filtered off and washed with ether. The yields and physical constants are given in Table 1.

LITERATURE CITED

1. G. I. Faerman and V. A. Kozeya, Uzb. Khim. Zh., 5, 107 (1957).
2. M. Kuraš, Chem. Obzor., 17, 41 (1941).
3. M. Kuraš, Chem. Obzor., 14, 145 (1939).
4. J. Terrema, US Patent 1,792,780; Chem. Abstr., 25, 2332 (1931).
5. T. A. Sycheva, I. N. Kiseleva, and M. N. Shukina, Khim. Geterotsikl. Soedin., No. 2, 205 (1966).
6. D. Haag, Ind. Patent 57,054; Chem. Abstr. 9959 (1961).
7. K. Davidkov, D. Simon, and B. A. Gylybov, Bulgarian Patent, 21,488 (1973).