SOME CHARACTERISTIC PROPERTIES OF 3-ALKYL-2-THIOTHIAZON-4-ONES AND OF INTERMEDIATES IN THEIR SYNTHESIS

N. M. Turkevich and B. S. Zimenkovskii

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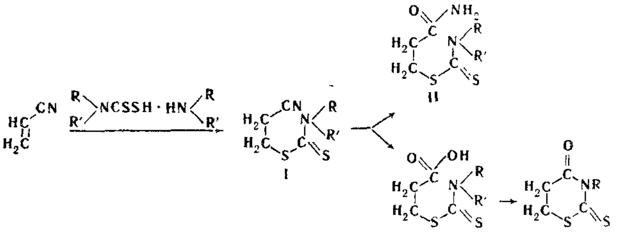
Acrylonitrile reacts with dithiocarbaminates to give nitriles of N-alkyl-S-thiocarbaminylthiohydracrylic acids, which are then hydrolyzed to the corresponding amides and acids. Dehydration of the latter gives 3-alkyl-2-thiothiazon-4-ones. The UV spectra of N-alkyl-S-thiocarbaminylthiohydracrylic acids, and amides and nitriles of them are characterized by two maxima in the 245–250 nm (thioamide band) and 266–280 nm (dithiocarbonate band) regions. Thiazan ring closure results in bathochromic shift of absorption maxima due to lengthening of the conjugated chain. The average values of the atomic refraction for sulfur in the molecules of the compounds investigated correspond to a thioketone structure.

3-Alkyl-3-thiothiazan-4-ones have been investigated by Seyden-Penne [1], Garraway [2], E. V. Vladzimirskaya [3], and Campaigne and Nargund [4]. These compounds were synthesized by dehydrating N-alkyl-S-thiocarbiminylthiohydracrylic acids, which in turn had been obtained by hydrolyzing the corresponding nitriles, or the products of reaction of β-chloropropionic acid with dithiocarbaminates. It is to be noted that 2-thiothiazan-4-ones are considered starting materials for preparing fungicides and pesticides [5, 6].

We aimed to investigate the UV absorption spectra of 3-alkyl-2-thiothiazan-4-ones and intermediates used in synthesizing them, and in the cases of such compounds as were liquids, to calculate the atomic refraction of the sulfur atoms. The substances investigated were synthesized according to the following plan.



This method gave 10 nitriles I, 7 amides II, 8 acids III, and 4 3-alkyl-2-thiothiazan-4-ones IV. The molecules of the nitriles of the N-alkyl-S-thiocarbaminylthiohydracrylic acids contain two chromophores with p—π conjugation, viz. thioamide and dithiocarbonate chromophores, which give rise to two absorption maxima in the UV spectrum (Table 1).

Replacement of the nitrile group by amide and carboxylic chromophores does not give rise to marked changes in the absorption spectra of the compounds studied (Table 2, Fig. 2), because aliphatic carboxylic acids and their amides have a very intense maximum only in the region below 220 nm [7]. The first maximum in the 245–250 nm region is connected with the presence of the thioamide chromophore, since one of the simplest thioamides, thiourea, has one absorption maximum at 241 nm (see Fig. 1).

The second maximum of the nitriles, at 266–280 nm, is to be assigned to a dithiocarbonate band, since β-alkoxythiocarbonylthiohydracrylic acids are characterized by a similar maximum [2].

Figure 2 and Tables 3 and 4 show that dehydration of N-alkyl-S-thiocarbaminylthiohydracrylic acids, giving a thiazanone ring, gives rise to marked changes in the UV absorption spectra. Characteristic of 3-alkyl-2-thiothiazan-4-ones are two absorption maxima which are, however, much displaced bathochromically. Thus the first maximum is in the region 270–274 nm, and the second in the 315–330 nm region. Such a large displacement of the maxima is connected with considerable increase in the p—π—p—π chain of conjugation.

Three of the compounds synthesized were liquids: 3-propyl-2-thiothiazan-4-one, 3-isobutyl-2-thiothiazan-4-one, and N-diethyl-S-thiocarbaminylthiohydracrylonitrile. Their molecular refractions were determined (Table 5) and then the increment for the two sulfur atoms in the molecules of the compounds calculated. Increments for sulfur atoms are known to vary greatly, depending on the type of compound, which is bound up with details of their structures. For all of the three compounds investigated the mean atomic refraction for sulfur was 9.7, corresponding to the increment for the thioketone structure [8]. Although in one of the compounds investigated one sulfur atom is an ether one (Batsanov [8] gives an increment of 8.0 for it) and the other a thioketone one, we found enhanced increment values, which are bound up with shift of a lone pair of electrons on the thioether sulfur atom. E. V. Vladimirskaya [9] found similar increased increments with thiazan-2,4-diones, and the corresponding S-carbaminylthiohydracrylic acids.

EXPERIMENTAL

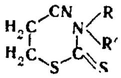
N-Alkyl-S-thiocarbaminylthiohydracrylonitriles (I). An equimolecular amount of CS_2 was added dropwise to a solution of 0.02–0.72 mole amine in 10–100 ml EtOH, which was stirred and held at 0° C. After a single phase formed, an equivalent (on the CS_2) amount of acrylonitrile in 1–10 ml glacial AcOH was added. Then the products were diluted with water, and the solid filtered off, washed with water, and recrystallized from water diluted with EtOH or MeOH. In the cases of the methyl and diethyl derivatives, the reaction products were extracted from the reaction mixtures with ether. Methylamine was brought to react as its hydrochloride, and ethylamine as its hydrobromide.

N-Alkyl-S-thiocarbaminylthiohydracrylamides (II). 0.55–3.0 g nitrile was stirred for 10 min at −5° C with 5–30 ml conc H_2SO_4. Then the reaction products were poured into 20 ml ice water, the crystals filtered off, washed with water, and recrystallized from water.

N-Alkyl-S-thiocarbaminylthiohydracrylic acids (III). 3–50 mM N-alkyl-S-thiocarbaminylthiohydracrylonitrile was refluxed for 1 hr in 3–60 ml dilute HCl (1:1). The solid precipitated on cooling was

Table 1

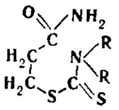
N-Alkyl-S-thiocarbaminylthiohydracrylonitriles (I)



R	R′	Mp, °C	λ_{max}, nm	lg ε	Formula	Found, %		Calculated, %		Yield, %
						N	S	N	S	
CH_3	H	39	245 265–267	3.91 3.92	$C_5H_8N_2S_2$	17.60	39.86	17.47	40.00	36.7
C_2H_5	H	91	248 270.5	3.84 3.85	$C_6H_{10}N_2S_2$	16.07	36.45	16.17	36.78	54.6
$CH_2CH=CH_2$	H	62	250 270	3.97 3.93	$C_7H_{10}N_2S_2$	14.67 C H	 44.69 5.42	15.04 C H	 45.12 5.41	80.6
$CH{<}^{CH_3}_{CH_3}$	H	96	250 270	3.90 3.91	$C_7H_{12}N_2S_2$	15.20	34.12	14.88	34.06	74.5
$CH_2CH_2CH_3$	H	67	250 270	3.85 3.85	$C_7H_{12}N_2S_2$	14.71	34.40	14.88	34.06	87.3
$CH_2CH{<}^{CH_3}_{CH_3}$	H	53	250 270	3.94 3.94	$C_8H_{14}N_2S_2$	14.21	31.75	13.85	31.70	76.8
CH_2COOH	H	85	250 270	3.88 3.86	$C_6H_8N_2O_2S_2$	13.59	31.12	13.71	31.39	38.0
CH_3	CH_3	43	245 275	3.89 3.97	$C_6H_{10}N_2S_2$	16.43 C H	 41.72 5.98	16.09 C H	 41.33 5.74	53.9
C_2H_5	C_2H_5	Liquid, bp 130° C (0.5 mm)	250 280	3.82 3.94	$C_8H_{14}N_2S_2$	13.98	31.42	13 83	31.70	37.8

Table 2

N-Alkyl-S-thiocarbaminylthiohydracrylamides (II)



R	R′	Mp, °C	λ_{max}, nm	lg ε	Formula	Found, %		Calculated, %		Yield, %
						N	S	N	S	
C_2H_5	H	118	250 270	3.98 3.99	$C_6H_{12}N_2OS_2$	14.61	33.47	14.56	33.35	54.5
$CH{<}^{CH_3}_{CH_3}$	H	129	250 270	3.93 3.93	$C_7H_{14}N_2OS_2$	13.89	31.01	13.58	31.10	70.0
$CH_2CH_2CH_3$	H	103	250 270	3.95 3.94	$C_7H_{14}N_2OS_2$	13.67	31.43	13.58	31.10	77.5
$CH_2CH{<}^{CH_3}_{CH_3}$	H	104	250 270	3.96 3.95	$C_8H_{16}N_2OS_2$	13.09	29.21	12.72	29.10	87.4
$CH_2CH=CH_2$	H	90	250 270	3.89 3.87	$C_7H_{12}N_2OS_2$	13.89	31.93	13.72	31.39	74.5
CH_3	CH_3	121	250 275	4.00 4.03	$C_6H_{12}N_2OS_2$	14.50	33.21	14.57	33.35	63.4
C_2H_5	C_2H_5	106	250 280	4.00 4.04	$C_8H_{16}N_2OS_2$	12.90	28.79	12.75	29.11	57.4

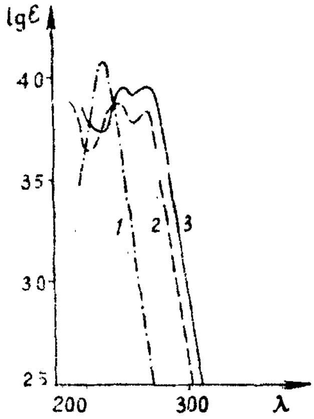


Fig. 1. Absorption spectrum plots for urea (1), N-carboxymethyl-S-thiocarbaminylthiohydracrylonitrile (2), N-n-propyl-S-thiocarbaminylthiohydracrylamide (3).

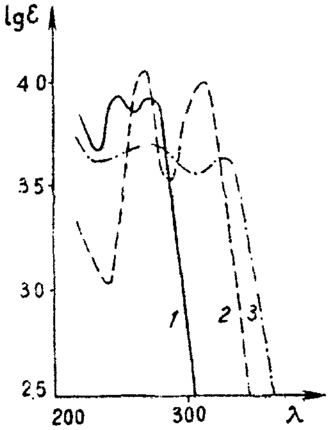
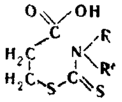


Fig. 2. Absorption spectrum plots of N-carboxymethyl-S-thiocarbaminylthiohydrylic acid (1), 3-n-propyl-2-thiothiazan-4-one, (2), and 3-carboxymethyl-2-thiothiazan-4-one (3).

Table 3

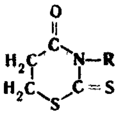
N-Alkyl-S-thiocarbaminylthiohydracrylic acids (III)



R	R′	Mp, °C	λ_{max}, nm	lg ε	Formula	Found, %		Calculated, %		Yield, %
						N	S	N	S	
CH_3	H	88	250 270.5	3.90 3.96	$C_5H_8NO_2S_2$	7,94	35.57	7.81	35.77	83.5
C_2H_5	H	99	250 271	3.87 4.00	$C_6H_{11}NO_2S_2$	6.91	33.14	7.25	33,17	45.5
$CH_2CH_2CH_3$	H	79	250 270	3.95 3.96	$C_7H_{13}NO_2S_2$	7.07	30.39	6.76	30.92	72.4
$CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	H	63	255 275	3.97 3.99	$C_7H_{13}NO_2S_2$	7.15	31.27	6.76	30 92	67.0
$CH_2CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	H	72	250 270	3.89 3.92	$C_8H_{15}NO_2S_2$	6.50	29.47	6.33	28.98	65.0
CH_3	CH_3	145	250 275	3.90 3.94	$C_6H_{11}NO_2S_2$	7.65	33.06	7.25	33.17	71.5
C_2H_5	C_2H_5	93	250 280	3.98 4.04	$C_8H_{15}NO_2S_2$	6.52	31.83	6.33	31.70	51.2
CH_2COOH	H	154	250 270	3.93 3.93	$C_6H_9NO_4S_2$	6.32	28.55	6.27	28.72	67.8

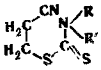
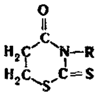
Table 4

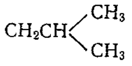
3-Alkyl-2-2-thiothiazan-4-ones (IV)



R	Mp, °C	λ_{max}, nm	lg ε	Formula	Found, %		Calculated, %		Yield, %
					N	S	N	S	
C_2H_5	66	270 315	4.10 4.03	$C_6H_9NOS_2$	8.34	36.28	7.99	36.57	81.5
$CH_2CH_2CH_3$	liquid	270 315	4.06 3.98	$C_7H_{11}NOS_2$	7.43	34.04	7.40	33.87	65.7
$CH_2CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	liquid	270 315	3.91 3.86	$C_8H_{13}NOS_2$	6.89	31.92	6.89	31.53	61.2
CH_2COOH	70 (decomp)	274 330	3.69 3.63	$C_6H_7NO_3S_2$	7.11 C H	35.86 3.60	6.82 C H	35.11 3.43	36 2

Table 5

Physicochemical Properties of S-Thiocarbaminylthiohydracrylonitriles  and 3-Alkyl-2-Thiothiazan-4-ones 

Compound	R	R′	d_4^{20}	n_D^{20}	MR	Atomic refraction of 2 atoms of S
I	C_2H_5	C_2H_5	1.1185	1.5725	59.66	19.41
IV	$CH_2CH_2CH_3$	—	1.2086	1.6059	54.00	20.25
IV	 $CH_2CH(CH_3)_2$	—	1.1736	1.5741	57.16	18.80

filtered off, washed with water, and recrystallized from water (in the case of the N-methyl derivative, from benzene-petrol ether 1:1).

3-Alkyl-2-thiothiazan-4-ones (IV). 0.1–5.0 g N-alkyl-S-thiocarbaminylthiohydracrylic acid was refluxed for 1 hr with 0.5–12.5 ml Ac_2O. Only the ethyl derivative gave crystals of reaction product (after cooling). In every other case the products had to be evaporated almost to dryness. The propyl and isopropyl compounds were extracted with ether, the extract dried over anhydrous Na_2SO_4, the ether taken off, and the residue vacuum distilled.

The UV absorption spectra were determined with an SF-4 spectrophotometer. 1–3 mg% solutions of the compounds investigated were made up in twice-distilled EtOH.

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L'vov Medical Institute
Institute of Organic Chemistry,
AS UkrSSR, Kiev