UDC 547.783.9 + 543.422.6

ELECTRONIC ABSORPTION SPECTRA OF 3-β-CARBOXYETHYLRHODANINE AND ITS 5-ARYLIDENE DERIVATIVES

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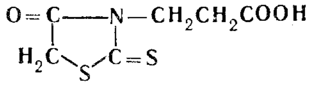
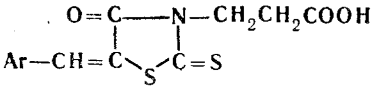
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 2, pp. 212-215, 1966

The UV spectra of 3-β-carboxyethylrhodanine and its 5-arylidene derivatives comprise four bands. The first absorption band with a peak at 239 mμ is not very characteristic of rhodanines. The second band, connected with the presence of the chromophore $>N-\underset{|}{C}=S$, is characterized by peaks in the 243-281 mμ region.

The peak of the third absorption band at about 300 mμ, is connected with the presence of an amide chromophore, which shifts bathochromically on introduction of a benzylidene group; subsequent introduction of nitro groups results in its being displaced hyposochromically. The most characteristic feature of the 5-arylidene derivatives is formation of a very intense K absorption band in the 360-466 mμ region, superimposed on the corresponding low-intensity 3-β-carboxyethylrhodanine absorption band.

Rhodanine (2-thiothiazolid-4-one) is characterized by two high-intensity absorption peaks in the UV region, at 252 and 295 mμ [1, 2]. The first peak is related to the presence of the $>N-\underset{|}{C}=S$ chromophore in the molecule, and it is bathochromically displaced 11 mμ as compared with the analogous thiourea peak (Fig. 1, curve 4). The second peak is ascribed to the presence of the –CONH– and CSS– chromophores. To investigate more thoroughly how the UV spectra varied in the rhodanine series, the spectra of 3-β-carboxyethylrhodanine (I) and its 5-arylidene derivatives (II) were obtained.


I


II

The spectral curve for compound I (Fig. 1) consists of four bands. The first (Ts band, [2]) has a high-intensity absorption peak below 220 mμ. The second (T band) is characterized by a maximum at 261 mμ. Comparing these maxima with the peaks for thiourea and rhodanine, it can be seen that introduction of a β-carboxyethyl group at position 3 in

UV Spectra of 3-β-Carboxyethylrhodanine and its Derivatives

Ar in formula II	Band							
	1st		2nd		3rd		4th	
	λ_{max}	lg ε	λ_{max}	lg ε	λ_{max}	lg ε	λ_{max}	lg ε
3-β-Carboxyethyl-rhodanine* (I)	<220	—	261	4.15	295	4.20	375—380	1.88
C_6H_5	235	3.88	272	3.97	303	3.88	377	4.53
o-$O_2NC_6H_4$	237	3.98	270	3.93	—	—	360	4.36
м-$O_2NC_6H_4$	229	4.24	255—263	4.13	—	—	371	4.46
n-$O_2NC_6H_4$	237	3.89	281	4.03	—	—	376	4.53
o-HOC_6H_4	235.5	3.77	279	3.91	296	3.90	395.5	4.42
n-ClC_6H_4	239	3.71	276	3.95	302—306	3.80	379.5	4.54
n-$(CH_3)_2NC_6H_4$	<220	—	259	3.90	299	4.11	466	4.59
$C_6H_5CH{=}CH$	<220	—	242.5	3.77	296.5	4.04	401	4.59
3-CH_3O-4-HOC_6H_3	<220	—	264.5	3.86	292	4.04	404.5	4.51
3,4-$(CH_3O)_2C_6H_3$	<220	—	262	3.90	292.5	3.96	405	4.52
3,4-$CH_2O_2C_6H_3$	<220	—	261.5	3.91	292	3.91	406	4.55
α-$C_{10}H_7$	<220	—	269.5	3.86	303	3.95	389.5	4.35
α-(β-HO)$C_{10}H_6$	232	4.59	—	—	302 342—345	4.02 4.07	410	4.23
9-$C_{14}H_9$	<220	—	253	4.04	291—295 335—337	2.89 3.22	385 430	2.77 2.87

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* Full name of compound.

the rhodanine molecule results in further bathochromic shift of the thione peak by 9 mμ. The third (A band) is characterized by a peak at 295 mμ. The UV spectrum curves for acetamide and urea (Fig. 1) show an evident hump in the region mentioned. The fourth absorption band with a low-intensity peak at 375–380 mμ, has been but little investigated for rhodanines, and may be connected with the presence of the chromophore –SCS–.

Introduction of a benzylidene group at position 5 in the molecule (II, Ar = C_6H_5) leads to bathochromic displacement of the first three bands, and to formation of a very intense fourth band, connected with the presence of a conjugated chain. The bathochromic shift of the first band is evidenced on the absorption curve (Fig. 2, curve 3) as a peak at 235 mμ, not found in the absorption curve of the starting compound I.

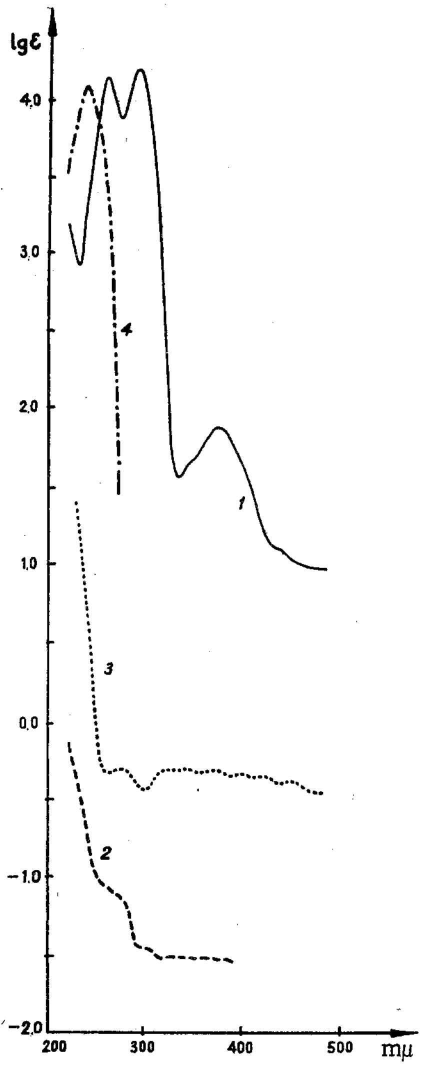

Fig. 1. Absorption spectrum curves: 1) 3-β-carboxyethylrhodanine; 2) urea; 3) acetamide; 4) thiourea.

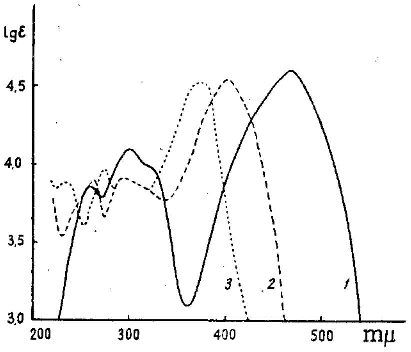

Fig. 2. Absorption spectrum curves: 1) 5-p-dimethylaminobenzylidene-; 2) 5-piperylidene 3) benzylidene-3-β-carboxyrhodanine.

Introduction of the benzylidene group leads to marked lowering of absorption intensity in the regions of the peaks of the second and third curves, and it is possible that this lowering is due to being situated adjacent to a very intense K band. The K band peak is superimposed on the corresponding low-intensity peak of the fourth band of the starting compound I, and this may be one of the reasons for the very high intensity of absorption ($\lg \varepsilon$ 4.53) in this region.

Introduction of a nitro group at the o-, m-, or p- position in the benzylidene group results in a 1–17 mμ (table) hypsochromic displacement of the K band peak, and to disappearance of the A band maxima. It should be mentioned that the latter, and the hypsochromic shift of the K band maxima is characteristic of nitro derivatives only.

The vanillidene (II, Ar = $4\text{-OH-3-CH}_3\text{OC}_6\text{H}_3$) veratrylidene (II, Ar = $3,4\text{-di-MeOC}_6\text{H}_3$) and piperylidene (II, Ar = $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3$) groups differ little among themselves chemically. The UV spectra of 5-vanillidene, 5-veratrylidene, and 5-piperylidene derivatives are almost identical. Compared with the benzylidene derivative a strong bathochromic shift of the K band by 27–29 mμ and hypsochromic shifts of the maxima of the A band (by 10–11 mμ), as well as of the T band (by 7–11 mμ) are found.

The most marked bathochromic shift of the peaks in the K band is found with 5-p-dimethylaminobenzylidene (II, Ar = $\text{Me}_2\text{NC}_6\text{H}_4$), 9-anthranylidene (II, Ar = $C_{14}H_9$), and β-hydroxynaphthylidene (II, Ar = $\beta\text{-HOC}_{10}\text{H}_6$) derivatives. The hydroxyl group, placed β- in the naphthylidene group, can shift all four bands bathochromically.

5 peaks are found in the curve for the 9-anthranylidene compound, due to superposition of absorption bands of compound I and of 9-anthraldehyde, characterized by maxima at 233.5 ($\lg \varepsilon$ 3.79).

From the results in the table it follows that a chlorine atom introduced in the p-position in the benzylidene group (II, Ar = p-ClC_6H_4), is practically without effect on the second, third and fourth absorption bands. At the same time replacement of the benzylidene group by the salicylidene (II, Ar = o-HOC_6H_4) or the cinnamylidene (II, Ar = = $C_6H_4CH{=}CH$) ones result in a considerable change in the appearance of the absorption curve.

Experimental

3-β-Carboxyethylrhodanine, mp 159°, was synthesized by treating the dipotassium salt of N-carboxyethyldithiocarbaminic acid with monochloroacetic acid. 5-Arylidene derivatives were prepared by condensing I with aromatic aldehydes in AcOH [3].

The spectrophotometric studies were made with an SF-4 spectrophotometer. The solutions of the 5-arylidene derivatives, of thiourea, and also of 9-anthraldehyde were made up at a concentration of ~ 1 mg in 100 ml MeOH. For elucidation of the low intensity peaks of I, use was made of solutions of 0.56 mg compound, 1002.18 mg urea, and 455.36 mg acetamide in 100 ml MeOH.

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30 November 1964

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