SYNTHESIS OF RHODANINE DERIVATIVES WITH POTENTIAL ANTIMETABOLITE ACTIVITY

IV. Electronic Absorption Spectra of the Products of Condensation of 3-β-Carboxyethylrhodanine with Oxo Compounds*

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The absorption spectra of 18 condensation products from 3-β-carboxyethylrhodanine and oxo compounds are investigated. Introduction of alkylidene groups into position 5 of the 3-β-carboxyethylrhodanine results in the second band maxima (at about 260 mμ) disappearing, and this is explained by the marked ability of these compounds to polarize and give polar structures. Loss of the conjugated bond gives rise to a considerable hypsochromic shift in the fourth band in comparison with 5-arylidene-3-α-carboxyethylrhodanines.

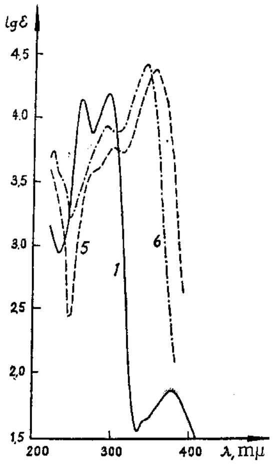
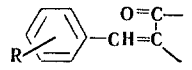


Fig. 1. UV spectra (plot number corresponds to compound number in table).

In one of our previous papers [1] we showed that the UV absorption spectra of 3-β-carboxyethylrhodanine (I) consists of four bands. The first, with a maximum below 220 mμ, is a benzenoid type band, the maximum at 261 mμ is ascribed to the presence of a thioamide chromophore, while a third band at 295 mμ is due to the superposition of amide and dithiocarbonate chromophores. With the 5-arylidene derivatives, a low intensity in the fourth band at 375–380 mμ is superimposed on a high-intensity K band, connected with the molecules of the compound containing a conjugated chain with 5 double bonds



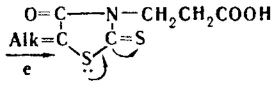
As the K band is most marked in the UV absorption spectra of 5-arylidene derivatives, it was definitely of interest to investigate the spectra of derivatives with a shortened or lengthened conjugated chain.

We determined the UV absorption spectra of 18 condensation products from 3-β-carboxyethylrhodanine and various oxo compounds, among them 8 aliphatic, 2 hydroaromatic, 3 heterocyclic, and 5 aromatic ones. In the latter case the substances contained benzene, naphthalene, anthracene, and acenaphthene rings.

The results in the table show that introduction of alkylidene substituents at position 5 in the 3-β-carboxyethylrhodanine results in the maximum in the second band vanishing (save in the case of a 5-α-carboxyethylidene derivative), and to considerably hypsochromic shift of the maximum in the 4th band, with simultaneous marked increase in its intensity.

In some cases the maxima in the first band are displaced bathochromically, and in consequence they appear in the absorption spectra plots which we drew starting at 220 mμ (Fig. 1). Among the groups which shift the maxima in the first band bathochromically, are β-methylpropylidene $(CH_3)_2CH{-}CH{=}$, α-methylpropylidene $C_2H_5{-}C(CH_3){=}$, and α-methyl-β-ethoxycarbonylethylidene $H_5C_2OOC{-}CH_2{-}C(CH_3){=}$. The 3rd band maxima lie in the region 287.5–298 mμ and are not so intense as they are for 3-β-carboxyethylrhodanine.

The disappearance of the thioamide maximum in the case of alkylidene derivatives of 3-β-carboxyethylrhodanine can be explained by the marked capacity of the alkylidene groups to enhance polarization of the rhodanine ring



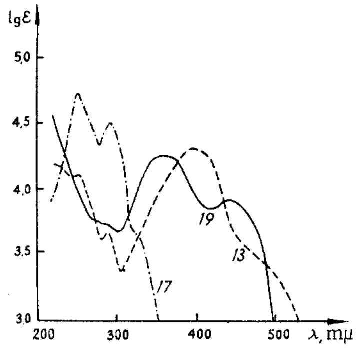


Fig. 2. UV spectra (plot number corresponds to the compound number in the table).

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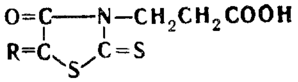
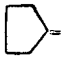
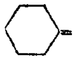
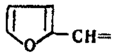
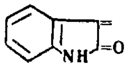
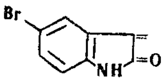
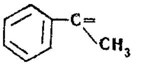
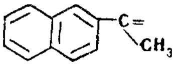
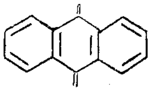
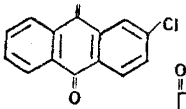
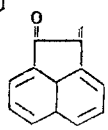
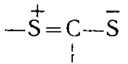
*For Part III see [4].

Table

Absorption Maxima (mμ) of 3-β-carboxyethylrhodanine and its Condensation Products with Oxo Compounds



Experiment number	R	1st band		2nd band		3rd band		4th band	
		λ_{max}	lg ε	λ_{max}	lg ε	λ_{max}	lg ε	λ_{max}	lg ε
1	H_2	<220	—	261	4.15	295	4.20	375—380	1.88
2	$CH_3—CH=$	<220	—	—	—	294	4.01	335	4.39
3	$CH_3—C(CH_3)=$	<220	—	—	—	289	3.93	343	4.45
4	$CH_3—C(COCH_3)=$	<220	—	—	—	hump	3.9	340	4.36
5	$CH_3—C(COOH)=$	<220	—	276	3.59	298	3.76	354	4.39
6	$CH_2(COOC_2H_5)—$ $—C(CH_3)=$	222	3.75	—	—	296	3.95	343	4.44
7	$CH_3—CH_2—C(CH_3)=$	221	3.77	—	—	290.5	3.94	344	4.46
8	$CH_3—CH(CH_3)—CH=$	222	3.77	—	—	296	3.99	336	4.39
9	$CH_3—(CH_2)_5—CH=$	<220	—	—	—	293	4.02	337	4.44
10		<220	—	—	—	289	3.90	345	4.48
11		221	3.71	—	—	289	3.92	346	4.49
12		237	3.54	287	3.97	hump	3.8	399	4.60
13		<220	—	255	4.10	291	3.66	398	4.30
14		<220	—	hump	4.1	296.5	3.93	391	4.30
15		<220	—	—	—	287.5	3.91	351	4.39
16		221	4.70	269	4.09	291	4.09	356—360	4.31
17		<220	—	253	4.73	295	4.50	hump	3.6
18		<220	—	256	4.81	296	4.10	326	3.85
19		<220	—	—	—	hump	3.7	356 370 442	4.26 4.24 3.91

Due to formation of polar structures containing the  $-\overset{+}{S}=\underset{|}{C}-\overset{-}{S}$ group, the specific weight of thioamide groups in the molecules of the compounds studied decreases, leading to vanishing of maxima in the thiomide band. It should be noted that polar structures for rhodanine derivatives are being increasingly used to explain structures of rhodanine derivatives [2,3].

It is of interest to note that, as expected, introduction of the COOH group α to the alkylidene substituent produces the opposite effect (due to drawing out of the electrons of the carboxyl) so that the absorption spectra curves for the pyrotartaric acid condensation product has a marked maximum in the thiomide band. This effect is not observed when an additional CH_2 group is introduced; such a group is known to reduce electron transfer considerably (see acetoacetic ester condensation product, Fig. 1).

The large hypsochromic shift of the 4th band maxima in comparison with 5-arylidene derivatives, can be explained by the considerable shortening of the conjugated chain in the molecules of the substances investigated. Likewise introduction of cyclopentylidene, cyclohexylidene, α-phenylethylidene, and oxoacenaphthylidene groups at position 5 affects the shift of electrons in the rhodanine ring in exactly the same as alkylidene derivatives. In all the cases mentioned the thioamide maximum is found to vanish, while with the first three compounds there is also a hypsochromic shift of the maxima in the 4th band. In comparison with 5-arylidene derivatives, this shift is due either to shortening of the conjugated chain (cyclopentylidene or cyclohexylidene group), or to the effect of the methyl group on the α carbon atom (acetophenone condensation product).

Up to the present the cause of the disappearance of the thioamide maximum in the case of the acenaphthaquinone derivative is unknown. Inclusion of the complex electron system of the 9-oxoacenaphthylidene-10 substituent in the conjugated chain, gives rise to 3 very intense maxima in the K band, i. e., at 356, 370, and 442 mμ. It is to be noted that these absorption maxima are missing from the electronic absorption spectra of acenaphthaquinone, which is characterized only by maxima at 226 (lg ε 4.53) and 305 mμ (lg ε 3.70).

All the condensation products from 3-β-carboxyethylrhodanine and heterocyclic oxo compounds (furfural, isatin, 5-bromoisatin), as well as from oxo compounds with condensed benzene rings (2-acetylnaphthalene, anthraquinone, and β-chloroanthraquinone) investigated by us, behave like typical 5-alkylidene-3-β-carboxyethylrhodanines. They are all characterized by well-defined maxima or inflections in the 2nd, 3rd, and 4th bands. The K band maxima lie in the 356–399 mμ region, and are displaced hypsochromically only with anthraquinone derivatives. (Fig. 2).

EXPERIMENTAL

The electronic absorption spectra were measured with a SF-4 spectrophotometer. 1 mg of the compound to be investigated was dissolved in 100 ml twice-distilled methanol.

REFERENCES

1. B. M. Turkevich, KhGS [Chemistry of Heterocyclic Compounds], 212, 1966.
2. E. V. Vladzimirskaya and Yu. M. Pashkevich, ZhOKh, 33, 3149, 1963.
3. N. M. Turkevich and A. F. Minka, ZhOKh, 35, 884, 1965.
4. B. M. Turkevich, KhGS [Chemistry of Heterocyclic Compounds], 698, 1966.

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