UV ABSORPTION SPECTRA OF 3-AMINORHODANINE DERIVATIVES

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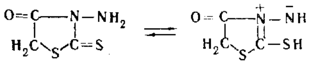
3-Aminorhodanine condenses readily with isothiocyanates to form unsymmetrical thioureas of the rhodanine series. The UV spectra of arylidene derivatives of 3-aminorhodanine consist of four bands: a short-wave band with a maximum up to 242 nm, a "thioamide" band with a maximum at 264-290 nm, a "dithiocarbonate" band with maxima at 290-370 nm, and a long-wavelength K band with maxima at 310-520 nm. The K absorption band is the most characteristic band for the arylidene derivatives of 3-aminorhodanine, and the maxima for 3',5-diarylidene derivatives are generally shifted to the short-wave region, while the maxima for the 5-monoarylidene derivatives are usually shifted to the long-wave region.

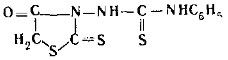
3-Aminorhodanine can exist in thione (or hydrazine) (I) and thiol (II) tautomeric forms [1,2]:



I II

The presence of hydrazine form I is indicated by the ready formation of hydrazones in alcohol [2] and the deamination of 3-aminorhodanine under the influence of HNO_2 [3]. The existence of the thiol form, however, is proved by the loss of the hydrazine properties of the preparation in ammoniacal media [2], by the acidic properties [1], and by the UV spectra [3,4]. In this connection, it seemed of interest to study the UV spectra of 3-aminorhodanine derivatives.

The starting materials for the synthesis of 3-aminorhodanine were the methyl and ethyl esters of S-(N-aminothiocarbamoyl)thioglycolic acid, which were obtained by the method in [5] and have only one absorption maximum at 272 nm. (A second short-wave maximum is situated below 220 nm.) Closing of the thiazolidine ring leads to 3-aminorhodanine with an absorption maximum at 295 nm (see Table 1), and the bathochromic shift of the maxima can be explained by transfer of electrons between the dithiocarbonate and thioamide chromophores.



III

The reaction of 3-aminorhodanine with phenyl isothiocyanate gave 3-phenylthioureidorhodanine (III), which has two absorption maxima at 258 and 320 nm. (A third short-wave maximum is located below 220 nm.) The first maximum can arbitrarily be called the "thioamide" maximum, since it is also characteristic of thiourea (241 nm). The first and second maxima are shifted by 7 nm and 25 nm, respectively, as compared with unsubstituted rhodanine (see Table 1).

We obtained 3',5-dicrotylidene-3-aminorhodanine (IV) by the condensation of 3-aminorhodanine with excess crotonaldehyde in glacial acetic acid. Since both conjugation chains are small and isolated in this compound, the position of the absorption maximum has changed only slightly in comparison with 3-aminorhodanine (see Table 1), but the absorption intensity has decreased considerably.

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TABLE 1. Absorption Maxima of 3-Aminorhodanine, the Starting Materials for Its Synthesis, and Some Derivatives

Compound	λ_{max}, nm (lg ε)			
	band I		band II	
3-Aminorhodanine	—	—	295	3,98
$H_2NNHCSSCH_2COOCH_3$	—	—	272	3,90
$H_2NNHCSSCH_2COOC_2H_5$	—	—	272	3,88
3-Phenylthioureidorhodanine	258	4,22	320	4,34
3',5-Dicrotylidene-3-aminorhodanine	—	—	290	3,30

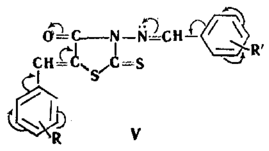
TABLE 2. Absorption Maxima of Monoarylidene Derivatives of 3-Aminorhodanine

Arylidene	mp, °C	λ_{max}, nm (lg ε)			
		band I	band II	band III	K band
$3'-C_6H_5CH$	136				335 (4,23)
$5-C_6H_5CH$	196	239 (4,01)	264 (3,94)		377 (4,49)
$3'-(p-ClC_6H_4CH)$	142				335 (3,59)
$5-(p-ClC_6H_4CH)$	204		275 (3,92)	310 (3,91)	375 (4,06)
$3'-(p-BrC_6H_4CH)$	140				335 (4,46)
$5-(p-BrC_6H_4CH)$	214				310 (4,33)
$3'-[p-(CH_3)_2NC_6H_4CH]$	164	240 (3,34)	280 (3,71)		375 (4,52)
$5-[p-(CH_3)_2NC_6H_4CH]$	216	235 (3,86)		315 (4,06)	470 (4,57)
$3'-[p-(C_2H_5)_2NC_6H_4CH]$	178	242 (3,34)	274 (3,79)		375 (4,51)
$5-[p-(C_2H_5)_2NC_6H_4CH]$	160		inflection	320 (4,00)	359 (4,00) 480 (4,35)
$3'-(p-O_2NC_6H_4CH)$	194		265 (4,06)		360 (4,48)
$5-(p-O_2NC_6H_4CH)$	176		270 (4,12)		370 (4,23)
$3'-(m-O_2NC_6H_4CH)$	168		280 (4,11)		325 (4,38)
$5-(p-O_2NC_6H_4CH)$	235	240 (4,14)		inflection	355 (3,82)
$3'-(o-HOC_6H_4CH)$	180			304 (4,05)	349 (4,15)
$5-(o-HOC_6H_4CH)$	204		290 (3,03)	inflection	340 (3,29)
$3'-(o-HOOCC_6H_4CH)$	192				337 (4,37)
$5-(o-HOOCC_6H_4CH)$	200		265 (2,82)		365 (3,41)
$3'-[3,4-(CH_3O)_2C_6H_3CH]$	142		inflection		345 (4,51)
$5-[3,4-(CH_3O)_2C_6H_3CH]$	136		265 (4,03)	290 (4,08) 330 (4,05)	405 (4,45)

TABLE 3. Absorption Maxima of 3',5-Diarylidene Derivatives (V) of 3-Aminorhodanine

R	R'	mp, °C	λ_{max}, nm (lg ε)			
			band I	band II	band III	K band
H	H	170			305 (4,29)	310 (4,40)
H	o-OH	150				330 (4,20)
p-Cl	p-Cl	181	225 (4,38)	inflection		320 (4,47)
p-Br	p-Br	201	230 (4,40)			320 (4,53)
$p-(CH_3)_2N$	$p-(CH_3)_2N$	266		270 (3,73)	360 (4,30)	465 (3,38)
$p-(C_2H_5)_2N$	$p-(C_2H_5)_2N$	200		275 (4,18)	370 (4,61)	480 (4,10)
$p-NO_2$	$p-NO_2$	175		266 (4,22)		355 (4,37)
$m-NO_2$	$m-NO_2$	265	241 (4,24)	inflection		316 (4,22)
o-OH	o-OH	200			305 (4,32)	335 (4,33)
o-OH	H	150			305 (4,29)	330 (4,20)
o-OH	$p-(CH_3)_2N$	204			305 (4,23)	345 (4,38) 464 (3,62)
o-COOH	o-COOH	238				311 (4,39)
$3,4-(CH_3O)_2$	$3,4-(CH_3O)_2$	209				315 (4,32)
$2-OH-3-CH_3O$	$2-OH-3-CH_3O$	229			330 (4,44)	415 (4,39) 520 (3,91)

3'-Arylidene-, 5-arylidene-, and 3',5-diarylidene derivatives (V) of 3-aminorhodanine were synthesized to study the effect of arylidene groupings on the UV spectra. The UV spectra of the arylidene derivatives (see Tables 2 and 3) consist of four bands.



V

All three of the first bands are only slightly characteristic. The first short-wave absorption band in most cases is situated below 220 nm, as in the case of unsubstituted 3-aminorhodanine, and its bathochromic shift to 242 nm is observed only in some arylidene derivatives. The maxima in this band are apparently associated with the presence of an amide chromophore, since amides of the aliphatic series have high intensity absorption also only below 220 nm.

The second absorption band with a maximum at 264-290 nm is associated with the presence of a thioamide chromophore (similar maxima are observed in the case of both thiourea and unsubstituted rhodanine), while the third band with maxima at 290-370 nm is associated with the presence of a dithiocarbonate chromophore (similar maxima are observed for thiocarbonylbisthioglycolic acid and unsubstituted rhodanine). In connection with the presence of an adjacent very-high-intensity K absorption band with maxima at 310-520 nm and also in conjunction with the transfer of electrons between the individual chromophores, the maxima in these bands are not always clearly expressed.

A K band, which is absent in the UV spectra of unsubstituted rhodanine and 3-aminorhodanine, develops as a consequence of the presence of conjugation chains that are in conjugation with the arylidene groupings. Since the conjugation chain in 5-arylidene derivatives is longer than in 3'-arylidene derivatives, the absorption maxima of the former compounds are generally shifted bathochromically by 10-15 nm. In addition, the two indicated conjugation chains are not conjugated, in connection with which a hypsochromic shift of the absorption maxima of 3',5-diarylidene derivatives (V) by 9-35 nm is observed. Bis(p-dialkylaminobenzylidene) derivatives constitute an exception to this observation.

EXPERIMENTAL

The UV spectra of ethanol solutions were obtained with an SF-4 spectrophotometer.

3-Phenylthioureidorhodanine. A mixture of 1.48 g (0.01 mole) of 3-aminorhodanine, 2.03 g (0.015 mole) of phenyl isothiocyanate, and 30 ml of alcohol was refluxed for 2 h. The alcohol was removed with a water aspirator, and the resinous residue was triturated thoroughly with ether to give 78% of yellow crystals with mp 163-165° (from alcohol). Found %: C 42.5; H 3.3; N 14.8. $C_{10}H_9N_3OS_3$. Calculated %: C 42.4; H 3.2; N 14.8.

3',5-Dicrotylidene-4-aminorhodanine. A mixture of 1.48 g (0.01 mole) of 3-aminorhodanine and 1.40 g (0.02 mole) of crotonaldehyde was refluxed in 30 ml of glacial acetic acid for 3 h. The precipitate that formed when the mixture was diluted with water was removed by filtration, washed with water and acetic acid, and saponified by refluxing in methanol to give 56% of a product with mp 204-205°. Found %: N 11.5; S 25.5. $C_{11}H_{12}N_2OS_2$. Calculated %: N 11.1; S 25.4.

Arylidene Derivatives of 3-Aminorhodanine. The 3'-arylidene derivatives were obtained by the reaction of 3-aminorhodanine with aromatic aldehydes in alcohol [2,6]; the 5-arylidene derivatives were obtained by condensation in ammoniacal media [2,7]. The 3',5-diarylidene derivatives were obtained by the condensation of the 3'-arylidene derivatives with aldehydes in ammoniacal media or by the condensation of the 5-arylidene derivatives in alcohol, and also by refluxing 3-aminorhodanine with excess aldehyde in glacial acetic acid [2,6].

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