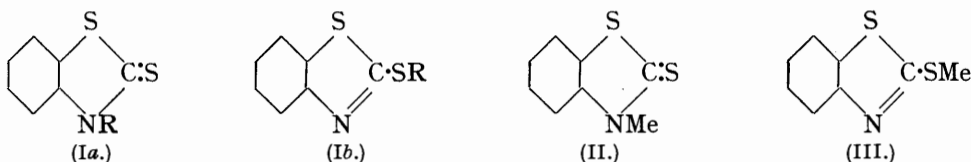


281. Absorption Spectra of Some Sulphur Compounds.

By R. A. MORTON and A. L. STUBBS.

Ultra-violet absorption spectra distinguish between the structures (Ia) and (Ib); and when R = H the structure corresponds to (a) rather than (b). Similarly (IVa) and (IVb) are markedly different. Comparisons with the spectra of *o*-hydroxycarbanil, 1-hydroxybenzthiazole derivatives, and substituted quinolines and quinolones support the interpretation.

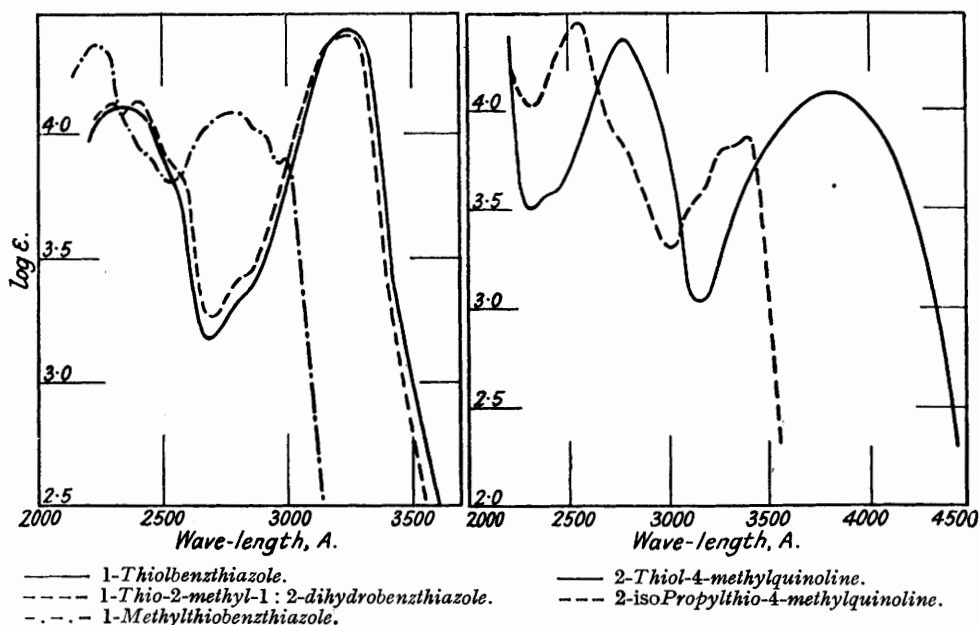
THE compound (I, R = H) may possess the alternative structures (Ia) and (Ib), but the methyl derivatives (II) and (III) exist as separate individuals. The unequivocal syntheses



by Mills, Clark, and Aeschlimann (J., 1923, 123, 2362) establish the structure of (II), so the isomeric compound prepared by the action of methyl sulphate on the sodium salt of the

FIG. 1.

FIG. 2.



thiol must have the structure (III) (cf. Sexton, this vol., p. 470). Comparison of the ultra-violet absorption spectra (Fig. 1 and Table I) of (I), (II), and (III) affords evidence that (I) is a thio-ketone.

TABLE I.

(I.)		(II.)		(III.)	
$\lambda_{\max.}$, $m\mu.$	$\log \epsilon_{\max.}$	$\lambda_{\max.}$, $m\mu.$	$\log \epsilon_{\max.}$	$\lambda_{\max.}$, $m\mu.$	$\log \epsilon_{\max.}$
325	4.43	324.5	4.41	300.5	3.92
~282	3.34	~282	3.43	~290	4.01
~252	3.84	~255	3.87	280	4.09
235	4.10	241	4.14	~244	3.92
		231	4.13	224	4.36

~ denotes inflection.

The compound (IV) may also be formulated as (IV*a*) or (IV*b*), but as its absorption spectrum differs widely from those of alkyl derivatives possessing the structure (V; R = Me, Et, or Pr^β) it must be a thio-ketone if the ethers can be proved to be substituted thiol-quinolines (Fig. 2).

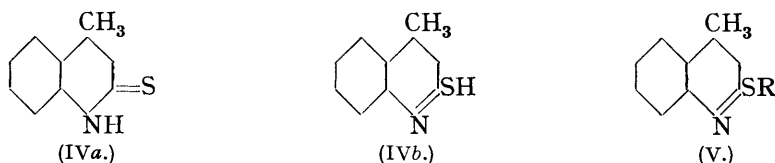


TABLE II.

$\lambda_{\max.}$	$\log \epsilon_{\max.}$	$\lambda_{\min.}$	$\log \epsilon_{\min.}$	$\lambda_{\max.}$	$\log \epsilon_{\max.}$	$\lambda_{\min.}$	$\log \epsilon_{\min.}$
	(IV.)				(V; R = Me.)		
383	4.1	316	3.03	339	3.81	—	—
278.5	4.36	—	—	~327	3.75	300.5	3.38
241	3.57	231.5	3.49	~277	3.77	—	—
				255	4.43	233	3.97
	(V; R = Et.)				(V; R = Pr ^β .)		
339	3.80	—	—	341	3.87	—	—
~327	3.76	300.5	3.30	~329	3.81	302	3.30
—	—	—	—	~312	3.52	—	—
256	4.43	231	3.94	~280	3.80	—	—
				255.5	4.44	233	4.02

~ denotes inflexion.

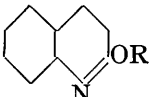
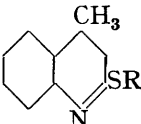
Discussion.—The data may be considered in relation to the effect of replacing oxygen by sulphur and also in relation to the theory of chromophoric groups. The absorption spectrum of *o*-hydroxycarbanil, like that of *o*-aminophenol, is essentially benzenoid, and

$\lambda_{\max.}$, m μ	286	232.7	273.6	292.5	245	325	235
$\log \epsilon_{\max.}$	3.6	3.86	3.71	3.63	3.95	4.43	4.1
	(Morton & McGookin, J., 1934, 901)	(Morton & Rogers, J., 1925, 127, 2698)	(Hunter & Parken, J., 1935, 1757)	(This paper)			

any absorption due to the carbonyl group seems to be masked. On replacing the ring oxygen by sulphur, $\lambda_{\max.}$ is displaced somewhat in the direction of longer wave-lengths, *i.e.*, to 292.5 m μ in 1-hydroxy-5-methylbenzthiazole (the 5-methyl group exercises but little effect on the spectrum). A further and larger displacement to 325 m μ occurs (in 1-thio-dihydrobenzthiazole) when the oxygen of the carbonyl group is replaced by sulphur. This is accompanied by a big increase in intensity of absorption ($\log \epsilon$ 3.63 \rightarrow $\log \epsilon$ 4.43). Replacement of methoxyl oxygen by sulphur results in a small wave-length displacement and a large increase in intensity of absorption :

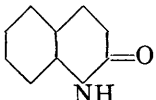
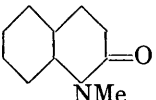
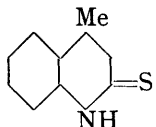
$\lambda_{\max.}$, m μ	296.2	291.2	~282.5	~260	300.5	~290	280	~244	224
$\log \epsilon_{\max.}$	3.0	3.0	3.05	3.9	3.92	4.01	4.09	3.92	4.36
	(Hunter and Parken, <i>loc. cit.</i>)								

The alkyl derivatives (V) may be compared with methoxy- and ethoxy-quinolines (Ault, Hirst, and Morton, J., 1935, 1653) :

		
$\lambda_{\text{max.}}$, m μ	322 308.5	339 327 etc. (Table II)
$\log \epsilon_{\text{max.}}$	3.57 3.65	3.81 3.75

It will be noticed that there is the same splitting of the long-wave absorption into two maxima, and that the wave-length displacement is not large when methoxyl oxygen is replaced by sulphur.

When carbostyryl (Morton and Rogers, *loc. cit.*; Ault *et al.*, *loc. cit.*) and its *N*-methyl derivative are compared with (IV) it is seen that replacement of carbonyl oxygen by sulphur again effects a large wave-length displacement :

			
$\lambda_{\text{max.}}$, m μ	327 296	328 270.5	383 278.5
$\log \epsilon_{\text{max.}}$	3.83 3.845	3.78 3.82	4.1 4.36

The spectroscopic evidence thus indicates that in alcoholic solution both (I) and (IV) exist as thio-ketones and that, irrespective of whether the structural problem be considered in terms of tautomerism or resonance, the alternative formulations can only play a very subordinate part. A similar conclusion is reached by Hunter and Parken (*loc. cit.*) in that "1-hydroxy-5-methylbenzthiazole" is largely ketodihydrobenzthiazole.

EXPERIMENTAL.

The absorption spectra were obtained in the ordinary way, using an arc between iron and nickel electrodes, or a high-tension spark between tungsten electrodes under water for a continuous-spectrum light source. ϵ is defined by the relation $\log_{10} I_0/I = \epsilon cd$ where c is the molar concentration and d the thickness in cm.

2-Thiol-4-methylquinoline (Roos, *Ber.*, 1889, **21**, 625; Rosenhauer, Hoffmann, and Heuser, *Ber.*, 1929, **62**, 2732).—2-Hydroxy-4-methylquinoline (Knorr, *Annalen*, 1886, **236**, 83) (35 g.) and phosphorus pentasulphide (35 g.) were intimately mixed and heated at 210° until completely molten. The cooled melt was boiled with 150 c.c. of concentrated hydrochloric acid until only sulphur remained undissolved. The solution was filtered through glass-wool and diluted with a large volume of water, and the mercaptoquinoline collected, washed with water, and recrystallised from alcohol and water; it formed small brown needles, m. p. 265° (yield 25 g.). Repeated crystallisation, followed by sublimation in a vacuum, yielded the mercaptan in pale brown needles, m. p. 274—275° (cf. Roos, m. p. 253°; Rosenhauer *et al.*, m. p. 266°).

2-Methylthio-4-methylquinoline.—2-Thiol-4-methylquinoline (15 g.) was dissolved in 10% aqueous sodium hydroxide (60 c.c.) and treated with methyl sulphate (12 c.c.) with intensive shaking. 30 c.c. of 10% alkali were added, and the mixture kept at room temperature for 3 hours. The oily product was extracted with chloroform, and the extracts washed with 2% aqueous alkali and finally water, and dried over sodium sulphate. The 2-methylthio-4-methylquinoline left on removal of the solvent was distilled in a vacuum; b. p. 170—177°/14 mm. (yield 13 g.); it solidified, and was crystallised from alcohol and water, separating in colourless prisms, m. p. 37° (Found: N, 7.8. $C_{11}H_{11}NS$ requires N, 7.4%).

2-Ethylthio-4-methylquinoline (cf. Roos, *loc. cit.*).—2-Thiol-4-methylquinoline (6.5 g.) was dissolved in 10% alkali (30 c.c.) and ethyl alcohol (20 c.c.), warmed to 40°, and treated with ethyl iodide. A red oil separated almost immediately. The reaction mixture was kept at 40—50° for 20 minutes, cooled, diluted with water, and extracted with chloroform. The extracts were washed with 2% alkali and finally with water, and then dried over sodium sulphate. The 2-ethylthio-4-methylquinoline left on removal of the solvent was distilled in a vacuum (Roos states that it decomposes on distillation, and gives no constants), b. p. 170—175°/14 mm.; yield 6—8 g. (Found: N, 7.4. $C_{12}H_{13}NS$ requires N, 6.9%).

2-isoPropylthio-4-methylquinoline.—2-Thiol-4-methylquinoline (16 g.) was dissolved in 8% aqueous alkali and alcohol (20 c.c.) and treated with *isopropyl* bromide (10 g.). The reaction

mixture was heated on a water-bath for 1 hour, the *isopropyl* derivative separating as a dark oil. The cooled reaction mixture was diluted with water and extracted with chloroform. The extracts were washed with 2% aqueous alkali and finally with water, and the *2-isopropylthio-4-methylquinoline* left on removal of the solvent was distilled in a vacuum; b. p. 170—173°/14 mm.; yield 9 g. (Found : N, 6.8. $C_{13}H_{15}NS$ requires N, 6.5%).

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