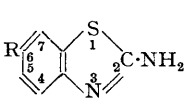
299. *The Ultra-violet Absorption Spectra of Some 2-Aminobenzthiazole and 2-Imino-3-methyl-2 : 3-dihydrobenzthiazole Derivatives.*

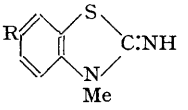
By J. R. Edisbury, R. F. Hunter, and A. D. Scott.

The ultra-violet absorption spectra of a number of 2-amino- and 2-imino-3-methyl-2 : 3 dihydro-benzthiazoles have been determined. There is a barely significant shift in absorption maximum towards the region of longer wave-length on replacing hydrogen by fluorine in the 6-position in 2-aminobenzthiazole, a marked shift when fluorine is replaced by chlorine, no further displacement when chlorine is replaced by bromine, and another small shift when iodine replaces bromine. Methylation of the aromatic nucleus causes small shifts towards the region of longer wave-length and a similar effect occurs on alkylation of the 2-amino-group.

The 2-imino-3-methyl-2 : 3-dihydrobenzthiazoles show two absorption bands, and the shift of that of higher wave-length which occurs on substitution of hydrogen by bromine in the 6-position is identical with that which occurs in the 2-aminobenzthiazole system.

In an investigation of the effect of substituents on the ultra-violet absorption of aromatic and aromatic heterocyclic compounds, the absorption spectra of a number of 2-aminobenzthiazole (I) and 2-imino-3-methyl-2 : 3-dihydrobenzthiazole (II) derivatives, and of 4-bromo-2-amino-


(I.)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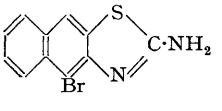
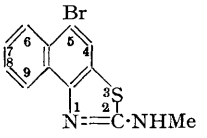

(III.)


(IV.)

ββ′-naphthathiazole (III) and 5-bromo-2-methylamino-β-naphthathiazole (IV) were examined. The results are summarised in the table below :

Compound.	Abs. maxima, mμ.	ε, max.
2-Aminobenzthiazole	263	12,900
6-Fluoro-2-aminobenzthiazole	264	11,400
6-Chloro-2-aminobenzthiazole	272	20,300
6-Bromo-2-aminobenzthiazole	272	15,500
6-Iodo-2-aminobenzthiazole	276	20,500
6-Chloro-4-bromo-2-methylaminobenzthiazole	280 and 233	19,000 and 38,500
2-Amino-4 : 6-dimethylbenzthiazole	269	15,900
2-*iso*Butylamino-4-methylbenzthiazole	272	13,250
2-Dimethylamino-4-methylbenzthiazole	283 and 230	24,000 and 12,900
2-Ethylamino-6-methylbenzthiazole	271	20,100
4-Bromo-2-amino-6-methylbenzthiazole	269	14,500
4-Bromo-2-*iso*butylamino-6-methylbenzthiazole	278	15,100
2-Imino-3-methyl-2 : 3-dihydrobenzthiazole	300 and 265	4850 and 8200
6-Bromo-2-imino-3-methyl-2 : 3-dihydrobenzthiazole	309 and 270	4900 and 9400
2-Imino-6-ethoxy-3-methyl-2 : 3-dihydrobenzthiazole	327 and 270	5650 and 7300
4-Bromo-2-amino-ββ′-naphthathiazole	265	48,800
5-Bromo-2-methylamino-β-naphthathiazole	258 and 340	41,500 and 10,800

In the 6-halogeno-2-aminobenzthiazoles, there is a barely significant shift towards the region of longer wave-length on passing from hydrogen to fluorine, a marked shift from fluorine to chlorine, no further displacement when chlorine is replaced by bromine, and finally another small shift when iodine replaces bromine (Fig. 1). This phenomenon is in general agreement with many of the physical properties of halogen-substituted compounds.

It is noteworthy that replacement of the 4-methyl group by bromine in 2-amino-4 : 6-dimethylbenzthiazole has practically no effect on the intensity of the absorption band whose maximum remains at the same wave-length (269 mμ) in 4-bromo-2-amino-6-methylbenzthiazole.

Methylation in the aromatic nucleus of the benzthiazole system causes a small shift of absorption maximum towards the region of longer wave-length. A similar effect occurs on alkylation of the 2-amino-group which increases with size of the alkyl substituent (cf. Burawoy, *J.*, 1939, 1177).

The appearance of the two absorption maxima in the 2-imino-3-methyl-2 : 3-dihydrobenzthiazoles and in 2-dimethylamino-4-methylbenzthiazole in all of which the semi-cyclic triad system [H]N·C:N ⇌ N:C·N[H] has been rendered static by substitution of " mobile " hydrogen by methyl (Hunter, *J.*, 1930, 125; Hunter and Jones, *ibid.*, p. 2190) (Fig. 2) is also interesting.

FIG. 1.

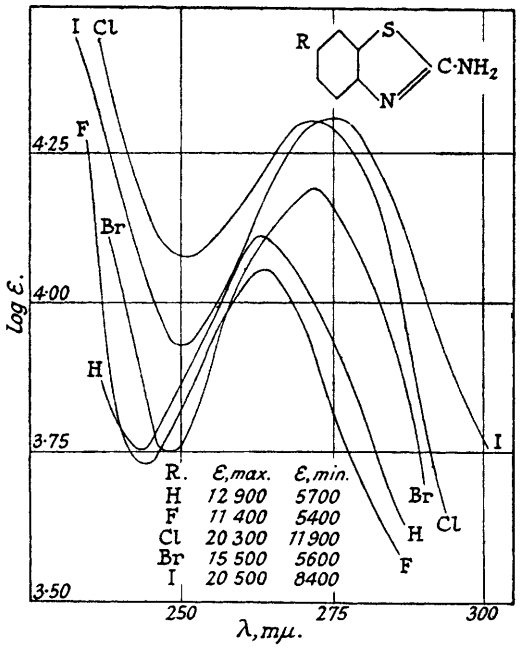
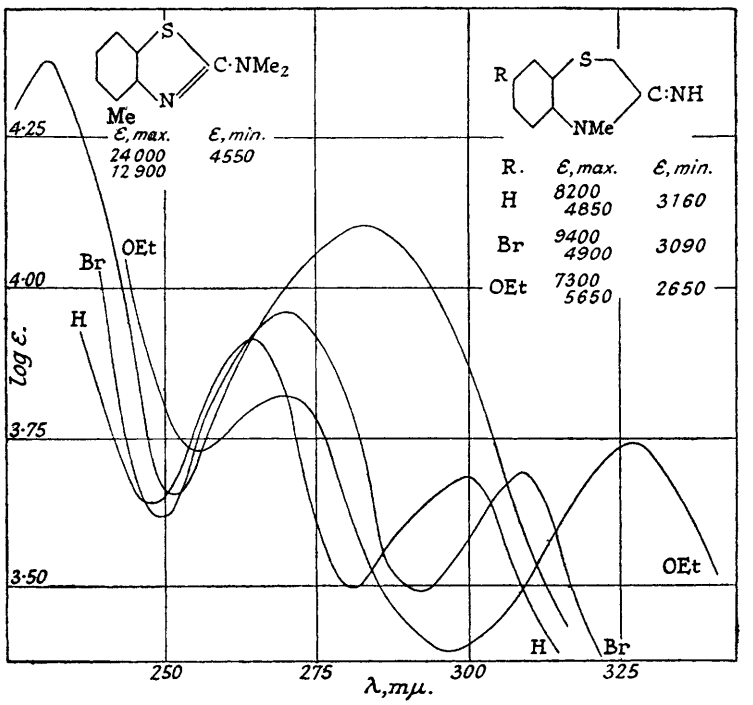


FIG. 2.



The shift of the absorption band of higher wave-length which occurs on substitution of hydrogen by bromine in the 6-position in 2-imino-3-methyl-2 : 3-dihydrobenzthiazole (9 mμ) is identical with that which occurs in the 2-aminobenzthiazole system.

The high absorption of 4-bromo-2-amino-ββ′-naphthathiazole and of 5-bromo-2-methylamino-β-naphthathiazole is evidently connected with the presence of the additional fused aromatic ring, the systems being essentially diheteroanthracene and phenanthrene respectively.

Experimental.

The specimens measured were either those described in the following references or prepared as described in these papers. Benzthiazoles: 2-amino- (Hunter, *J.*, 1926, 1385); 6-fluoro-2-amino- (Dyson, Hunter, Jones, and Styles *J. Indian Chem. Soc.*, 1931, **8**, 147); 6-chloro-2-amino- (Dyson, Hunter, and Morris, *J.*, 1927, 1186); 6-bromo-2-amino- (Hunter, *loc. cit.*); 6-iodo-2-amino- (Dyson, Hunter, Jones, and Styles, *loc. cit.*); 6-chloro-4-bromo-2-methylamino- (Dyson, Hunter, Jones, and Styles, *loc. cit.*); 2-amino-4 : 6-dimethyl- (Hunter and Pride, *J.*, 1929, 943); 2-*iso*butylamino-3-methyl- (Dyson, Hunter, Jones, and Styles, *loc. cit.*); 2-dimethylamino-4-methyl- (Hunter and Styles, *J.*, 1927, 1209); 2-ethylamino-6-methyl- (Dyson, Hunter, Jones, and Styles, *loc. cit.*); 4-bromo-2-amino-6-methyl- (Hunter, *J.*, 1926, 1385); 4-bromo-2-*iso*butylamino-6-methyl- (Dyson, Hunter, Jones, and Styles, *loc. cit.*); 2-imino-3-methyl-2 : 3-dihydro- (Hunter, *J.*, 1926, 1385); 6-bromo-2-imino-3-methyl-2 : 3-dihydro- (Hunter, *J.*, 1930, 125); 2-imino-6-ethoxy-3-methyl-2 : 3-dihydro- (Hunter and Jones, *J.*, 1930, 2190). 4-Bromo-2-amino-ββ′-naphthathiazole (Hunter and Jones, *J.*, 1930, 941). 5-Bromo-2-methylamino-β-naphthathiazole (Chiragh Hasan and Hunter, *J. Indian Chem. Soc.*, 1933, **10**, 82).

The compounds were dissolved in absolute alcohol and diluted as necessary.

Measurements of ultra-violet light absorption were made on a Hilger (E 498) quartz medium spectrograph with Spekker photometer, using a condensed spark between tungsten-steel electrodes. Kodak Type IV 0 plates were used in most instances for the purpose of providing adequate photographic contrast.

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