# The Near-ultra-violet Absorption Spectra of Some Heterocyclic Compounds. Part II.\* Benzothiazoles.

By A. CERNIANI and R. PASSERINI.

## [Reprint Order No. 5014.]

The work of Part I \* on benzoxazoles is supplemented by a similar study of benzothiazole and its derivatives. The suggestions made for benzoxazoles concerning the locations of chromophores, their resonance when overlapped, and effect of hydrogen bonding are confirmed for the benzothiazole series. A general bathochromic shift without intensification, from benzoxazole to benzothiazole compounds, which is found in the bands assigned to the benzoring chromophore, is attributed to a shift of relative conjugating power of O and S from the order O>S in the ground state of the carbon  $2p\pi$  shell, towards the order O<S, as the  $2p\pi$  shell becomes enlarged in electronically excited states.

For comparison with the spectra (Part I \*) of benzoxazole and its substitution products, the near-ultra-violet absorption spectra of benzothiazole and a series of analogous derivatives are now described. These spectra are generally so similar to those obtained in the preceding investigation that a sufficient account of the present work can be given by pointing out the correspondances in general terms and discussing in detail only the more important differences.

Benzothiazole and 2-Methylbenzothiazole (Table 1, Nos. 1 and 2; Fig.).—The spectrum of benzothiazole has been described by Lutskii and Sidorov (cf. Chem. Abs., 1948, 42, 2516), whose absorption curve differs markedly from that now recorded. The spectrum of 2-methylbenzothiazole has been described by Behaghel and Schneider (Ber., 1936, 69, 88) and by Lutskii and Sidorov (loc. cit.), and, more exactly by Kiprianov and Rozum (cf. Chem. Abs., 1952, 46, 3400), whose results agree well with those now given. The present results for the two compounds are mutually confirmatory, since the two spectra are almost identical, as would be expected.

The main difference between the spectra of benzoxazole and benzothiazole—a difference which runs all through the spectra of their derivatives, with certain exceptions pointed out below—is that, relatively to the oxygen compound, the sulphur compound shows bathochromic shifts of the bands, without intensification. The first band-system of benzothiazole, which, like that of benzoxazole, is assigned as a transition to the  $B_{2u}$ -derived state of the benzo-ring chromophore, has its main maximum at 285 m $\mu$  (instead of 270 m $\mu$ ), the vibrational structure being similar in spacing and intensity distribution to that of the band-system of benzoxazole. The second electronic absorption, the upper state of which we associate, as before, with the benzene state classed as either  $B_{1u}$  or  $E_{2g}$ , appears at

• Part I, preceding paper.

### TABLE 1.

### (All spectra measured in ethyl-alcoholic solution.) 2-X-Substituted benzothiazoles.

				log		log					log		log
] «	X = H	M. p.*	λ <sub>max.</sub> 216 252 285 294	ε <sub>max</sub> . 4·38 3·76 3·22 3·13	λ <sub>min.</sub> 242 272 291	ε <sub>min.</sub> 3·80 3·17 3·19	11 ª	X = SMe	M. p.* 52°	$\lambda_{max.}$ 224 (244) 278 (287) 200	$\epsilon_{max.}$ 4·31 3·94 4·12 4·06 2.04	λ <sub>min.</sub> 253 297	ε <sub>min.</sub> 3∙78 3∙91
2 ª	CH3		218 252 283 293	4·34 3·87 3·20 3·14	244 277 289	3·76 3·10 3·00	12•	SPh	—	299 223 281 300	3·94 4·41 4·08 3·96	254	3∙86
3 •	C <sub>6</sub> H <sub>5</sub>	112— 113°	226 248 256	4·31 3·89 3·90	222 244 252	4·30 3·85 3·88	131	S•C <sub>6</sub> H <sub>4</sub> Me- <i>o</i>	—	221 276 300	4·54 4·20 4·05	252 298	3.99 4.04
4 <sup>b</sup>	C <sub>6</sub> H₄•OH- <i>o</i>	1 <b>31</b> — 132	297 249 258	4·29 3·79 3·85	201 246 253	3·85 3·74 3·77	14,			277 300	4·06 3·93	299 299	3.92
50	C. H. •OH-4	991	288 333 251	4·12 4·20	262 308 248	3·72 3·95 3·70	159	S•C <sub>6</sub> H₄Me- <i>p</i>	72	224 282 300	4·46 4·12 3·99	254 298	3.89 3.98
5-	C <sub>8</sub> 114 <sup>.</sup> O11- <i>p</i>	222	$251 \\ 258 \\ 320 $	3.71 3.70 4.37	$\frac{248}{256}$ $264$	3.69 3.66	16 *	NHPh	160	222 (238) 302	4·29 4·24 4·39	254	3.61
6 <sup>s</sup>	C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> - <i>m</i>	184	224 254 296— 300	$4 \cdot 42 \\ 4 \cdot 16 \\ 4 \cdot 23$	240 260	4∙05 4∙11	175	NH•C6H4Me-0	127.5	224 (235) 284	4·29 4·20 4·18	252	3.78
7 <sup>b</sup>	C <sub>6</sub> H₄·NO₂- <i>p</i>	228	222 (246) 333	4·36 3·93 4·30	276	<b>3</b> ∙59	187	NH•C <sub>6</sub> H <sub>4</sub> Me-m	124	220 (235) 304	4·39 4·24 4·40	254	3.59
8,	C <sub>6</sub> H <sub>4</sub> ·NH <sub>2</sub> -m	140	230 296	4·44 4·22	266	<b>4</b> ·05	191	NH∙C <sub>6</sub> H₄Me-p	182— 183	222 (245) 303	4·33 4·14 4·40	254	3.66
9.8	$C_6H_4$ ·N $H_2$ - $p$	150	222 (252) 356	4·30 3·69 4·56	274	3∙41	20 5	NH·C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> -m	189— 190	235 306 360	4·35 4·46 3·16	254 335	4∙01 3∙09
10 °	C <sub>6</sub> H <sub>4</sub> ·NMe <sub>2</sub> -p	173	223 (258) 356	4·32 3·80 4·56	280	3.31	21 i	NH·C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> -p	223	231 266 372	4·46 4·13 4·42	244 302	4∙02 3∙44
	6-Nitro-2-X-benzothiazoles.												
22 •	Н	176°	219 285	4·21 3·97	254	3.43	30 •	NHPh	247°	$219 \\ 232 \\ 273$	4·35 4·33 4·33	228 246 301	4·33 3·94 3·53
23 •	CH <sub>3</sub>	175	$\frac{218}{292}$	4.32	255	3.38				373	4.30	001	0.00
24 ª	C <sub>6</sub> H <sub>5</sub>	188	225 261 326	4·40 3·96 4·38	252 277	3∙94 3∙92	31 <sup>*</sup>	NH•C <sub>6</sub> H₄Me- <i>o</i>	215— 216	222 262 364	4·39 4·08 4·23	244 294	$3.91 \\ 3.41$
25 J	SMe	126	222 (244) 330	4·34 4·07 4·22	274	3.44	32 f	NH•C <sub>6</sub> H <sub>4</sub> Me-m	222	220 (230) 273	4·36 4·28 4·24	246 304	3∙85 3∙44
26 <sup>f</sup>	SPh	104	223 (245) 328	4·46 4·12 4·24	278	<b>3</b> ·59	33 ª	NH•C <sub>6</sub> H₄Me-p	242	375 222 (234)	4·29 4·33 4·31	246 306	3·90 3·52
275	S•C <sub>6</sub> H₄Me- <i>o</i>	101	224 (245) 328	4.53 4.17 4.90	276	<b>3</b> ∙68	0 4 4	NULC II NO	050	274 378	4·28 4·30	040	4.14
281	S•C <sub>6</sub> H₄Me-m	132— 134	224 (245)	4·54 4·18	276	3.73	34	NT ·U <sub>6</sub> H <sub>4</sub> ·NU <sub>2</sub> - <i>m</i>	200	230 267 360	4·37 4·34 4·33	240 298	3.65
29	S•C <sub>6</sub> H₄Me-p	144— 146	328 225 (245) 328	4·30 4·57 4·20 4·28	280	<b>3</b> ∙69	351	NH•C <sub>6</sub> H₄•NO₂- <i>p</i>	280	227 (245) (337) 382	4·42 4·13 4·10 4·61	286	3.43
											~		

Specimen kindly supplied by Prof. Colonna. <sup>b</sup> Bogert and Corbitt, J. Amer. Chem. Soc., 1926, 48, 783. <sup>c</sup> Bogert and Taylor, Chem. Abs., 1932, 26, 1281. <sup>d</sup> Hofmann, Ber., 1887, 20, 1791. <sup>e</sup> Brooker et al., J. Amer. Chem. Soc., 1941, 63, 3192. <sup>f</sup> See p. 2264. <sup>e</sup> Illuminati and Gilman, J. Amer. Chem. Soc., 1949, 71, 3351. <sup>k</sup> Hofmann, Ber., 1879, 12, 1130. <sup>e</sup> Hunter and Jones, J., 1930, 2190. Hasan, Hunter, and Firdaus, J., 1936, 1672. <sup>k</sup> Drozdov and Stavroskaja, Chem. Abs., 1940, 34, 103.
\* B. p.s of compounds as numbered were : (1) 95°/6 mm.; (2) 237°; (12) 183—187°/3 mm.; (13) 235—237°/17 mm.; (14) 245°/17 mm.

252 m $\mu$  (instead of 231 m $\mu$ ). A third absorption, whose upper state may be derived from the benzene  $E_{1\mu}$  state, could be seen in the spectrum of benzoxazole only in the first onset, but in that of benzothiazole comes well into the observed spectral range with a maximum at 216 m $\mu$ .

These bathochromic shifts would be expected from the assignments suggested. In benzoxazole there is some conjugation between the oxygen 2p electrons and the benzenoid  $2p\pi$  shell. In benzothiazole, for stereoelectronic reasons, somewhat weaker conjugation is expected between the sulphur 3p electrons and the carbon  $2p\pi$  shell. These statements apply to the ground state. But in the  $B_{2u}$ -derived excited states, in which the  $2p\pi$  shell is swollen, and also concentrated more over the atoms and less over the bond centres, sulphur conjugation gains a relative stereoelectronic advantage over oxygen conjugation, with the result that this upper state is depressed towards the ground state, with reduction in the transition energy, more in the sulphur than in the oxygen compound. Similar reasoning can be applied to the still higher states and transitions of the benzo-ring



chromophore. There seems to be no reason for expecting any substantial intensification, such as usually accompanies the more familiar bathochromic shifts due to extensions of conjugation.

2-Phenylbenzothiazole (Table 1, No. 3; Fig.).—As with benzoxazole, so with benzothiazole, the effect of a 2-phenyl substituent is to submerge the  $B_{2u}$ -like system, ascribed to the benzo-ring chromophore, in a much stronger, broad band of somewhat greater wave-length, while the shorter-wave part of the spectrum, containing the second and the third absorption assigned to the benzo-chromophore, remains almost unaffected by the substituent.

It is significant that, whereas in the shorter-wave absorptions of 2-phenylbenzothiazole, the already discussed bathochromic shifts, relatively to the spectrum of the oxygen analogue, are repeated, yet the long-wave band has an almost identical position and intensity in the two spectra ( $\lambda 297$ —299 mµ, log  $\varepsilon 4.3$ ). This is consistent with its assignment to the different, nearly independent, benzylidene-imine chromophore.

Hydroxy-, Nitro-, Amino-, and Dimethylamino-derivatives of 2-Phenylbenzothiazole (Table 1, Nos. 4-10). Apart from general similarities and differences, such as have been illustrated above, the spectra of these substituted 2-arylbenzothiazoles are so similar to those of the benzoxazole analogues that the analysis in the preceding paper may be considered to apply.

However, data are given for the hydroxy-compounds (cf. Table 1 of Part I), in confirmation of the theory of hydrogen-bonding in the *o*-hydroxyphenyl compounds with the hetero-nitrogen atom. If we had tried to set up the alternative hypothesis of conjugation with the hetero-oxygen atom, it could not have been carried over into the benzothiazole series, since hydrogen-bonding with thiazole sulphur is inconceivable, the unshared electrons of neutral sulphur (in any form) having no noticeable affinity for protons.

2-Methylthio-, 2-Arylthio-, and 2-Arylamino-benzothiazoles (Table 1, Nos. 11-21). The ultra-violet spectrum of 2-methylthiobenzothiazole has been described by Morton and Stubbs (J., 1939, 1321), whose results agree with ours. The spectrum of 2-phenylthiobenzothiazole is closely similar. These spectra, and that of 2-anilinobenzothiazole, as well as the spectra of all the derivatives having methyl or nitro-groups in the 2-phenylthioor 2-phenylamino-residue, are similar to the spectra of the corresponding benzoxazole compounds, apart from general differences, as already illustrated, and one further noteworthy difference. In general, then, the relevant discussion in the preceding paper may be considered to apply. The new point is that the long-wave absorption in the 2-thiocompounds, which was, and is, assigned to the introduced thioamide chromophore, is broader in the benzothiazole than in the benzoxazole series. Tentatively, we ascribe the broadening to a resonance, consequent on the presence of two identical atoms (sulphur) similarly involved in the thioamide (now dithiocarbamate) structure in the benzothiazole.

TABLE 2.

			Found :	Regd. :			
Benzothiazoles	М.р.	Formula	N, %	N, %			
2-o-Tolylthio-	*	C <sub>14</sub> H <sub>11</sub> NS	5.45	5.4			
2-m-Tolylthio-	†	,,	5.5	5.4			
2-o-Toluidino-	127°	$C_{14}H_{12}N_{2}S$	11.8	11.65			
2-m-Toluidino-	124		11.8	11.65			
2-m-Nitroanilino-	190	C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> N <sub>3</sub> S	15.6	15.5			
6-Nitro-2-phenylthio-	104	$C_{13}H_8O_8N_3S$	9.9	9.7			
6-Nitro-2-o-tolylthio-	102	$C_{14}H_{10}O_{2}N_{2}S_{2}$	9·4	9.3			
6-Nitro-2-m-tolylthio-	134		9.5	9· <b>3</b>			
6-Nitro-2-p-tolylthio-	146	**	9.5	9.3			
6-Nitro-2-m-toluidino-	<b>222</b>	$C_{14}H_{11}O_{2}N_{3}S$	15.0	14.7			
* B. p. 237°/17 mm.	† B. p. 245°/17 mm.						

6-Nitrobenzothiazole, and its 2-Methyl-, 2-Phenyl-, 2-Methylthio-, 2-Arylthio-, and 2-Arylamino-derivatives (Table 1, Nos. 22—35).—The importance of these spectra is that they confirm the rule, deduced in the preceding paper, that large separations between the longer- and shorter-wave absorptions appear when a 6-nitro-group is present simultaneously with an unsaturated 2-substituent, thus supporting the presumed locations of the chromophores by the observation of electronic splittings resulting from their overlap.

#### EXPERIMENTAL

The specimens measured were either obtained as noted in the references under Table 1, or prepared as here described. Except for 6-nitro-2-*m*-nitrophenylbenzothiazole, all the products detailed in Table 2 were obtained by heating under reflux equimolecular ethanolic solutions of 2-chloro- or 6-nitro-2-chloro-benzothiazole and the appropriate potassium mercaptide or aniline derivative. The products were purified by distillation under reduced pressure, or by crystallisation after evaporation of the ethanol.

For the preparation of 6-nitro-2-m-nitrophenylbenzothiazole, equivalent amounts of 2-chloro-6-nitrobenzothiazole and m-nitroaniline were heated in an oil-bath at 160—190° for 2 hr. The product was crystallised, first from acetic acid, and then from nitrobenzene, forming yellow needles, m. p. 257° (Found : N, 17.8.  $C_{18}H_8O_4N_4S$  requires N, 17.7%).

Light-absorption measurements were made as indicated in Part I.

The authors thank Professor M. Colonna for furnishing the spectral data for the first three compounds listed in Table 1 (cf. Fig.), and Professor C. K. Ingold, F.R.S., for helpful discussion of the spectroscopic data.

Istituto di Chimica Industriale dell' Universita, Bologna.

[Received, January 6th, 1954.]