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

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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 benzo-ring 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 Lutskiĭ 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 Lutskiĭ 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 mμ (instead of 270 mμ), 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

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* Part I, preceding paper.

TABLE 1.

(All spectra measured in ethyl-alcoholic solution.)

2-*X*-Substituted benzothiazoles.

	X =	M. p.*	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
1[a]	H	—	216	4·38	242	3·80
			252	3·76	272	3·17
			285	3·22	291	3·19
			294	3·13		
2[a]	CH_3	—	218	4·34	244	3·76
			252	3·87	277	3·10
			283	3·20	289	3·00
			293	3·14		
3[a]	C_6H_5	112—	226	4·31	222	4·30
		113°	248	3·89	244	3·85
			256	3·90	252	3·88
			297	4·29	261	3·83
4[b]	C_6H_4·OH-*o*	131—	249	3·79	246	3·74
		132	258	3·85	253	3·77
			288	4·12	262	3·72
			333	4·20	308	3·95
5[b]	C_6H_4·OH-*p*	221—	251	3·71	248	3·70
		222	258	3·70	256	3·69
			320	4·37	264	3·66
6[b]	C_6H_4·NO_2-*m*	184	224	4·42	240	4·05
			254	4·16	260	4·11
			296—	4·23		
			300			
7[b]	C_6H_4·NO_2-*p*	228	222	4·36	276	3·59
			(246)	3·93		
			333	4·30		
8[b]	C_6H_4·NH_2-*m*	140	230	4·44	266	4·05
			296	4·22		
9[b]	C_6H_4·NH_2-*p*	150	222	4·30	274	3·41
			(252)	3·69		
			356	4·56		
10[c]	C_6H_4·NMe_2-*p*	173	223	4·32	280	3·31
			(258)	3·80		
			356	4·56		
11[d]	SMe	52°	224	4·31	253	3·78
			(244)	3·94	297	3·91
			278	4·12		
			(287)	4·06		
			299	3·94		
12[e]	SPh	—	223	4·41	254	3·86
			281	4·08		
			300	3·96		
13[f]	S·C_6H_4Me-*o*	—	221	4·54	252	3·99
			276	4·20	298	4·04
			300	4·05		
14[f]	S·C_6H_4Me-*m*	—	221	4·43	254	3·91
			277	4·06	299	3·92
			300	3·93		
15[g]	S·C_6H_4Me-*p*	72	224	4·46	254	3·89
			282	4·12	298	3·98
			300	3·99		
16[h]	NHPh	160	222	4·29	254	3·61
			(238)	4·24		
			302	4·39		
17[f]	NH·C_6H_4Me-*o*	127·5	224	4·29	252	3·78
			(235)	4·20		
			284	4·18		
18[f]	NH·C_6H_4Me-*m*	124	220	4·39	254	3·59
			(235)	4·24		
			304	4·40		
19[i]	NH·C_6H_4Me-*p*	182—	222	4·33	254	3·66
		183	(245)	4·14		
			303	4·40		
20[f]	NH·C_6H_4·NO_2-*m*	189—	235	4·35	254	4·01
		190	306	4·46	335	3·09
			360	3·16		
21[i]	NH·C_6H_4·NO_2-*p*	223	231	4·46	244	4·02
			266	4·13	302	3·44
			372	4·42		

6-Nitro-2-*X*-benzothiazoles.

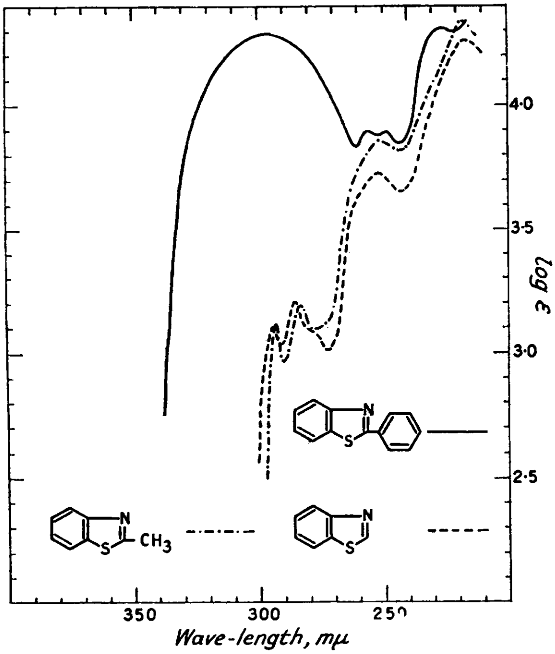
	X =	M. p.*	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
22[a]	H	176°	219	4·21	254	3·43
			285	3·97		
23[a]	CH_3	175	218	4·32	255	3·38
			292	4·07		
24[a]	C_6H_5	188	225	4·40	252	3·94
			261	3·96	277	3·92
			326	4·38		
25[j]	SMe	126	222	4·34	274	3·44
			(244)	4·07		
			330	4·22		
26[f]	SPh	104	223	4·46	278	3·59
			(245)	4·12		
			328	4·24		
27[f]	S·C_6H_4Me-*o*	101	224	4·53	276	3·68
			(245)	4·17		
			328	4·29		
28[f]	S·C_6H_4Me-*m*	132—	224	4·54	276	3·73
		134	(245)	4·18		
			328	4·30		
29	S·C_6H_4Me-*p*	144—	225	4·57	280	3·69
		146	(245)	4·20		
			328	4·28		
30[a]	NHPh	247°	219	4·35	228	4·33
			232	4·33	246	3·94
			273	4·33	301	3·53
			373	4·30		
31[k]	NH·C_6H_4Me-*o*	215—	222	4·39	244	3·91
		216	262	4·08	294	3·41
			364	4·23		
32[f]	NH·C_6H_4Me-*m*	222	220	4·36	246	3·85
			(230)	4·28	304	3·44
			273	4·24		
			375	4·29		
33[a]	NH·C_6H_4Me-*p*	242	222	4·33	246	3·90
			(234)	4·31	306	3·52
			274	4·28		
			378	4·30		
34[f]	NH·C_6H_4·NO_2-*m*	256	230	4·37	246	4·14
			267	4·34	298	3·65
			360	4·33		
35[f]	NH·C_6H_4·NO_2-*p*	280	227	4·42	286	3·43
			(245)	4·13		
			(337)	4·10		
			382	4·61		

[a] Specimen kindly supplied by Prof. Colonna. [b] Bogert and Corbitt, *J. Amer. Chem. Soc.*, 1926, **48**, 783. [c] Bogert and Taylor, *Chem. Abs.*, 1932, **26**, 1281. [d] Hofmann, *Ber.*, 1887, **20**, 1791. [e] Brooker *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3192. [f] See p. 2264. [g] Illuminati and Gilman, *J. Amer. Chem. Soc.*, 1949, **71**, 3351. [h] Hofmann, *Ber.*, 1879, **12**, 1130. [i] Hunter and Jones, *J.*, 1930, 2190. Hasan, Hunter, and Firdaus, *J.*, 1936, 1672. [k] 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 mμ (instead of 231 mμ). A third absorption, whose upper state may be derived from the benzene E_{1u} 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 mμ.

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 (λ 297—299 mμ, log ε 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-phenylthio- or 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-thio-compounds, 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.

Benzothiazoles	M. p.	Formula	Found : N, %	Reqd. : N, %
2-*o*-Tolylthio-	—*	$C_{14}H_{11}NS$	5·45	5·4
2-*m*-Tolylthio-	—†	,,	5·5	5·4
2-*o*-Toluidino-	127°	$C_{14}H_{12}N_2S$	11·8	11·65
2-*m*-Toluidino-	124	,,	11·8	11·65
2-*m*-Nitroanilino-	190	$C_{13}H_9O_2N_3S$	15·6	15·5
6-Nitro-2-phenylthio-	104	$C_{13}H_8O_2N_2S$	9·9	9·7
6-Nitro-2-*o*-tolylthio-	102	$C_{14}H_{10}O_2N_2S_2$	9·4	9·3
6-Nitro-2-*m*-tolylthio-	134	,,	9·5	9·3
6-Nitro-2-*p*-tolylthio-	146	,,	9·5	9·3
6-Nitro-2-*m*-toluidino-	222	$C_{14}H_{11}O_2N_3S$	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. $C_{13}H_8O_4N_4S$ requires N, 17·7%).

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

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