The Near-ultra-violet Absorption Spectra of Some Heterocyclic Compounds. Part I. Benzoxazoles.

By R. Passerini.

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The ultra-violet absorption spectra of benzoxazole and many mono- and di-substituted derivatives have been investigated to 210 mμ, the substituents being CH_3, C_6H_5, NO_2, SR, and NR_2 (R = H, alkyl, aryl, or acyl). Interpretations are offered on the basis of essentially localised chromophores, with resonance interaction between them in suitable structural circumstances.

Following previous work on the electronic spectra of some benziminazoles (Mangini Montanari, and Passerini, *Atti Accad. Lincei*, 1952, **12**, 411), a systematic survey of the spectra of heterocyclic compounds is being undertaken, and this paper relates to benzoxazoles. Earlier records of these spectra (Behaghel and Schneider, *Ber.*, 1936, **69**, 93; Ramart-Lucas and Vantu, *Bull. Soc. chim.*, 1936, **3**, 1165) are too fragmentary, and such few spectra as are recorded are inadequate for the discussions which follows. The new data are recorded in Tables 1 and 2, and in the figure.

Benzoxazole and 2-Methylbenzoxazole (Table 1, Nos. 1 and 2).—These spectra are closely similar. The first absorption system, around 270 mμ, is obviously derived from the B_{2u} benzene system, and shows the characteristic vibrational structure. Thus the benzo-ring, and not the hetero-ring, is regarded as the basic chromophore. The moderate bathochromic shift and intensification, relative to the benzene system at 255 mμ, would be a normal result of weak conjugation by the hetero-atoms with the benzo-ring. Similar effects are found in anisole (Robertson, Sheriff, and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 1539; Cerniani, Passerini, and Righi, *Gazzetta*, 1954, **84**, in the press), benzofuran

(Andrisano and Pappalardo, *ibid.*, 1953, **83**, 108), and benziminazole (Steck, Nachod, Ewing, and Gorman, *J. Amer. Chem. Soc.*, 1948, **70**, 3406; Mangini *et al.*, *loc. cit.*).

The second absorption system at 231 mμ has about the position and intensity to be expected if it is derived from the second absorption system of benzene, which, according to our present knowledge, may belong to either species B_{1u} or E_{2g}, and has its onset at 203 mμ. This tentative argument is somewhat strengthened by the consideration that it seems possible to interpret the spectra of all the derivatives described below without

TABLE 1.

(Solutions are in ethyl alcohol except where otherwise indicated.)

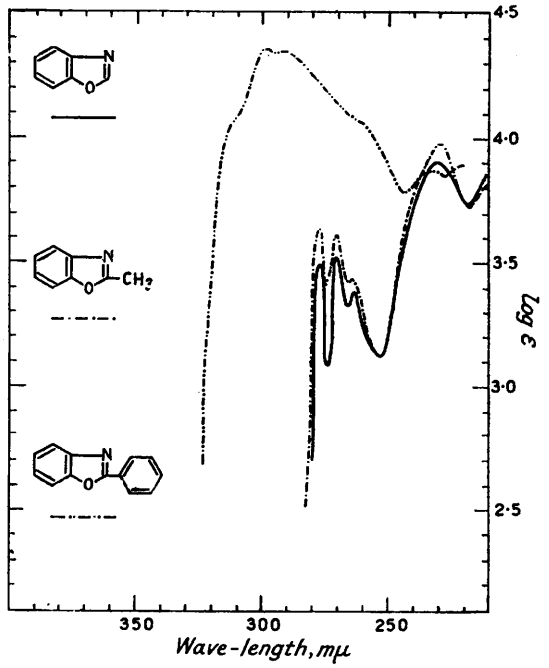
X =	M. p.	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
2-*X*-Benzoxazoles.					
1[a] H	182·5° *	231	3·90	218	3·74
		263	3·38	253	3·12
		270	3·53	266	3·32
		276	3·51	274	3·08
2[b] CH_3	201 *	231	3·97	218	3·73
		264	3·43	253	3·12
		270	3·61	266	3·42
		276	3·64	275	3·40
3[c] C_6H_5	102	234	3·86	227	3·85
		(260)	4·05	243	3·78
		292	4·34	295	4·33
		299	4·35		
		(310)	4·08		
4[d] C_6H_4Me (*o*)	69	236	3·88	233	3·87
		(270)	4·13	243	3·86
		292	4·30		
		(313)	4·10		
5[d] C_6H_4Me (*m*)	71	240	3·83	234	3·84
		(270)	4·13	244	3·78
		294	4·36	296	4·35
		(310)	4·00		
6[e] C_6H_4Me (*p*)	114	240	3·83	230	3·76
		(275)	4·13	244	3·79
		295	4·36	298	4·35
		302	4·37		
		(313)	4·10		
7[f] C_6H_4·OH (*o*)	124	263	4·05	245	3·72
		272	4·11	266	4·05
		281	4·17	277	4·08
		285	4·17	283	4·15
		293	4·30	288	4·10
		319	4·23	299	3·96
		331	4·18	326	4·18
5-Nitro-2-*X*-benzoxazoles.					
16[d] H	127	224	4·39	250	3·59
		270	3·84		
		(335)	2·60		
17[e] CH_3	154	226	4·42	252	3·56
		274	3·84		
		(335)	2·83		
6-Nitro-2-*X*-benzoxazoles.					
21[h] H	125	282	4·01	242	3·20
22[g] CH_3	151	290	4·04	246	3·39
5-Methyl-2-*p*-nitrophenylbenzoxazole.					
25[f]		234	4·12	222	4·06

X =	M. p.	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
7 C_6H_4·OH (*o*) aq. N-HCl	—	(263)	4·06	276	4·10
		274	4·13	288	4·12
		286	4·18	298	3·99
		292	4·30		
		318	4·26		
		(339)	4·19		
C_6H_4·O⁻ (*o*) aq. N-NaOH	—	220	4·40	260	3·92
		286	4·06	306	3·00
		352	4·08		
8[d] C_6H_4·OH (*p*)	250°	(273)	4·07	240	3·43
		305	4·47		
9[c] C_6H_4·OMe (*p*)	99	(275)	4·13	238	3·54
		306	4·51		
10[c] C_6H_4·NO_2 (*m*)	211	222	4·20	218	4·20
		265	4·27	244	4·06
		295	4·32	275	4·24
11[c] C_6H_4·NO_2 (*p*)	268	232	4·13	218	4·01
		327	4·33	268	3·53
12[c] C_6H_4·NH_2 (*m*)	178	228	4·31	244	4·15
		256	4·19	270	4·12
		296	4·36		
		(310)	3·77		
13[c] C_6H_4·NH_2 (*p*)	170	222	4·07	254	3·26
		(276)	3·74		
		327	4·50		
14[c] C_6H_4·NHAc (*p*)	212	(225)	4·15	247	3·50
		316	4·51		
15[f] C_6H_4·NMe_2 (*p*)	183	230	4·02	270	3·24
		(308)	3·97		
		345	4·66		
18[c] C_6H_5	172	214	4·16	232	3·86
		269	4·48		
19[f] C_6H_4·NO_2 (*p*)	258	232	4·18	216	4·12
		(300)	4·20	255	4·03
		324	4·27		
20[f] C_6H_4·NHAc (*p*)	259	225	4·22	248	3·85
		310	4·50		
23[c] C_6H_5	180	258	4·09	238	3·95
24[f] C_6H_4·NO_2 (*p*)	221	332	4·50	252	3·86
		334	4·33	273	3·64

[a] Bamberger, *Ber.*, 1903, **36**, 2051. [b] Light & Co., redistilled. [c] Stephens and Bower, *J.*, 1949, 2971. [d] See p. 2260. [e] Holljes and Wagner, *J. Org. Chem.*, 1944, **9**, 31. [f] Specimen kindly supplied by Dr. F. F. Stephens of Glaxo Laboratories. [g] Phillips, *J.*, 1930, 2685. [h] *Chem. Zentr.*, 1927, II, 1308; cf. F.P. 575,663. * B. p.s.

assuming that a specific excitation of the aromatic π shell of the hetero-ring is under observation.

5- *and* 6-*Nitro-benzoxazole and* -2-*methylbenzoxazole* (Table 1, Nos. 16, 17, 21, and 22).—These four spectra are similar. The first absorption appears as a moderately strong, structureless band near 270 mμ. This is a normal result of that strong conjugation between a nitro-group and a benzene ring, which is best regarded as producing a combined nitrophenyl chromophore (Mangini and Passerini, *J.*, 1952, 1168). The insensitiveness of this absorption to the position of the nitro-group shows that through-conjugation with the hetero-atoms is weak: if it were strong, as, *e.g.*, in *p*-nitrophenol, we should expect a large further bathochromic shift (cf. Burawoy and Chamberlain, *J.*, 1952, 2310). The fact that the spectra are scarcely changed in concentrated sulphuric acid points in the same direction. Theoretically, such through-conjugation should be weak, since the only non-polar, non-bridged (and therefore the main) valency structure of the hetero-ring (I) stereo-



electronically restricts nitrogen, as well as oxygen, conjugation to that fundamentally involved in the π-shell of the hetero-ring.

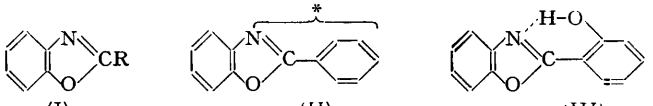
2-*Phenyl-*, 2-o-, -m-, *and* -p-*Methyl-*, 2-o- *and* -p-*Hydroxy-phenyl-, and* 2-p-*Methoxy-phenyl-benzoxazole* (Table 1, Nos. 3—9).—The spectra of all these 2-aryl derivatives are generally similar, with one notable exception mentioned below, and they differ remarkably from the spectra of the non-arylated benzoxazoles. This exception apart, they are characterised by a strong and very broad first absorption near 300 mμ. It is believed that this contains, as a weaker component, possibly to be seen in the shoulders on the short-wave sides of the main bands, the already discussed first band-system of the benzo-ring chromophore. The stronger and longer-wave absorption is ascribed to the newly introduced benzylidene-imine chromophore [with asterisk in (II)]. There are no stereo-electronic restrictions on conjugation between the phenyl ring and the hetero-ring, and, for the reason mentioned in the preceding paragraph, we thus expect conjugation to extend mainly to the nitrogen atom. The interaction is strong enough to justify our regarding it as producing a new combination chromophore. However, the C:N-unit is only weakly electronegative, and thus through-conjugation with *para*-situated hydroxyl or methoxyl groups modifies the spectrum only slightly.

It is the *ortho*-hydroxyl substituent which produces the striking spectral modification, breaking the broad band up into two band systems, of which the short-wave one shows well-developed vibrational structure, while the long-wave one is moved slightly to longer waves and is weakened. It may be suggested that these effects arise from hydrogen bonding (III), which, by charging the nitrogen atom positively, reduces the benzylidene-imine conjugation, and allows the benzo-ring absorption to appear separately, perhaps with a superimposed first absorption (B_{2u} type) of the phenyl ring chromophore, acting to some extent independently.

m- *and* p-*Amino-*, p-*Acetamido-, and* p-*Dimethylamino-benzoxazole* (Table 1, Nos. 12—15).—The three forms of *p*-amino-substituent produce bathochromic shifts of the long-wave band ascribed above to the benzylidene-imine chromophore. With methoxy- and hydroxy-substituents included for comparison, the displacements are in the order $NMe_2 > NH_2 > NHAc > OMe,OH > H$, the maxima appearing respectively at 345, 327, 316, 306, 305, and 299 mμ. The order of the groups is that of *o* : *p*-orienting power in electrophilic substitution, as far as this is known (Ingold and Ingold, *J.*, 1926, 1310). Evidently the *p*-amino-group, except when acylated, can enter strongly into the benzylidene-imine conjugation.

The *m*-amino-group cannot, of course, do so; and accordingly, the spectrum of this substitution-product is very different. It consists of a dominant long-wave band, which, from its position and intensity, may be correlated with the main band, ascribed to the benzylidene-imine chromophore in the unsubstituted 2-phenyl compound, and two overlapped shorter-wave systems, which might arise from the aniline and the benzo-ring chromophores.

5-, 6-, 3'-, *and* 4'-*Nitro-derivatives of* 2-*Phenylbenzoxazole* (Table 1, Nos. 10, 11, 18—20, and 23—25).—A *m*- or *p*-nitro-substituent in the phenyl ring produces spectral effects sufficiently similar to those of correspondingly situated amino-groups to render detailed discussion unnecessary. Just as the nitro-group like the amino-group is conjugated heavily with the simple benzene ring, so both groups must be considered to form united and more complex chromophores with the benzylidene-imine system.



(I) (II) (III)

The 5- and 6-nitro-derivatives of 2-phenyl- or of substituted 2-phenyl-benzoxazoles show spectra which, in first approximation, can be understood as superposed effects of excitation of the already discussed chromophores, separately present in 5- or 6-nitro-benzoxazole and in 2-phenylbenzoxazole. In second approximation, however, the nitro-benzo- and benzylidene-imino-chromophores interact, with the result that the two bands are found, not at 300 and 280 mμ, but further apart, with certain transfers of intensity between them. The separation is relatively small in the 5-nitro-compounds, but considerable in the 6-nitro-derivatives, the two bands in 6-nitro-2-phenylbenzoxazole itself appearing at 322 and 258 mμ. This larger separation is to be expected, since the 6-nitro-group of the one elementary chromophore is formally conjugated with the imino-nitrogen atom of the other, and hence resonance between the unit chromophores, thus overlapped, is readily possible.

2-*Methylthio- and* 2-*Phenylthio-benzoxazole* (Table 2, Nos. 1 and 2).—The spectra of these two benzoxazoles are similar. They show that the 2-thio-group modifies the benzoxazole spectrum similarly to the 2-phenyl group. The main difference is that the long-wave band-system, near 280 mμ, now attributed to the introduced thioamide type of conjugation is narrower than that of the benzylidene-imine chromophore, and does not wholly overlap the benzo-ring system, which can be seen near 250 mμ.

2 *Anilinobenzoxazole* (Table 2, No. 4).—This spectrum is similar to those of the 2-thio-compounds, except that the long-wave system, which must here be attributed to the newly introduced amidine type of conjugation, appears at slightly longer wave-length,

TABLE 2.

2-*X*-Substituted benzoxazoles.

X =	M. p.*	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
1[a] SMe	—	249	4·07	236	3·75
		278	4·09	264	3·81
		286	4·06	282	3·96
2[b] SPh	—	247	4·09	228	3·96
		280	4·10	265	3·96
		286	4·11	283	4·09
3[b] S·C_6H_4Me (*p*)	—	247	4·18	232	4·01
		279	4·16	268	4·02
		286	4·17	283	4·13
4[c] NHPh	175°	261	4·31	235	3·54
		288	4·41	272	4·11
		296	4·40		
5[d] NH·C_6H_4Me (*m*)	145°	264	4·30	235	3·57
		290	4·42	272	4·12
		296	4·41		
6[d] NH·C_6H_4Me (*p*)	182	263	4·32	235	3·56
		288	4·44	272	4·13
7[e] NH·C_6H_4·NO_2 (*m*)	192—194	259	4·38	230	3·93
		287	4·50	272	4·26
		354	3·13	320	2·95
8[b] NH·C_6H_4·NO_2 (*p*)	230—231	245	4·21	224	3·91
		276	3·78	272	3·76
		284	3·72	282	3·71
		356	4·31	294	3·44

6-Nitro-2-*X*-benzoxazoles.

X =	M. p.*	$\lambda_{max.}$	log $\varepsilon_{max.}$	$\lambda_{min.}$	log $\varepsilon_{min.}$
9[f] SMe	123—125°	243	4·03	227	3·97
		321	4·18	265	3·43
10[b] SPh	121—122	241	4·13	228	4·07
		320	4·22	274	3·78
11[b] S·C_6H_4Me (*o*)	106—108	242	4·12	232	4·07
		318	4·17	282	3·84
12[b] S·C_6H_4Me (*m*)	110—112	241	4·10	230	4·06
		320	4·19	273	3·76
13[b] S·C_6H_4Me (*p*)	142—143	240	4·12	234	4·11
		322	4·23	271	3·61
14[b] NHPh	224—225	261	4·30	225	3·84
		359	4·29	292	3·38
15[b] NH·C_6H_4Me (*o*)	172—173	254	4·14	226	3·96
		354	4·24	284	3·36
16[b] NH·C_6H_4Me (*m*)	214—215	262	4·29	226	3·85
		364	4·28	296	3·39
17[b] NH·C_6H_4Me (*p*)	215—216	263	4·27	226	3·86
		366	4·24	298	3·44
18[e] NH·C_6H_4·NO_2 (*m*)	234	260	4·37	226	4·09
		349	4·30	298	3·79
19[b] NH·C_6H_4·NO_2 (*p*)	299—300	228	4·19	218	4·14
		366	4·49	272	3·58
		466	3·64	428	3·45

[a] Beilenson and Hamer, *J.*, 1939, 143. [b] Cerniani and Passerini, *Annali*, 1954, **44**, 3. [c] Kalchoff, *Ber.*, 1883, **16**, 1825. [d] Deck and Dains, *J. Amer. Chem. Soc.*, 1933, **55**, 4986. [e] See p. 2261. [f] Bower and Stephens, *J.*, 1951, 325.

* B. p.s. of compounds as numbered were: (1) 139—140°/20 mm.; (2) 193—196/14 mm.; (3) 215—216/14 mm.

about 292 mμ, and is somewhat stronger. The shorter-wave system, which may be again ascribed to the benzo-ring chromophore, now appears at 260 mμ.

Methyl- and Nitro-substitution Products of 2-Phenylthio- and 2-Anilino-benzoxazole (Table 2, Nos. 3 and 5—19).—The spectra of these derivatives present no unexpected features, and could be discussed on lines similar to those above.

EXPERIMENTAL

Compounds already recorded in the literature have been prepared as indicated in the footnotes to Tables 1 and 2. New substances were prepared as follows. 2-o-*Tolylbenzoxazole* was prepared by Hölljes and Wagner's general method (*J. Org. Chem.*, 1944, **9**, 31) for benzoxazole syntheses. *o*-Aminophenol (5 g.) and *o*-tolunitrile (5 g.) were heated in a sealed tube at 190—200° for 5 hr. The product was distilled under reduced pressure, b. p. 163—166°/15 mm.; it crystallised from aqueous ethanol (charcoal) in pale yellow needles, m. p. 69° (Found: N, 6·7. $C_{14}H_{11}ON$ requires N, 6·7%). 2-m-*Tolylbenzoxazole*, similarly prepared, had b. p. 190°/15 mm., and on crystallisation from aqueous ethanol formed pale yellow plates, m. p. 71° (Found: N, 6·7%). 2-p-*Hydroxyphenylbenzoxazole* was prepared by heating *o*-aminophenol with *p*-cyanophenol at 190—200° for 5 hr. The product was extracted with ethanol (100 ml.) by distillation of which it was obtained as a solid, which crystallised from aqueous ethanol in pale pink needles, m. p. 250° (Found: N, 6·7. $C_{13}H_9O_2N$ requires N, 6·6%). A suspension in sodium hydroxide solution (2N) of 2-*p*-hydroxyphenylbenzoxazole was treated with methyl sulphate, the mixture being kept alkaline to phenolphthalein. After 30 min., 2-*p*-methoxyphenylbenzoxazole was removed and crystallised from ethanol; it had m. p. 99° (cf. Stephens and Bower, *J.*, 1950, 1722). 5-*Nitrobenzoxazole* was obtained by distillation at 15 mm. of 2-formamido-4-nitrophenol (5 g.). Crystallisation from ethanol yielded prisms, m. p. 127° (Found: N, 17·1. $C_7H_4O_3N_2$ requires N, 17·1%). For the preparation of 2-m-*nitroanilinobenzoxazole*, 2-chlorobenzoxazole (3 g.) and *m*-nitroaniline (2·7 g.) were heated at 150—160° for 1 hr. The residue, after extraction

with acetic acid, was crystallised from ethanol (charcoal); it had m. p. 193—194° (Found: N, 16·7. $C_{13}H_9O_3N_3$ requires N, 16·5%). For the preparation of 6-*nitro*-2-m-*nitrophenylbenzoxazole* a solution of 2-chloro-6-nitrobenzoxazole (Cerniani and Passerini, *Annali*, 1954, **44**, 3) in ethanol (50 ml.) was boiled with a solution of *m*-nitroaniline (3·5 g.) in ethanol (30 ml.) under reflux for 2 hr. The solid product, removed by filtration, was crystallised from acetic acid, and had m. p. 232—234° (Found: N, 18·7. $C_{13}H_8O_5N_4$ requires N, 18·7%).

Light-absorption Measurements.—A Beckman model D.U. Spectrophotometer was used, hydrogen and tungsten lamps being employed as light sources. Spectra were taken in solutions of concentration 1 in 10^5, in 95% ethanol, or, as noted in the Tables, in N/1-aqueous hydrochloric acid or N/10-aqueous sodium hydroxide. Readings were taken 2 mμ apart. The wavelengths were measured to 0·25 mμ in the important regions of the spectra.

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ISTITUTO DI CHIMICA INDUSTRIALE DELL' UNIVERSITA,
BOLOGNA.

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