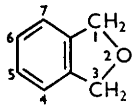
875. *Phthalans. Part II.* Ultraviolet and Infrared Spectra.*

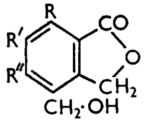
By W. R. Allison, W. R. Logan, G. T. Newbold, and T. J. Ross.

Some new phthalans are described and aspects of the ultraviolet and infrared spectra of these and known members are discussed. An infrared band assignment characteristic of the phthalan ring is put forward.

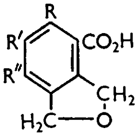
Apart from the parent phthalan (I), which has been prepared by the action of alkali on *o*-xylylene bromide [1] and by pyrolysis of *o*-xylylene glycol,[2] members of this series without substituents in the 1- or 3-position were unavailable until the discovery of the isomerisation of 4-hydroxymethylphthalides to phthalan-4-carboxylic acids, *e.g.*, (IIa) to (IIIa).[3-7] This paper discusses the ultraviolet and infrared spectra of these compounds and others derived from them.



(I)

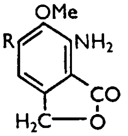


(II)

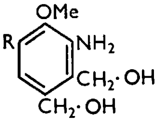


(III)

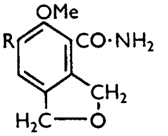
	R	R′	R″
a:	OMe	OMe	H
b:	OMe	Me	H
c:	OMe	OMe	Me
d:	OMe	OMe	OMe
e:	OMe	H	OMe



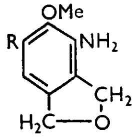
(IV)



(V)



(VI)



(VII)

a: R = OMe
b: R = Me

Ultraviolet spectra of 4-hydroxymethylphthalides were compared with those of the corresponding phthalan-4-carboxylic acids in five cases. The isomerisation showed no significant consistent trend in the wavelength positions of maxima or in the intensity of the long-wavelength band or of the middle band where present. It was notable, however, that the low-wavelength band (212—221 mμ) showed a marked decrease in intensity ($\Delta\varepsilon$ 5—15 × 10^3) on passing from the phthalide derivative to the isomeric phthalan while the wavelength position did not exhibit a consistent trend: (IIa) 214 ⟶ (IIIa) 213, $\Delta\varepsilon = -8400$;[3] (IIb) 212 ⟶ (IIIb) 214, $\Delta\varepsilon - 15{,}000$;[5,8] (IIc) 214 ⟶ (IIIc) 212, $\Delta\varepsilon - 12{,}000$;[4] (IId) 218 ⟶ (IIId) 216, $\Delta\varepsilon - 5200$;[4] and (IIe) 221 ⟶ (IIIe) 216 mμ, $\Delta\varepsilon - 9000$.[6]

In order to ascertain the effect of ring closure of an *o*-bishydroxymethylbenzene to a

---

* Part I, *J.*, 1958, 304.

[1] Willstätter and Veraguth, *Ber.*, 1907, **40**, 965.

[2] Entel, Ruof, and Howard, *J. Amer. Chem. Soc.*, 1952, **74**, 441.

[3] Brown and Newbold, *J.*, 1952, 4878.

[4] Blair and Newbold, *J.*, 1954, 3935.

[5] Blair, Logan, and Newbold, *J.*, 1956, 2443.

[6] Logan and Newbold, *J.*, 1957, 1946.

[7] Blair, Logan, and Newbold, *J.*, 1958, 304.

[8] Brown and Newbold, *J.*, 1953, 1285.

phthalan upon the ultraviolet spectrum two corresponding pairs of compounds were prepared. The amino-dimethoxy-dialcohol (Va) and the amino-methoxy-methyl-dialcohol (Vb) were prepared by reduction of the corresponding phthalides (IVa) [9] and (IVb) [4] with lithium aluminium hydride. No hydrogenolysis of the alcohol group *ortho* to the amino-group was noted in either reduction.[7, 10] 4-Amino-5 : 6-dimethoxyphthalan (VIIa) was prepared by conversion of 5 : 6-dimethoxyphthalan-4-carboxylic acid (IIIa) by way of the acid chloride into the amide (VIa), followed by Hofmann degradation. The aminophthalan (VIIa) was unaffected by hot dilute acid under conditions which converted 5 : 6-dimethoxyphthalan-4-carboxylic acid (IIIa) into 4-hydroxymethylmeconin (IIa). 5-Methoxy-6-methylphthalan-4-carboxylic acid (IIIb) was transformed in a similar way without isolation of the acid chloride into the amide (VIb), and hence into 4-amino-5-methoxy-6-methylphthalan (VIIb). A comparison between the ultraviolet spectra of the amino-alcohols (V) and the corresponding aminophthalans (VII) shows that a hypsochromic shift occurs in the long-wavelength band on ring closure from the alcohol to the phthalan, together with a fall in intensity, *i.e.*, (Va) $\longrightarrow$ (VIIa) $\Delta m\mu - 8$, $\Delta\varepsilon - 1450$ and (Vb) $\longrightarrow$ (VIIb) $\Delta m\mu - 15$, $\Delta\varepsilon - 1000$.

The infrared spectra of thirteen phthalans prepared in this Department have been examined, together with those of phthalan and tetrahydrophthalan,[2] for a band which might be characteristic of the phthalan ring. As a result, a band at 910—900 cm.$^{-1}$, usually narrow and of medium strength, has been assigned to this structural unit. This band is comparable with the symmetrical ring-stretching vibration at 913 cm.$^{-1}$ shown by tetrahydrofuran.[11] The stronger asymmetrical ring-stretching vibration shown by tetrahydrofuran at 1098—1075 cm.$^{-1}$ was not characteristic in the phthalan spectra. The assignments are given in the Table. Two examples in the Table need comment: 5 : 6-dimethoxyphthalan-4-carboxyl chloride shows a normal band in Nujol mull but this is 21 cm.$^{-1}$ less in solution, while 4-amino-5-methoxy-6-methylphthalan shows a normal value in solution with a doublet at a lower frequency in Nujol mull. A phthalan suspected of being substituted in the benzene ring should therefore be examined in both media before a conclusion is drawn. In order to test the specificity of the assignment the positions of bands (Nujol mull in cm.$^{-1}$) between 950 and 850 cm.$^{-1}$ in a number of related compounds are given: 4-hydroxymethyl derivatives of meconin (923 w, 880 m, 871 m), 7-methoxy-6-methylphthalide (918 w, 896 w, 883 w), 5 : 6 : 7-trimethoxyphthalide (897 w), 6 : 7-dimethoxy-5-methylphthalide (871 w), 5 : 7-dimethoxyphthalide (882 w); the 3 : 4- (942 w, 922 w, 853 m) and 4 : 5-dimethoxy- (877 m), 4-methoxy-5-methyl- (895 m), 3-amino-4 : 5-dimethoxy- (946 w), 3-amino- (897 m broad), and 3-amino-4-methoxy-5-methyl- (935 w, 833 m) derivative of *o*-bishydroxymethylbenzene. Other compounds examined were

Infrared bands of phthalans in the 11 μ *region.*

Substituents in (I)				Max. (cm.$^{-1}$) (in Nujol)	Max. (cm.$^{-1}$) (in CCl_4)
4	5	6	7		
H	H	H	H [2]	904 *	—
CO_2H	H	H	H	904	—
CO_2H	OMe	OMe	H	906, 900 †	909
COCl	OMe	OMe	H	902	881
CO_2Me	OMe	OMe	H	901, 909	910
$CO{\cdot}NH_2$	OMe	OMe	H	906	907
NH_2	OMe	OMe	H	902	906
CO_2H	OMe	Me	H	909	907
$CO{\cdot}NH_2$	OMe	Me	H	905	907
NH_2	OMe	Me	H	891, 894	906
CO_2H	OMe	H	OMe	904	908
CO_2Me	OMe	H	OMe	902	907
CO_2H	OMe	OMe	OMe	905	909
CO_2H	OMe	OMe	Me	906	911
Hexahydrophthalan [2]				904 *	—

* Medium not specified; frequency estimated from published curves in ref. 2. † Inflexion.

---

[9] McRae, VanOrder, Griffiths, and Habgood, *Canad. J. Chem.*, 1951, **29**, 282.

[10] Conover and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 3586.

[11] Jones and Sandorfy in " Technique of Organic Chemistry," Ed. Weissberger, Interscience, New York, 1956, Vol. IX, p. 437; Barrow and Searles, *J. Amer. Chem. Soc.*, 1953, **75**, 1175.

m-dioxano(4′ : 5′-6 : 7)phthalide (887 m in CCl_4), 2-aminobenzyl alcohol (932 m), 3-amino-2-methylbenzyl alcohol (904 m broad). 2-Methylbenzyl alcohol shows no band in this region.[2]

Experimental

Infrared spectra were measured on a Grubb–Parsons S4 spectrometer with sodium chloride optics. Accuracy in the 11 μ region was checked by frequent reference to the 11·038 μ band [12] of polystyrene film. Light petroleum, where used, had b. p. 60—80°.

5 : 6-*Dimethoxyphthalan-4-carboxyl Chloride*.—5 : 6-Dimethoxyphthalan-4-carboxylic acid [3] (1·0 g.) was refluxed on the steam-bath for 1 hr. with thionyl chloride (5 c.c.), and the excess of thionyl chloride distilled off under reduced pressure. After being kept overnight *in vacuo* over sodium hydroxide the solid residue was crystallised from benzene–light petroleum (charcoal) to give the *acid chloride* (500 mg.) as blades, m. p. 102·5—103·5° (Found: C, 54·7; H, 4·6. $C_{11}H_{11}O_4Cl$ requires C, 54·4; H, 4·5%).

5 : 6-*Dimethoxyphthalan-4-carboxyamide*.—The crude acid chloride from the acid (1·0 g.) was treated in dry ether (20 c.c.) with liquid ammonia (50 c.c.) in portions. The solution was allowed to evaporate overnight; water (50 c.c.) was added to the residue and the mixture extracted with chloroform (3 × 50 c.c.). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The residue crystallised from chloroform–light petroleum, to give the *amide* (600 mg.) as needles, m. p. 134—135° (Found: C, 59·2; H, 5·9; N, 6·6. $C_{11}H_{13}O_4N$ requires C, 59·1; H, 5·7; N, 6·3%), $\lambda_{max.}$ 209 (ε 27,000) and 308 mμ (ε 3300) in EtOH. The amide sublimes at 130°/10^{-4} mm. Infrared absorption bands in Nujol were at 3413, 3175 (NH_2), and 1669 cm.$^{-1}$ (CO).

4-*Amino*-5 : 6-*dimethoxyphthalan*.—Finely powdered 5 : 6-dimethoxyphthalan-4-carboxyamide (740 mg.) was added at 0° to a portion (10 c.c.) of the hypobromite solution prepared by the addition of bromine (2·05 c.c.) to a stirred ice-cold 10% solution of potassium hydroxide (100 c.c.). After 20 min. at room temperature, the solution was heated to 80° (bath-temperature) for 15 min. The cooled solution was extracted with ether (3 × 25 c.c.) and the combined ethereal extracts were washed with 5% hydrochloric acid (2 × 50 c.c.). Basification of the acid washings with 10% aqueous sodium hydroxide, followed by isolation using ether and crystallisation from benzene–light petroleum, gave 4-*amino*-5 : 6-*dimethoxyphthalan* (500 mg.) as plates, m. p. 96—97·5° (Found: C, 61·5; H, 6·4. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%). $\lambda_{max.}$ in EtOH 212 (ε 39,300), 240 (ε 8450), and 284 mμ (ε 1400). Infrared absorption bands in Nujol were at 3413, 3333, and 3195 cm.$^{-1}$ (NH_2). The aminophthalan (200 mg.) was refluxed with 3N-hydrochloric acid (5 c.c.) for 2¼ hr. The cooled solution was basified, and the product isolated in ether and crystallised from benzene–light petroleum to give unchanged material as plates, m. p. and mixed m. p. 96—97·5° (160 mg.).

5-*Methoxy*-6-*methylphthalan*-4-*carboxyamide*.—5-Methoxy-6-methylphthalan-4-carboxylic acid [5] (1·1 g.) was converted into the amide as described above. 5-*Methoxy*-6-*methylphthalan*-4-*carboxyamide* (0·75 g.) separated from ethanol (charcoal) as prismatic needles, m. p. 174—176° (Found: C, 63·75; H, 6·1 $C_{11}H_{13}O_3N$ requires C, 63·75; H, 6·3%), $\lambda_{max.}$ 209·5 (ε 22,500), and 295 (ε 2300), inflexion at 238 mμ (ε 5600), in EtOH, $\nu_{max.}$ in Nujol 3401, 3175 (NH_2) and 1664 cm.$^{-1}$ (CO).

4 *Amino*-5-*methoxy*-6-*methylphthalan*.—By method used for the preparation of 4-amino-5 : 6-dimethoxyphthalan, 5-methoxy-6-methylphthalan-4-carboxyamide (514 mg.) gave the corresponding *amino-compound* (190 mg.), crystallising from light petroleum as needles, m. p. 74—76° (Found: C, 67·15; H, 7·3. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3%), $\lambda_{max.}$ in EtOH, 213 (ε 40,000) and 276 mμ (ε 1000), $\nu_{max.}$ in Nujol 3420, 3330, and 3236 cm.$^{-1}$ (NH_2).

Methyl 5 : 7-*Dimethoxyphthalan*-4-*carboxylate*.—5 : 7-Dimethoxyphthalan-4-carboxylic acid [6] was esterified in methanol by ethereal diazomethane, to give the *methyl ester*, needles, m. p. 150—151° (from methanol) (Found: C, 60·2; H, 6·0. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%), $\lambda_{max.}$ 218 (ε 23,700), 257 (ε 11,500), and 300 mμ (ε 5300) in EtOH.

1 : 2-*Bishydroxymethyl*-4-*methoxy*-5-*methylbenzene*.—To a boiling partial solution of lithium aluminium hydride (0·83 g.) in ether (140 c.c.) a solution of 6-methoxy-5-methylphthalide (1·38 g.) in tetrahydrofuran (50 c.c.) was added dropwise with stirring. After 2½ hours' refluxing the mixture was cooled to 0° and the excess of hydride decomposed by ice. The

---

[12] Plyer and Peters, *J. Res. Nat. Bur. Stand.*, 1950, **45**, 462.

mixture was made alkaline with 10% sodium hydroxide solution (60 c.c.), and the ethereal layer separated. The aqueous layer was extracted with ether (5 × 60 c.c.). The combined ether extracts were washed with water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from benzene–light petroleum gave 1 : 2-*bishydroxymethyl*-4-*methoxy*-5-*methylbenzene* (1·1 g.), m. p. 71·5—72·5° (Found: C, 66·2; H, 7·7. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%), $\lambda_{max.}$ 209 (ε 12,200), 231 (ε 9150), and 280 mμ (ε 1850) in EtOH.

3-*Amino*-1 : 2-*bishydroxymethyl*-4-*methoxy*-5-*methylbenzene*.—7-Amino-6-methoxy-5-methylphthalide[4] (2·0 g.) was reduced with lithium aluminium hydride (1·2 g.), as described in the preceding experiment, to the *alcohol* (1·2 g.) which separated from benzene–light petroleum as rosettes of needles, m. p. 119° (Found: C, 60·9; H, 7·5. $C_{10}H_{15}O_3N$ requires C, 60·9; H, 7·7%), $\lambda_{max.}$ 219 (ε 43,400) and 291 mμ (ε 2000) in EtOH. The OON-*triacetyl derivative*, formed by the action of acetic anhydride and pyridine on the steam-bath for ½ hr., crystallised from benzene–light petroleum as needles, m. p. 167—168° (Found: C, 59·9; H, 6·9. $C_{16}H_{21}O_6N$ requires C, 59·4; H, 6·55%), $\lambda_{max.}$ 207 (ε 36,800) and 273·5 (ε 760), infl. 230 mμ (ε 10,300) in EtOH.

3-*Amino*-1 : 2-*bishydroxymethyl*-4 : 5-*dimethoxybenzene*.—7-Amino-*m*-meconin[9] (1·0 g.) was reduced, as in the preceding experiment, to the alcohol (750 mg.) which separated from acetone–light petroleum as prismatic needles, m. p. 112° (Found: C, 56·25; H, 7·0. $C_{10}H_{15}O_4N$ requires C, 56·3; H, 7·1%), $\lambda_{max.}$ 213 (ε 39,800), 292 (ε 2850), infl. 238 mμ (ε 6600) in EtOH.

We thank the Department of Scientific and Industrial Research for an Award (to W. R. A.).

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW.

[*Received, July* 11*th*, 1958.]