79. 1-*Phenylnaphthalenes. Part III.* The Effect of Substituents and their Position on the Absorption Spectra of* 1-*Phenylnaphthalene-*2 : 3-*dicarboxylic Anhydrides.*

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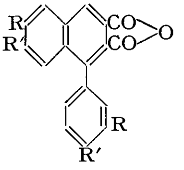
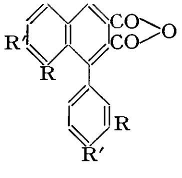
Structures proposed for some alkoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydrides are supported by their absorption spectra. Shifts in the absorption bands are observed with the change in the position of the alkoxyl group. The importance of directional effects in connection with the absorption of light is shown.

THIS investigation was primarily designed to establish the structure of some di- and tetra-alkoxy-1-phenylnaphthalene-2 : 3-dicarboxylic anhydrides, which could not be easily verified by chemical means.[1] The study was then extended to other 1-phenylnaphthalene-2 : 3-dicarboxylic anhydrides previously synthesised by Baddar,[2] and Baddar and El-Assal,[3] in order to correlate their structure with their electronic absorption spectra. The measurements were carried out on a Beckman D.U. spectrophotometer with glacial acetic acid or light petroleum solutions.

Results and Discussion.—The spectrographic results are given in the Table. The spectra of the 6-alkoxy-1-*m*-alkoxyphenylnaphthalene-2 : 3-dicarboxylic anhydrides are similar; they differ from those of the 8-alkoxy-1-*m*-alkoxyphenylnaphthalene-2 : 3-dicarboxylic anhydrides (Fig. 1). This is taken to be a good support to the structure

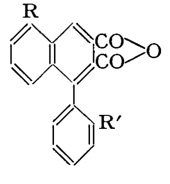
(I*a*) : R = R′ = H
(I*b*) : R = OMe, R′ = H
(I*c*) : R = OEt, R′ = H
(I*d*) : R = OPr^i, R′ = H
(I*e*) : R = R′ = OMe
(I*f*) : R = R′ = OEt
(I*g*) : R = H, R′ = OMe

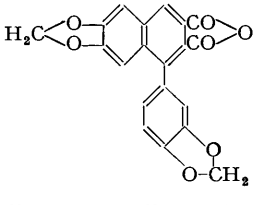




(II*a*) : R = OMe, R′ = H
(II*b*) : R = OEt, R′ = H
(II*c*) : R = OPr^i, R′ = H
(II*d*) : R = R′ = OEt

(III*a*) : R = R′ = OMe
(III*b*) : R = OMe, R′ = H
(III*c*) : R = H, R′ = OMe





(IV)

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* Part II, *J.*, 1955, 1714.

[1] Baddar, Fahim, and Galaby, *J.*, 1955, 465.

[2] Baddar, *J.*, 1947, 224.

[3] Baddar and El-Assal, *J.*, 1948, 1267; 1951, 1844.

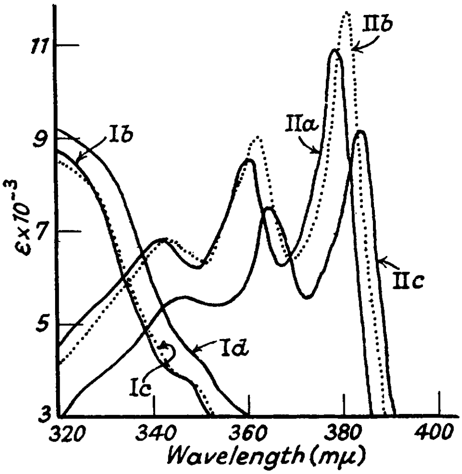
assigned to 6-*iso*propoxy-1-*m*-*iso*propoxyphenylnaphthalene-2 : 3-dicarboxylic anhydride (I*d*) which was not established by chemical means.[1]

The 8-alkoxy-isomers (II*a*, *b*, and *c*) (Fig. 1) show three related maxima, which proves the correctness of the structure assigned to them.[1] The slight bathochromic shift from the methoxy-isomer (II*a*) to the *iso*propoxy-isomer (II*c*) may be attributed to the increase in the electron-repelling character (+*I*) of the alkyl group.

The curves for the 6-alkoxy-compounds (I*b*, *c*, and *d*) have broadly similar features to those of the parent non-substituted anhydride (I*a*) with an all-over increase in intensity and a relatively small shift towards the red (Figs. 2, 3, and 4).

The 8-alkoxy-derivatives (II*a*, *b*, and *c*) (Figs. 2, 3, and 4) and the 5-methoxy-derivatives (III*a* and *b*) (Fig. 5) reveal on comparison with the parent anhydride (I*a*) a bathochromic shift, smaller than that of the 6-alkoxy-isomers, at wavelengths shorter than 290 mμ and a more extended shift for the absorption at longer wavelengths with a minimum at *ca.* 300 mμ, which is not observed in the 6-alkoxy-compounds (Figs. 2, 3, and 4). This difference in absorption is reflected in the colour of these compounds; thus, whereas the 6-alkoxy-derivatives are colourless, the 8- and 5-alkoxy-isomers are yellow.

FIG. 1.



The curve for the yellow 7-methoxy-1-*p*-methoxyphenylnaphthalene-2 : 3-carboxylic anhydride (I*g*) (Fig. 5) is close to those of the 6-alkoxy-anhydrides (I*b*, *c*, and *d*) at wavelengths shorter than 310 mμ. In the near ultraviolet there is a shift towards the red and intensity is also higher; here the curve nearly coincides with a synthetic curve (curve *c*, Fig. 2) for an equimolecular mixture of (II*a* and I*b*).

The curves for the yellow 6 : 7-dialkoxy- (I*e* and *f*) and 6 : 7-methylenedioxy-1-(3 : 4-methylenedioxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride (IV) (Fig. 6) are similar to that for (I*g*) (Fig. 5) in the general features, but the bathochromic shift and the increase in intensity are smaller than in (I*g*) because of the steric inhibition of resonance exerted by the alkoxyl group at the *meta*-position of the phenyl nucleus on that at the *para*-position.[4]

This effect, however, is least pronounced in the case of the bismethylenedioxy-derivative (IV), since the two oxygen atoms attached to the phenyl group are fixed together by the $-CH_2-$ bridge.

The curve for the colourless 7 : 8-diethoxy-1-(3 : 4-diethoxyphenyl)naphthalene-2 : 3-dicarboxylic anhydride (II*d*) (Fig. 6) is in agreement with those for the preceding tetra-alkoxy-compounds (I*e*, I*f*, and IV) in the far ultraviolet only, and with those for the 6-alkoxy-derivatives (I*b*, *c*, and *d*) in the near ultraviolet. This may be the result of inhibition of resonance of the phenyl group as a whole with the naphthalene nucleus, caused by the 8-ethoxyl group.

[4] Burawoy and Chamberlain, *J.*, 1952, 3734.

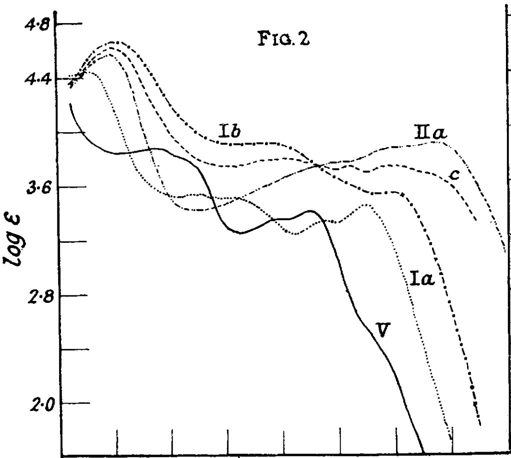


Fig. 2

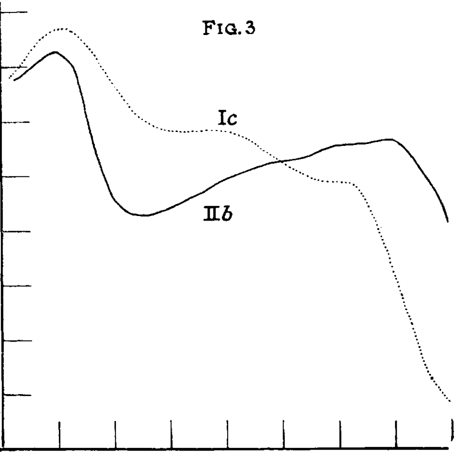


Fig. 3

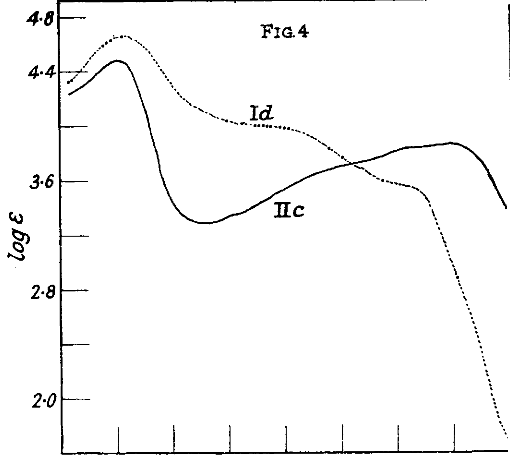


Fig. 4

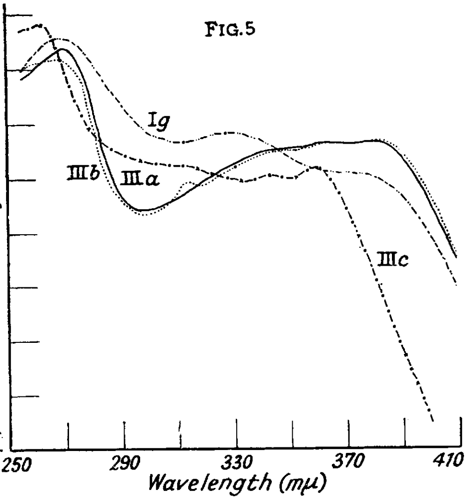


Fig. 5

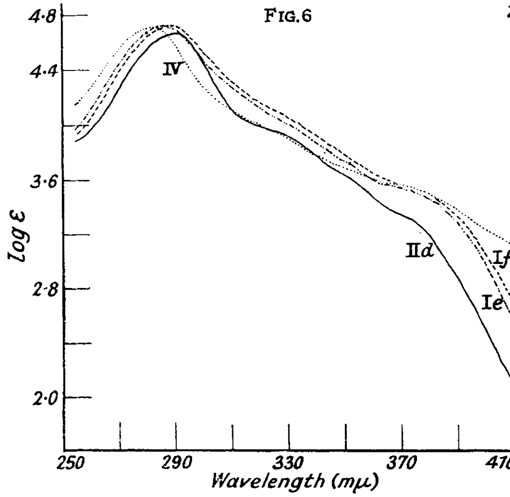


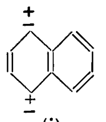
Fig. 6

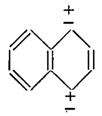
	Solvent : light petroleum *					Solvent : glacial acetic (" AnalaR ")				
Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε	Fig.	$\lambda_{max.}$ (mμ)	ε	$\lambda_{min.}$ (mμ)	ε	Fig.
I*a*	—	—	—	—	—	360	2740	350	2070	2
						346·5	2120	336	1710	
						∼308	3180	295	3290	
						299 ‡	3380			
						261	27,840			
V	—	—	—	—	—	340	2510	315	1740	2
						∼332	2200	271	6450	
						286 ‡	7548			
I*b*	∼320	8700	—	—	1	370 ‡	3430	364	3340	2
	∼347	3830				325 ‡	8060	316	7990	
						270	46,090			
I*c*	∼320	8500	—	—	1	∼367	3580	315	8280	3
	∼347	3830				325 ‡	8440			
						273	47,200			
I*d*	∼320	9200	—	—	1	∼367	3790	—	—	4
	∼348·5	4400				∼321	9840			
						274	45,100			
II*a*	342	6800	349	6190	1	386	7820	300	2645	2
	360	8550	367	6210		∼370	7375			
	378	10,850				∼355	5770			
						270	37,070			
II*b*	343·5	6820	351	6300	1	387	7100	300	2100	3
	362	9020	369	6350		∼375	6650			
	381	11,710				∼355	5190			
						270	32,410			
II*c*	346·5	5600	355	5380	1	389	7145	303	1970	4
	364	7530	372	5500		∼375	6710			
	384	9165				∼355	5195			
						271	30,260			
I*e*	—	—	—	—	—	∼366	3545	—	—	6
						∼320	12,870			
						286·5	51,770			
I*f*	—	—	—	—	—	∼370	3645	—	—	6
						∼320	14,310			
						288·5	52,000			
II*d*	—	—	—	—	—	∼370	2200	—	—	6
						∼320	9810			
						290	45,800			
IV	—	—	—	—	—	∼366	3720	—	—	6
						∼320	10,080			
						283	51,260			
III*a*	—	—	—	—	—	380	7250	298	2300	5
						375—362 †	7070			
						∼350	6520			
						270	35,400			
III*b*	—	—	—	—	—	382	7350	318·5	3470	5
						374—365 †	7050	298	2140	
						∼350	6220			
						314 ‡	3670			
						270	29,200			
III*c*	—	—	—	—	—	359·5	4660	351	3900	5
						344 ‡	4130	334·5	3760	
						∼308	4940			
						262	53,200			
I*g*	—	—	—	—	—	∼375	4200	310	7250	5
						329	8440			
						∼305	7510			
						269	42,280			

* I.P. for analytical purpose, b. p. 60—80° (B.D.H.). ∼ Approx. wavelength of inflexion ‡ Poor persistence. † Very close bands of poor persistence.

The variations in the absorption of light caused by the introduction of alkoxyl groups in 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride can be understood if we assume that the electronic excitations are parallel to those in the naphthalene molecule, and if we consider these variations in relation to the direction of excitation.[5]

In the naphthalene molecule four extreme structures (i—iv) contribute to the state of the molecule. In (i) and (ii) the polarisation is directed along the vertical axis and in (iii) and (iv) along the diagonal axis.


(i)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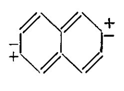
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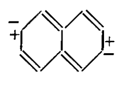
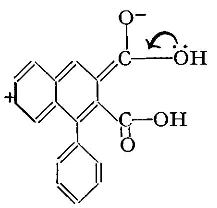
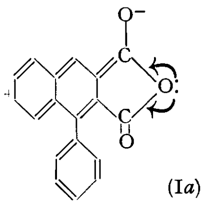

(iv)

The absorption spectrum of 1-phenylnaphthalene is considered to be similar to that of naphthalene.[6] The introduction of the 2- and 3-carboxyl groups in 1-phenylnaphthalene brings in more extended and more stabilised conjugation along the diagonal axis as shown by (V), since the negative charge is transferred from a carbon to an oxygen atom, and this should be associated with a bathochromic shift (Fig. 2). The larger shift noted for the anhydride (I*a*) as compared with the dicarboxylic acid (V) arises because inhibition of resonance caused by the free hydroxyl group in (V) is larger than that caused by the anhydride oxygen atom in (I*a*).

In the curves of the alkoxy-anhydrides one may discriminate between two regions of absorption, *viz.*, at 260—290 mμ and in the near ultraviolet at 360—390 mμ. It is possible to allocate the absorption in the two regions to electronic excitations along the vertical and the diagonal direction, respectively. Various workers visualised the effect of orientation of the molecules in the electronic field on their spectra.[7]


(V)


(I*a*)

The alkoxy-anhydrides fall into three types :

Type I : anhydrides II*a*, *b*, and *c* ; and III*a* and *b*.

Type II : anhydrides I*b*, *c*, and *d* ; II*d* ; and III*c*.

Type III : anhydrides I*e*, *f*, and *g* ; and IV.

The main excited structures of the three types are shown on p. 400 .

In type I, the main excitation is oriented vertically along ring *a*, and it is connected with the shifts 360→390 mμ in comparison with the parent anhydride. In type II, the main contributing coplanar structures are those resulting from excitation along the diagonal axis involving rings *a* and *b* ; the effect of this excitation is reflected in the shifts 260→290 mμ. In type III both the diagonal and the vertical excitation (along ring *b*) lead to coplanar structures, which contribute to the actual state of the molecule, and the result is the combined effect.

Comparison of the curves of these alkoxy-anhydrides with those of 1-phenylnaphthalene and 2-phenylnaphthalene [6,8] reveals the similarity of type I curves to that of 1-phenylnaphthalene on the one hand, and the close relation of type II curves to 2-phenylnaphthalene on the other, although all type I and type II curves are for 1-phenylnaphthalene derivatives. The difference in the curves of 1- and 2-phenylnaphthalene has been assigned

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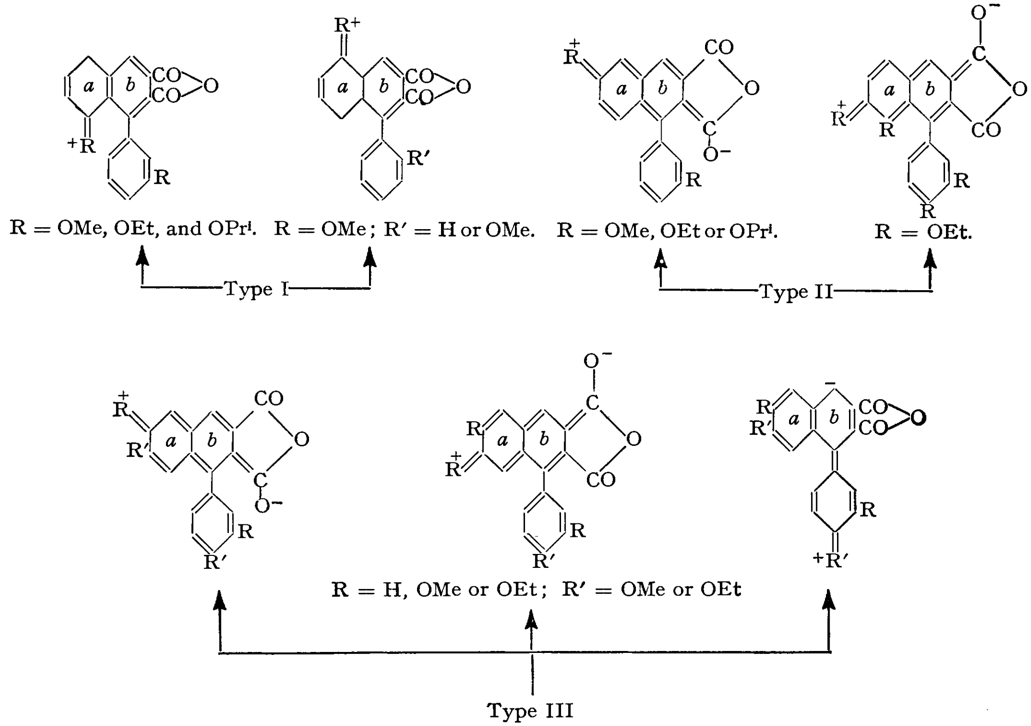
[5] Jones, *Chem. Rev.*, 1947, **41**, 353.

[6] *Idem, ibid.*, 1943, **32**, 1.

[7] Scheibe, *Kolloid Z.*, 1938, **82**, 1 ; *Angew. Chem.*, 1939, **52**, 631 ; Lewis and Bigeleisen, *J. Amer. Chem. Soc.*, 1943, **65**, 520, 2102, 2107 ; Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273 ; Zechmeister, LeRosen, Schroeder, Polgár, and Pauling, *J. Amer. Chem. Soc.*, 1943, **65**, 1940 ; Zechmeister, *Chem. Rev.*, 1944, **34**, 267 ; and Mulliken, *J. Chem. Phys.*, 1939, **7**, 364.

[8] Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.



to a coplanarity effect.[6] Friedel, Orchin, and Reggel,[8] however, attributed the bathochromic shifts and the greatly decreased fine structure in the spectrum of 1-phenylnaphthalene (compared with that of naphthalene) to an appreciable contribution from coplanar resonance structures involving the phenyl and the naphthalene ring. This conclusion receives support from the curves for type III anhydrides in the present series. It, therefore, appears that coplanarity effects are not the factor that governs the general features of the spectrum of the phenylnaphthalenes. Most probably this factor lies in the directional effects.

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