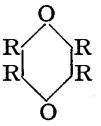
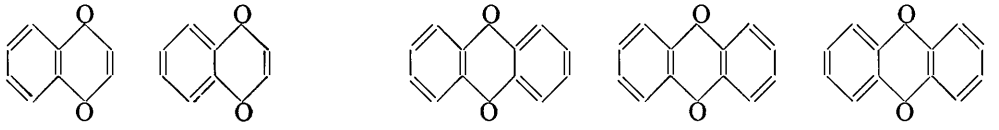
35. *Absorption Spectra in Relation to Quinones: 1 : 4-Naphthaquinone, Anthraquinone, and Their Derivatives.*

By R. Alan Morton and W. Trevor Earlam.

The spectra of 1 : 4-naphthaquinone and its alkyl substitution products are accounted for by the summation of effects due to (*a*) $C_6H_4<^{CO\cdot R}$ ($\lambda\lambda_{max.}$ 2500 and 3300 A.) and (*b*)  ($\lambda\lambda_{max.}$ 2620, 2720 A. quinonoid, and $\lambda_{max.}$ *ca.* 4000 A. carbonyl). The spectra of hydroxy-derivatives reflect similar summations, complicated somewhat by hydrogen bonding in α-hydroxy-compounds.

The spectrum of anthraquinone is reproduced closely by $2a + b$. In the hydroxyanthraquinones, the two bands ascribed to *a* can vary independently, as also can the quinonoid and carbonyl bands of *b*. α-Substitution, with its concomitant hydrogen bonding, favours fixation of Kekulé forms so as to diminish the quinonoid element in *b* and enhance the importance of the carbonyl aspect. This tendency is reversed in β-substitution products.

1 : 4-Naphthaquinone and anthraquinone possess, in terms of resonance, hybrid structures, the extreme forms being :



Apart from the C·C:O single bonds, all the carbon–carbon linkages possess some degree of double-bond character, and a knowledge of the precise electron-density distribution might well afford a basis for predicting many properties. Such knowledge is not easily gained, but some advance is possible by the careful interpretation of absorption spectra.

Morton and Stubbs (J., 1940, 1347) have shown that salicylaldehyde and *o*-hydroxyacetophenone are spectroscopically similar, having maxima near 3250 A., log ε 3·5, and 2550 A., log ε 4·0, characteristic of the benzenoid chromophore $C_6H_4<^{CO\cdot R}$. Klingstedt (*Compt. rend.*, 1923, **176**, 1550), Light (*Z. physikal. Chem.*, 1926, **122**, 414), and Scheibe (*Ber.*,

1926, **59**, 2617) have shown that simple quinones, *e.g.*, 1 : 4-benzoquinone, show: (i) resolved absorption in the visible region with low ε values (1—20), (ii) a marked inflexion at 2800—2900 A. of moderate intensity, log ε *ca.* 2·5, and (iii) an intense band, $\lambda_{max.}$ 2410 A., log ε 4·30. In *p*-xyloquinone the absorption is similar, but the 2410 A. maximum is displaced to 2500 A.

Macbeth, Price, and Winzor (J., 1935, 325) found that 1 : 4-naphthaquinone shows a marked inflexion at 3900—4600 A., log ε 1·9—1·6, a well-defined band at $\lambda_{max.}$ 3340 A., log ε 3·44, an inflexion at 2560 A., log ε 4·13, and a sharp maximum at 2460 A., log ε 4·28 (solvent, alcohol). Our data for hexane solutions are shown in Table I. Introduction of alkyl groups has interesting effects which have been important in recent work on the *K* vitamins. Webb (see Fieser *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 1927) and Ewing, Vandenbelt, and Kamm (*J. Biol. Chem.*, 1939, **131**, 352), in extending the work of several groups of investigators, recorded four maxima in the region 2400—2800 A. for disubstituted products.

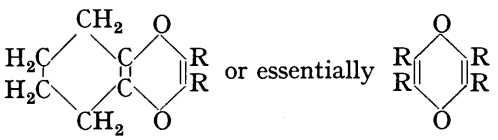
TABLE I.

	$\lambda_{max.}$, A.	log $\epsilon_{max.}$		$\lambda_{max.}$, A.	log $\epsilon_{max.}$
1 : 4-Naphthaquinone (Fig. 1)	2410	4·32	2-3 : Dimethyl-1 : 4-naphthaquinone	2430	4·26
	2460	4·37		2490	4·26
	2510	4·28		2600	4·28
	2560	4·12		2690	4·28
	3300	3·44		3300	3·38
2-Methyl-1 : 4-naphthaquinone	2440	4·29	Vitamin-K_1	2430	4·37
	2500	4·29		2490	4·39
	2630	4·30		2600	4·38
	3340	3·38		2700	4·36
				3250	3·52
2-Ethyl-1 : 4-naphthaquinone	2450	4·31	Vitamin-K_2	2430	4·20
	2500	4·34		2490	4·24
	2550	4·33		2600	4·18
	2670	4·26		2700	4·18
	3300	3·4		3250	3·45

It is clear from the work of Macbeth *et al.* (*loc. cit.*) that an inflexion 4000— 4500 A., log ε < 2, is also common to substances of this type, but many workers omit to study solutions sufficiently concentrated for the absorption in this region to be recorded. Ewing *et al.* confirmed earlier observations on the spectra of certain reduction products of vitamins-K_1 and -K_2, and concluded that when the quinonoid part of the molecules was retained, only the maxima at 2600 and 2700 A. persisted (measurements at 4000—4500 A. were apparently not feasible):

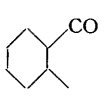
	Reduced vitamin-K_1 ($C_{31}H_{50}O_2$).	Reduced vitamin-K_2 ($C_{40}H_{60}O_2$).
$\lambda_{max.}$, A.	*ca.* 2600, 2700	2600, 2700
log $\epsilon_{max.}$	4·23	4·12

The absorptive part of both substances is

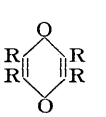


α-Tocopherylquinone, obtained by oxidation of α-tocopherol by means of ferric chloride, contains the same chromophoric grouping and shows $\lambda\lambda_{max.}$ 2625 and 2725 A., log ε 4·23 (Karrer and Geiger, *Helv. Chim. Acta*, 1940, **23**, 455).

The substituted 1 : 4-naphthaquinones (Table I) thus exhibit spectra little different from the simple summation *a* + *b*:

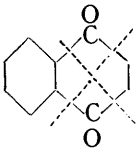
(*a*) 

$\lambda_{max.}$, A.	log $\epsilon_{max.}$
2430	4·02
2495	4·025
3290	3·63

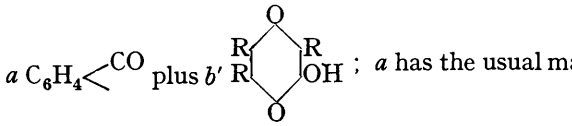
(*b*) 

$\lambda_{max.}$, A.	log $\epsilon_{max.}$
ca. 2600	*ca.* 4·2
2706	
~4000—4500	*ca.* 2·0

Chromophore *a* is potentially perhaps capable of functioning twice (see inset), but from the ε values only appears to count once.



The foregoing interpretation may be extended to the hydroxynaphthaquinones studied by Macbeth, Price, and Winzor (*loc. cit.*). Our data on naphthazarin are in good agreement. The figures in Table II, with those of Cooke, Macbeth, and Winzor (J., 1939, 878), lead to the view that the structure (I) (present also in lapachol, lomatiol, *iso*lomatiol, dihydroxyhydrolapachol, α-lapachone, and phthiocol) can be regarded chromophorically as



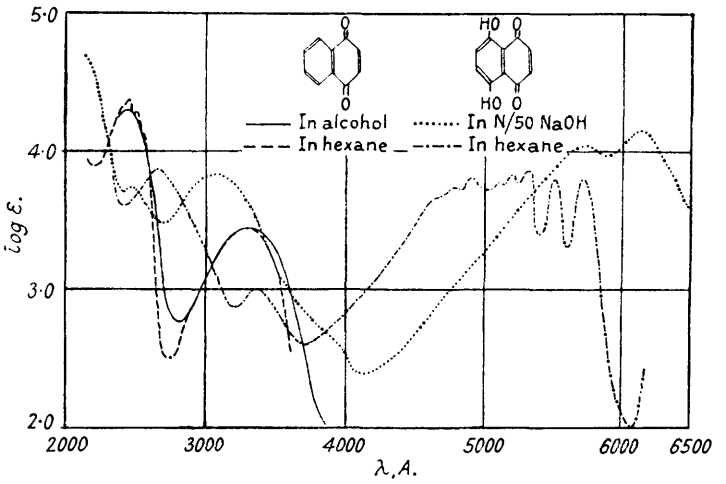
a has the usual maxima whilst *b'* has the quinonoid absorption at 2600—2700 A. displaced to *ca.* 2800 A., log $\epsilon_{max.}$ 4·2, and the carbonyl absorption at 3900—4500 A. increased in intensity from log ε 2 to 3, *i.e.*, about tenfold. Such an increase in ε also follows the introduction of hydroxyl into benzene (cf. Morton and Stubbs, *loc. cit.*). The counteracting effect of acetylation is common to both the benzenoid and the quinonoid chromophore.

TABLE II.

	$\lambda_{max.}$, A.	log $\epsilon_{max.}$			$\lambda_{max.}$, A.	log $\epsilon_{max.}$	
2-Hydroxy-1 : 4-naphthaquinone (lawsone)	2440	4·20	*a*	5 : 8-Dihydroxy-1 : 4-naphthaquinone (naphthazarin) (Fig. 1)	2470	3·73	*a*
	2760	4·20	*b*		2540	3·84	*a*
	3310	3·45	*a*		2700	3·92	
	~3950	3·30			2840	3·84	*b*
	4600	2·0	*b*		2980	3·52	
2 : 3-Dihydroxy-1 : 4-naphthaquinone (*iso*naphthazarin)	2700	4·12	*b*		3380	2·95	*a*
	2820	4·05	*b*		4500	3·50	*b*
	3350	3·31	*a*		4850	3·75	*b*
	4450	3·26	*b*		5130	3·85	*b*
	~3900—5100				5620	3·60	*b*
5-Hydroxy-1 : 4-naphthaquinone (juglone)	2490	4·12	*a*		6250	2·92	*b*
	2620	4·00	*b*				
	3390	3·18	*a*				
	4250	3·6					
	~4950	2·8	*b*				

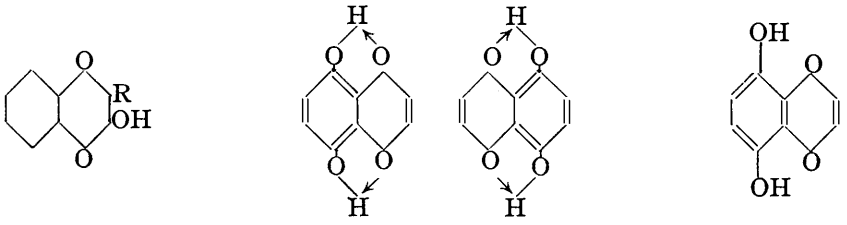
~ denotes inflexion.

FIG. 1.



In juglone (Macbeth, Price, and Winzor, J., 1935, 325) chromophore *a* appears with somewhat diminished intensity, and the long-wave absorption of the quinonoid chromophore is displaced to 4250 A., log ε *ca.* 3·6. In naphthazarin the benzenoid absorption is weakened still more, whilst the quinonoid absorption at 2600—2700 A. is displaced some-

what and that at 3900—4500 A. is displaced considerably. Resonance here involves the extremes (II) and (III), and hydrogen bonding favours fixation of (II) rather than (III).



(I.) (II.) (III.)

The data of Lugg, Macbeth, and Winzor (J., 1937, 1039) on hydroxyjuglone, hydroxydroserone, naphthapurpurin, and their acetates show clearly how acetylation restores a normal benzenoid absorption: $\lambda\lambda_{max.}$ 3450—3500, 2500—2600 A., log $\epsilon_{max.}$ 3·4—3·5 and *ca.* 4·0 respectively. In these acetates the quinonoid contribution to the observed absorption is of minor significance.

1 : 2-Naphthaquinones show spectra capable of similar interpretation. Goldschmidt and Graef (*Ber.*, 1928, **61**, 1858) studied the parent substance, and Macbeth, Price, and Winzor (*loc. cit.*) the 4-methoxy-derivative. Later (J., 1939, 878) Cooke, Macbeth, and Winzor discussed a series of 1 : 2-naphthaquinones from natural products. From these studies the *a* bands at 2500—2600, log ε 4·35—4·5, and *ca.* 3330 A., log ε *ca.* 3·2, are easily recognised. An inflexion near 2700—2860 A., log ε 3·8—4·0, is less intense than the absorption of 1 : 4-naphthaquinones in the same region, but selective absorption at 4000—4200 A. is well marked and more intense (log ε 3·3—3·4 as compared with log ε *ca.* 2) than that of the 1 : 4 analogues. It is sometimes possible to record weak selective absorption near 5000 A., log ε 2·0; this is obviously carbonyl absorption. The 1 : 2-naphthaquinones do not exhibit the well-resolved absorption in the region 2700—2800 A. characteristic of the ethenoid linkages in the quinonoid chromophore of 1 : 4-quinones.

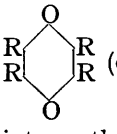
The spectrum of anthraquinone (Table III, Fig. 2) can now be accounted for readily.

TABLE III.

Anthraquinone.

	In alcohol.		In ether.*		
	$\lambda_{max.}$, A.	log $\epsilon_{max.}$	$\lambda_{max.}$, A.	log $\epsilon_{max.}$	
b	4050	1·95	4200	1·75	
			4060	1·88	resolved
			3970	1·95	absorption
			3770	2·05	
a	3255	3·75	3235	3·74	
b	2720	4·31	2715	4·18	
b	2628	4·31	2630	4·22	
a	2525	4·71	2515	4·70	
a	2435	4·52	2420	4·51	

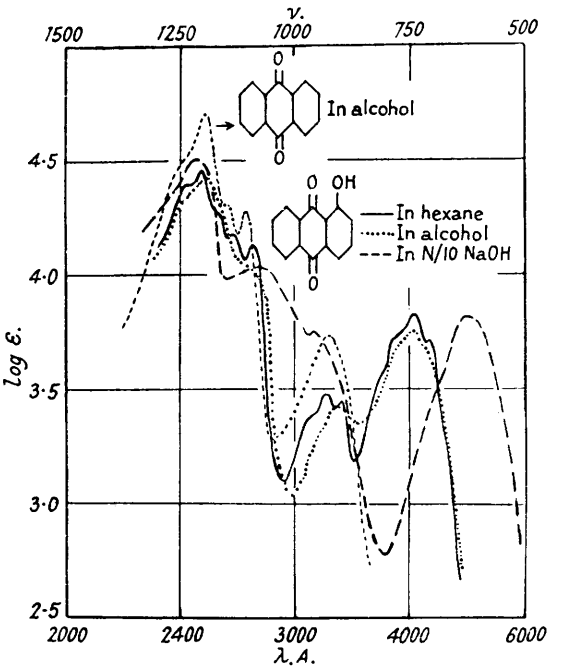
* Cf. Anderson (*J. Amer. Chem. Soc.*, 1933, **55**, 2094) where log values are too high by 1·0 throughout the spectrum.

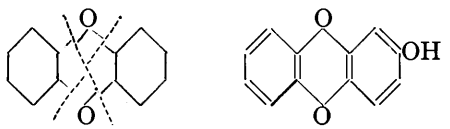
The *a* bands are due to the chromophore $C_6H_4{<}^{CO\cdot R}$ and are much more intense than in *o*-hydroxyacetophenone and salicylaldehyde, suggesting that the chromophore functions twice in anthraquinone (IV). The *b* bands are quinonoid in origin and correspond almost exactly with those already ascribed to  (cf. α-tocopherylquinone, p. 160).

Introduction of hydroxyl groups into anthraquinone produces considerable effects which vary with the position and number of substituents. It will be convenient to note first a group of distinct effects: (i) Displacement of maxima in the direction of longer

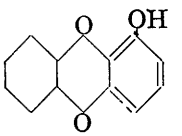
wave-lengths without influencing the probability of the relevant electronic process, *i.e.*, no change in $\varepsilon_{max.}$; (ii) marked increase or decrease in $\varepsilon_{max.}$ not accompanied by wave-length displacements; (iii) an alteration in the relative importance of the benzenoid and the quinonoid contributions to the absorption exerted by the resonance hybrid. In all cases hydroxyl groups bring about an increase in the absorption shown by anthraquinone near 4050 A., log ε *ca.* 2; this increase is least (log ε 3·15—3·55) for β-substituted products and greatest for αα′- (1 : 4-; 1 : 8-; 1 : 5-) derivatives, whilst 1- and 1 : 2-derivatives occupy an intermediate place. This absorption is attributed to the carbonyl group within the quinonoid chromophore. The wave-length displacements vary in the same sense, and, in fact, the β-substituted products differ little from the parent substance in this respect. The anthraquinone maxima at 2628 and 2720 A., log ε 4·31, are likewise due to the quinonoid factor; intensities of absorption for these bands show decreases in 1-, 1 : 5-, 1 : 8-, and 1 : 4-derivatives, and increases in 2- and 2 : 6-derivatives, whereas the two tendencies practically cancel out in alizarin. These effects are the reverse of those occurring at longer wave-lengths (> 4050 A.). The latter absorption in anthraquinone is analogous to the low-intensity long-wave absorption shown by 1 : 4-benzoquinone and 1 : 4-naphthaquinone and must concern an electronic process located in the carbonyl group. On the other hand, the 2628 and 2720 A. maxima of anthraquinone owe their appearance to the –C:C– link in the quinonoid chromophore. On this basis the quinonoid element in the absorption spectrum becomes more important in β- and less important in α-hydroxyanthraquinones, implying some degree of fixation of Kekulé forms (V), (VI), and (VII). It is interesting that if chelation occurs as a result of hydrogen bonding, the resulting resonance, *e.g.*, (VIII) and (IX), requires a weakening of quinonoid character, in so far as (X) tends to be eliminated.

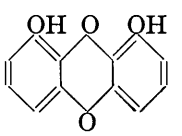
FIG. 2.

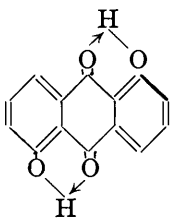


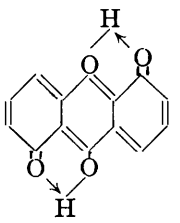

(IV.)

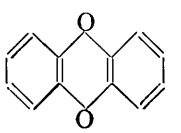
(V.)


(VI.)


(VII.)


(VIII.)


(IX.)


(X.)

The benzenoid element in the spectrum of anthraquinone ($\lambda_{max.}$ 3250 A., log ε 3·75; 2525 A., log ε 4·71) reappears in the hydroxy-derivatives. In 1-hydroxy- and 1-methoxy-

anthraquinone the maxima are little displaced but intensities are roughly halved; 2-hydroxyanthraquinone shows the 3300 A. maximum at log ε 3·55, approximately the intensity at which it occurs in *o*-hydroxyacetophenone, whereas the short-wave maximum (2410 A., log ε 4·31) is twice as intense as the corresponding band. It is therefore to be concluded that as a result of substitution the two benzenoid maxima can vary independently of one another. The 1 : 2-derivatives listed in Table IV show practically undisplaced

TABLE IV.

Hydroxyanthraquinones.

	$\lambda_{max.}$, A.	log $\epsilon_{max.}$		$\lambda_{max.}$, A.	log $\epsilon_{max.}$
1-Hydroxy-	4230	3·71	2-Hydroxy-	3780	3·55
	4060	3·83	in EtOH		
(erythroxyanthraquinone)	~3860	3·74	(Fig. 3)	3300	3·55
(Fig. 2)	3350	3·45		2830	4·46
in EtOH or hexane	3220	3·48		2710	4·55
	~3120	3·4			
	2760	4·13		2410	4·31
	2660	4·18			
	~2560	4·28			
	2500	4·46			
	2435	4·4			
in 0·1N-NaOH	4840	3·82			
	3150	3·75			
	2780	4·03			
	2480	4·51			
1-Methoxy-	3710	3·68	2-Methoxy-	3660	3·45
	~3590	3·63	(Fig. 3)		
in hexane (Fig. 3)	3300	3·5		3300	3·54
	3180	3·49			
	~3050	3·39		2810	4·38
(alcoholic solution shows	2705	4·1		2690	4·54
less resolution)	~2610	4·17			
	2500	4·49		~2300—2500	4·0—4·2
	~2460	4·42			
1 : 5-Dihydroxy-	4370	3·98	2 : 6-Dihydroxy-	~3850	3·35
	4180	3·98		3490	3·90
(anthrarufin)	~3970	3·81	(anthraflavin)	3015	4·28
	~3300	2·75	(Fig. 5)	2742	4·53
in EtOH	2870	3·98		~2650	4·38
	2760	3·98			
	2530	4·24			
	2250	4·57			
1-Hydroxy-5-methoxy-	4000	3·89	2 : 6-Dimethoxy-	3850	3·15
	~3220	3·05	(Fig. 5)	3460	3·87
in EtOH	~2800	3·9		2990	4·35
	2540	4·26		2715	4·55
	2230	4·53		2630	4·40
1 : 5-Dimethoxy-	3870	3·98			
(Fig. 10)	~3200	3·0			
	2650—2760	4·2—4·08			
	255	4·39			
1 : 5-Dihydroxy-	4800	4·1	1 : 4-Dihydroxy-	5200	3·942
				5075	3·942
in 1% NaOH				4980	3·95
	2800	4·2	(quinizarin)	4860	4·02
				4740	3·99
	2300	4·55	in hexane (Fig. 6)	4590	3·95
1 : 8-Dihydroxy-	4565	4·1		3355	3·27
	4455	4·14		3250	3·40
	4315	4·22		2910	3·34
(chrysazin) (Fig. 7)	4210	4·17			
	4110	4·16		2800	4·06
in hexane	2840	4·24		2567	4·23
(in EtOH, similar, but	2740	4·15		2500	4·46
less resolution)	2540	4·36		~2450	4·43
1-Hydroxy-8-methoxy-	4310	3·84			
(Fig. 7)	4100	3·90	1 : 2-Dihydroxy-	4350	3·79
	2810	3·96			
	~2700	4·02	(alizarin)	3310	3·55
	2550	4·24	in EtOH (Fig. 8)	2800	4·3
				2510	4·5

TABLE IV (*contd.*).

	$\lambda_{max.}$, A.	log $\epsilon_{max.}$
1 : 8-Dimethoxy (Fig. 7) very similar to 1 : 5-dimethoxy, but 3200 rather more pronounced.		
1 : 2-Dimethoxy- (Fig. 8)	3740	3·71
	~3300	3·5
	~2800	4·28
	~2700	4·3
	2510	4·46
1 : 2-Dihydroxy-	6075	4·15
	5640	4·22
in 1% NaOH (Fig. 8)		
	273·5	4·52
	229	4·25
1-Hydroxy-2-methoxy-	4410	3·80
	4250	3·83
	3270	3·54
	2790	4·14
in EtOH (Fig. 9)	~2600	
	2545	4·46
	2465	4·53
	2310	4·30
in hexane	4780	3·25
	4495	3·71
	4250	3·83
	4045	3·73
	~3580	3·14
	3300	3·45
	3210	3·49
	~2960	3·7
	2790	4·17
	2690	4·18
	2620	4·31
	2460	4·54
	~2330	4·33
in 1% NaOH	5130	3·83
	3200	3·78
	2850	4·03
	2560	4·54

absorption at 3300 A., log ε 3·5, and *ca.* 2500 A., log ε 4·5; 1 : 4-dihydroxyanthraquinone, which is similar in that it possesses one unsubstituted ring, also exhibits $\lambda\lambda_{max.}$ 3250 and

FIG. 3.

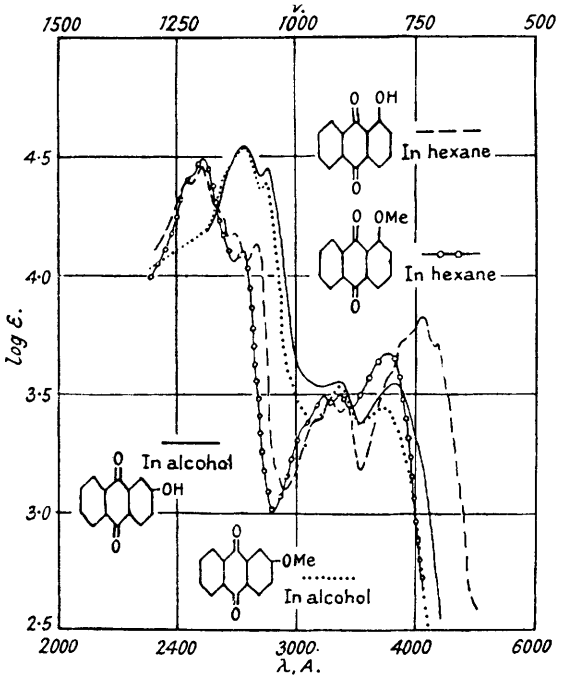
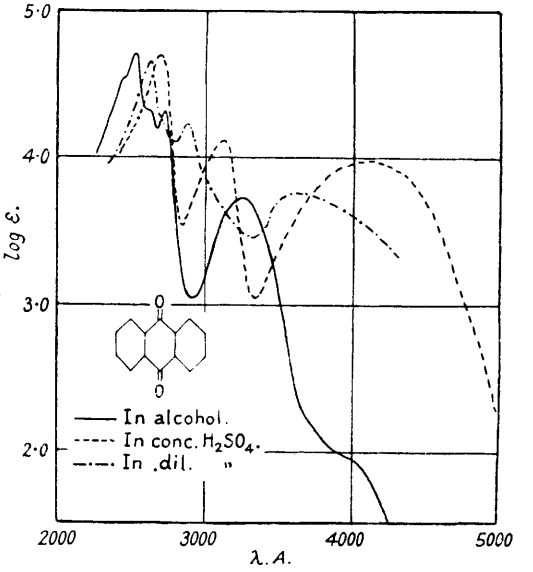


FIG. 4.



2500 A. at similar intensities. On the other hand, 1 : 5-dihydroxyanthraquinone shows the 3300 A. maximum undisplaced but very appreciably reduced in both intensity and persistence, whilst the 2500 A. maximum is also less intense. The 1 : 8-derivatives show no

selective absorption at 3300 A. but the 2500 A. band remains at log $\varepsilon_{max.}$ 4·3. In all the above instances wave-length displacements are small, but in 2 : 6-dihydroxyanthraquinone

FIG. 5.

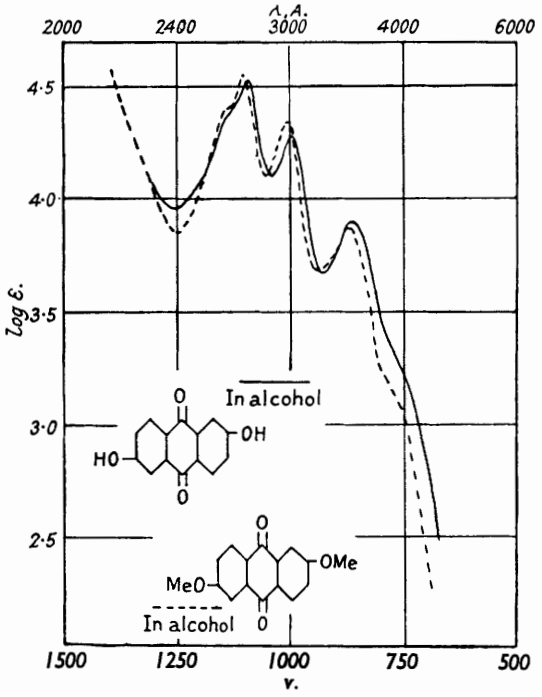


FIG. 6.

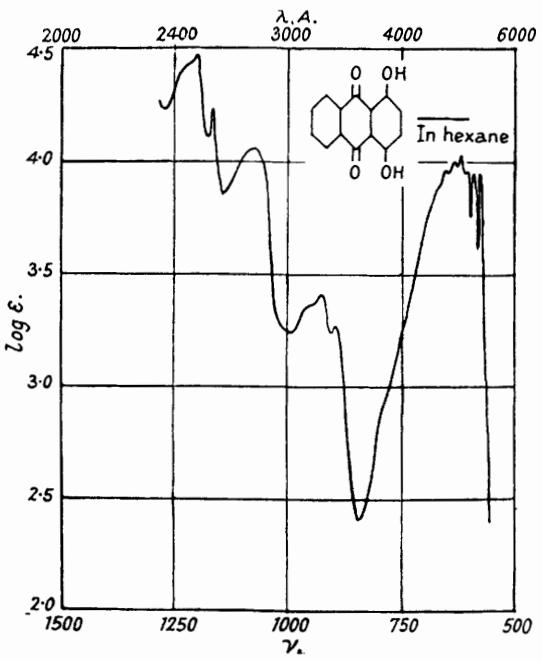


FIG. 7.

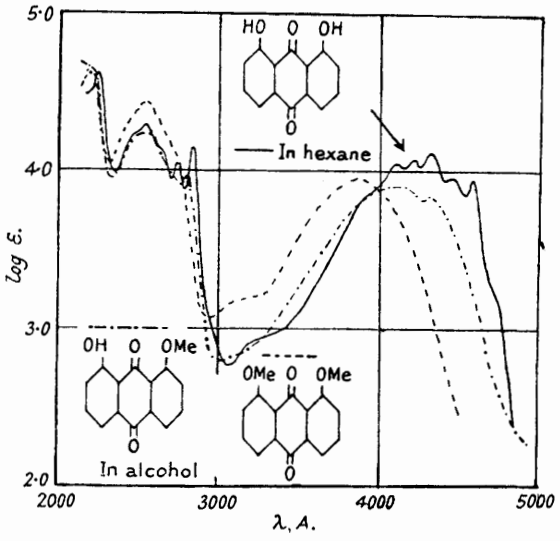
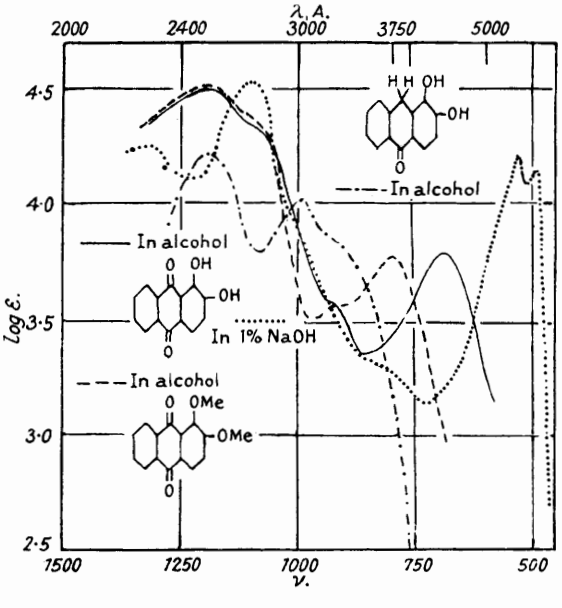


FIG. 8.



the 3250 band is moved to 3490 A., with log ε raised to 3·9; the 2500 A. band is also displaced but lacks persistence.

Although it would be unwise to stress the absolute intensities of absorption in the extreme ultra-violet (because the effects of different chromophores overlap), yet the changes are qualitatively easy to recognise.

FIG. 9.

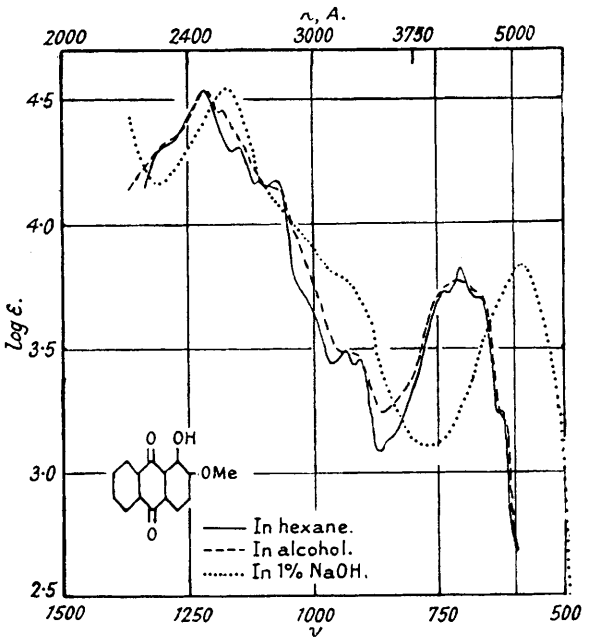
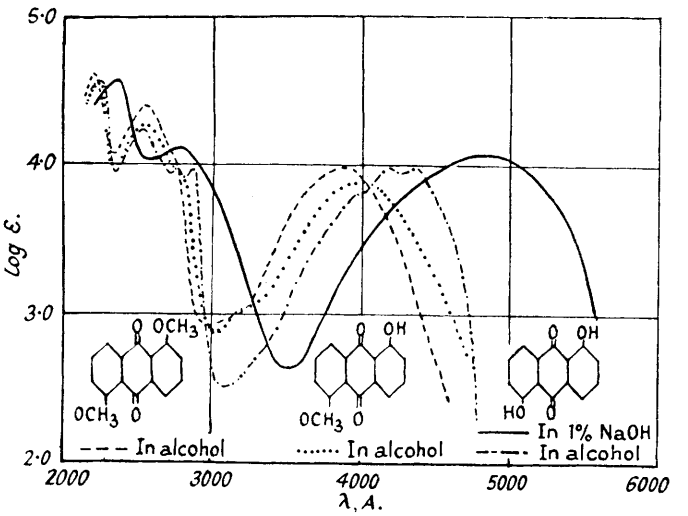
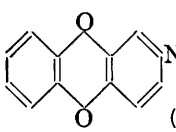


FIG. 10.



Lauer and Horio (*J. pr. Chem.*, 1936, **145**, 279) have studied the aminoanthraquinones; the data in Table V, being obtained by reading their published curves, are approximate. The *a* bands of $C_6H_4\langle^{CO}$ are shown in both cases, but the quinonoid bands (2628, 2725 A., displaced to 2750—3000 A.) are very much stronger in the β-derivative, again indicating that substitution in the 2-position tends to fix a Kekulé form (**XI**) with the 1 : 2 link having a predominantly double-bond character.



(XI.)

TABLE V.

1-Aminoanthraquinone.

		$\lambda_{max.}$, A.	log $\epsilon_{max.}$
In hexane		4450	3·75
		~4250	3·6
	a	3300	3·2
		2950	3·65
		2750	4·05
	a	2450	4·6
In EtOH		4700	3·78
		~4100	3·05
	a	3250	3·7
		~2920	3·7
		2850	4·05

2-Aminoanthraquinone.

		$\lambda_{max.}$, A.	log $\epsilon_{max.}$
In hexane		4300	3·4
		4050	3·57
	a	3250	3·80
		2870	4·50
	a	2350	4·6
In EtOH		4300	3·6
		3950	3·25
	a	3300	4·0
		~3180	3·85
	a	2970	4·3
	a	2450	4·5

1-Nitroanthraquinone.

$\lambda_{max.}$, A.	log $\epsilon_{max.}$
3250	3·63
2550	4·57

2-Nitroanthraquinone.

$\lambda_{max.}$, A.	log $\epsilon_{max.}$
3230	3·74
2605	4·60

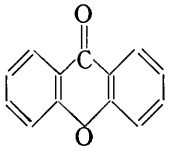
The nitroanthraquinones (data for which were obtained for us by Mr. Z. Sawires) are both very similar in respect of absorption spectra to anthraquinone. The quinonoid maxima at 2620 and 2730 A. are not detectable, but this may be due (particularly in the 2-nitro-derivative) to a masking effect of the somewhat displaced band in the region 2500—2600 A. It is clear, however, that the nitro-group does not enhance the visible absorption in the same way as the amino-group. Horio and Lauer (*loc. cit.*) have also studied a number of hydroxyanthraquinones. Their data are in fairly good agreement with those recorded here, but the curves for solutions in sodium hydroxide and in concentrated sulphuric acid are drawn upside-down and the ε values are meaningless. In addition to the substances studied by us, they record data for the longest wave-lengths of maximum absorption in 2 : 3-, 2 : 6-, 2 : 7-, 1 : 3-, and 1 : 6-dihydroxyanthraquinones.

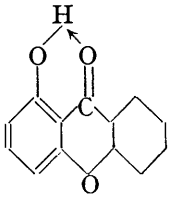
TABLE VI.

	$\lambda_{max.}$, A.	log $\epsilon_{max.}$
Benzophenone	3330	1·85
	2860	2·90
	2500	4·30
2-Hydroxy-5-methylbenzophenone	3420	3·20
	2510	4·04
p-Methoxybenzophenone	*no* 3420 max.	
	250	4·05
Xanthone	3350	4·02
	a 3226	3·84
	2833	3·73
	2762	3·58
	a 2469	4·4
Deoxyalizarin (Fig. 8)	330	3·8
	3000	4·0
	2500	4·2
o-Methoxybenzophenone	3420	3·20
	2510	4·04
m- ,, ,,	*no* 3420 max.	
	2560	4·05
1-Hydroxyxanthone	3640	3·56
	3390	3·36
	2500	4·28

The task of interpretation may be approached from another angle, beginning with benzophenone (Table VI), where the 3330 A. band is of such low intensity that it can be related to the 3280 A. maximum common to acetophenone and benzaldehyde and due to the carbonyl group. The 2860 and 2500 A. maxima are benzenoid, and in the *o*-hydroxy- and -methoxy-derivatives the former is displaced to 3420 A., *i.e.*, rather further than in salicylaldehyde and *o*-hydroxyacetophenone. Xanthone is interesting in that it shows the maxima already noted as characteristic of $C_6H_4<^{CO}$ (*a*) and in addition shows two maxima, 2833 and 2762 A., which are much more intense than the 2860 A. absorption of benzophenone. If the form (XII) plays any considerable part in the resonance hybrid, these two bands might well correspond with the quinonoid maxima discussed earlier. Some support is given to this suggestion by the absence of the bands from the spectrum

of 1-hydroxyxanthone. This compound, with its tendency towards hydrogen bonding (XIII), would be less markedly quinonoid.

(XII.) 

 (XIII.)

Deoxyalizarin exhibits selective absorption made up of the $C_6H_4<^{CO}$ *a* spectrum, superimposed upon a well-defined band with $\lambda_{max.}$ *ca.* 3000 A.; this is not resolved into two components, and more than one explanation of its origin could be advanced.

The spectroscopic data were obtained by using Hilger E_3 instruments with sectorphotometers. In one arrangement a long-focus sectorphotometer was used in conjunction with a D.C. arc between electrodes of iron and nickel, and in another, a short-focus sectorphotometer with a high-tension (Tesla) spark between tungsten electrodes under water. The latter source gives a continuous spectrum.

All the compounds were carefully purified but the methods used are not described in detail since they were rarely new, and in no case resulted in new criteria of purity.

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UNIVERSITY OF LIVERPOOL. [*Received, December 23rd,* 1940.]