127. *Studies in Light Absorption. Part I. p-Benzoquinones.*

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The selective visible and ultra-violet light absorption of *p*-benzoquinone in several solvents and of 26 alkyl-, methoxy-, halogeno-, and amino-substituted *p*-benzoquinones in *n*-hexane and in chloroform are recorded and discussed.

ALTHOUGH the visible and the ultra-violet light absorption of *p*-benzoquinone and its simple substitution derivatives have been studied (Dobbie, Lauder, and Walker, *Brit. Assoc. Rep.*, 1903, 126; Baly and Stewart, J., 1906, **89**, 502, 618; Hartley and Leonard, J., 1909, **95**, 34; Hartley, *ibid.*, p. 54; Hantzsch and Hein, *Ber.*, 1915, **48**, 167; 1919, **52**, 493; Lifschitz *et al.*, *Ber.*, 1915, **48**, 1730; 1916, **49**, 2050; *Rec. Trav. chim.*, 1924, **43**, 269, 403, 654; Purvis, J., 1923, **123**, 1841; Marchlewski and Moroz, *Bull. Soc. chim.*, 1924, **35**, 473; Seshan, *Proc. Indian Acad. Sci.*, 1936, **3**, 172), yet only few extensive or accurate data are available for the solution spectra (Klingstedt, *Compt. rend.*, 1923, **176**, 1550; Light, *Z. physikal. Chem.*, 1926, **122**, *A*, 414;

Scheibe, *Ber.*, 1926, **59**, 2617; Anderson, *J. Amer. Chem. Soc.*, 1933, **55**, 2094) and these relate to benzoquinone and alkylbenzoquinones only. Brull and Griffi's data (*Gazzetta*, 1939, **69**, 28) for the visible-light absorption of a number of substituted benzoquinones would appear to be wholly in error. Naphthaquinones and anthraquinones have been covered more fully (Macbeth and Winzer, J., 1939, 878; Morton and Earlam, J., 1941, 154; Doisy, Binkley, and Thayer, *Chem. Rev.*, 1941, **28**, 477).

The fundamental theoretical interest attaching to the quinone chromophore as intermediate between aliphatic and benzenoid systems and as the basic structure of many dyes, and the empirical value of light-absorption data for purposes of identification and quantitative estimation, appeared to warrant a detailed study, particularly in view of the increasing recognition of the biochemical importance of *p*-benzoquinones (Cooper *et al.*, *J. Soc. Chem. Ind.*, 1924, **43**, 352; 1927, **46**, 59; *Biochem. J.*, 1928, **22**, 317; Gulland, *ibid.*, 1932, **26**, 32; Oxford and Raistrick, *Chem. and Ind.*, 1942, **61**, 128; Oxford, *Biochem. J.*, 1942, **36**, 438; Alexander and Barton, *ibid.*, 1943, **37**, 463).

Apart from the inaccuracy of the experimental methods available at the time, most of the earlier studies are invalidated by the use of hydroxylic solvents. Solutions of *p*-benzoquinone itself and of alkyl- and halogen-substituted benzoquinones in water, alcohols, and ethers are unstable, especially to light, forming mainly quinols and so-called anilic acids (Ciamician and Silber, *Ber.*, 1901, **34**, 1531; Hartley, *loc. cit.*; Scheibe, *Ber.*, 1926, **59**, 2617). The instability increases with increasing substitution, ethyl-alcoholic solutions of some polyhalogenoquinones undergoing change in visible colour within a few minutes of dissolution. Alkylquinones react more slowly than halogenoquinones, the time of half-change of toluquinone in daylight at room temperature being of the order of one day, whereas with benzoquinone the reaction takes several weeks. In methyl alcohol, on the other hand, optical change can be detected within a few minutes.

The light-absorption properties of *p*-benzoquinone in a number of solvents and of 26 substituted benzoquinones in *n*-hexane and in chloroform solutions have been measured in the range 2100—6000 A. These solutions were in all cases optically stable for at least 24 hours. Fine-structure narrower than *ca.* 20—50 A. (depending on the wave-length region and the height of the subsidiary bands) was not detectable by the method employed, but this is no disadvantage, for interest is focused on the assignment of " band-envelopes " to electronic transitions rather than on vibrational analysis. Except with the higher members of the monoalkyl series, the differences in the extinction curves of isomers or homologues are always sufficiently great for identification purposes. Beer's law was invariably obeyed within the experimental error ($\pm$ 2% in ε) and the range of concentrations (0·01—1% w/v) employed.

Benzoquinone itself shows three bands : a high-intensity band near 2450 A. ($\varepsilon \sim 25,000$), a medium-intensity band near 2850 A. ($\varepsilon \sim 500$), and a resolved low-intensity band near 4350 A. ($\varepsilon \sim 20$) (these three bands are subsequently referred to as A, B, and C) (Table I). The order of solvents in which the wave-length position of the band maxima increases is different for the three bands. The intensities similarly show small, apparently random variations. It is clear that there is no simple relationship between band position, extinction coefficient, and

TABLE I.

Light absorption of p-*benzoquinone in various solvents.*

	A.		B.		C.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
n-Hexane	2420	24,300	2810	400	4340	19·8
					4570	19·6
					4790	12·0
*cyclo*Hexane	2420	17,900	2850	420	4350	20·8
					4570	22·3
					4730	12·8
Chloroform	2450	23,200	2810	470	4370	21·6
			2910	470	4510	21·6
Ethyl ether	2410	18,700	No band		4320	18·3
					4540	18·3
Dioxan	2415	16,000	No band		4350	20·8
	2440	15,700			4480	20·4
Ethyl alcohol	2420	17,700	2960	425	4350	19·2
Water	2470	21,500	2920	330	4360	20·4
1м-HCl	2450	22,700	2910	315	4380	22·8
	2490	21,800				

fine-structure resolution on the one hand, and dielectric constant, dipole moment, or other physical property of the solvent on the other (cf. Scheibe and Fromel, " Hand- und Jahrbuch der Chemischen Physik," 1936, **9**, 314). It is notable, however, that band B, which in the case of benzoquinone is of the nature of a " step-out " rather than a pronounced maximum, disappears almost completely in ethyl ether and in dioxan, both highly solvating solvents.

The data for the substituted benzoquinones are given in Table II and Figs. 1, 2, and 3, and the rather complex substitution effects are summarised in Table III. The variation in the intensity of band B in the methyl, chloro- and bromo-series, which is of particular interest, is represented graphically in Fig. 4. Change of solvent from hexane to chloroform has little effect on the intensity and fine structure resolution, and on the

TABLE II.

Light absorption of substituted p-benzoquinones.

| | Solvent : n-hexane. | | | | | | Solvent : chloroform. | | | | | |
| | A. | | B. | | C. | | A. | | B. | | C. | |
Substituents.	λ_{max}., A.	ε_{max}.	λ_{max}., A.	ε_{max}.	λ_{max}., A.	ε_{max}.	λ_{max}., A.	ε_{max}.	λ_{max}., A.	ε_{max}.	λ_{max}., A.	ε_{max}.
I. Me	2450	23,400	3080	760	4340 4550 4750	22·6 22·6 13·4	2520	24,200	3150	740	4360 4500	28·5 27·0
II. Et	2440	23,500	3070	860	4340 4530	34·2 33·4	2480 2560	20,200 19,600	3180	890	4370 4720	34·0 24·1
III. n-C₁₂H₂₅	2445 2490	17,300 16,900	3070 3165	800 725	Not determined		2505 2560	18,400 18,000	3160 3250	865 865	Not determined	
IV. n-C₁₄H₂₉	2450 2500	18,200 17,600	3070	1030	4390	40·6	2515 2560	18,500 18,000	3170 3250	1020 1020	4360 4780	52·3 35·8
V. n-C₁₆H₃₃	2455 2505	20,800 19,600	3080	980	4350	43·0	2510 2555	20,200 17,900	3090 3250	895 895	4340	51·0
VI. n-C₁₈H₃₇	2450 2510	22,700 20,200	3090 3160	880 850	Not determined		2505 2560	20,700 18,600	3090 3200	815 870	Not determined	
VII. 2 : 3-di-Me	2500 2555	20,800 19,700	3030 3080	375 375	4330	21·4	Not determined					
VIII. 2 : 6-di-Me *	2500	14,000	3030	175	4240	23·0	Not determined					
IX. 2 : 5-di-Me	2500 2560	22,200 21,100	3050	295	4370	22·6	2555 2620	23,800 20,700	3060	310	4340	29·8
X. 2-Me-5-Prβ	2505 2550	20,800 20,200	3070	300	4380	25·7	2565 2610	22,800 20,800	3160	290	4380	29·8
XI. Tri-Me	2530 2600	19,800 19,400	3270	470	4350	32·7	2585	22,300	3380	415	4340	41·0
XII. Tetra-Me	2585 2640	21,000 20,500	3305	210	4320	24·6	2640 2690	21,700 21,400	3390	240	4350	32·6
XIII. 5-MeO-2-Me	2580	18,900	3480	815	No band		2640	19,200	3600	725	No band	
XIV. 2 : 6-di-MeO	Insoluble						2880	15,400	3320	1670	,,	
XV. Cl	2510	19,100	3150	970	No band		2580	19,600	3230	815	~4150	27·3
XVI. 2 : 6-di-Cl	2690	20,000	3270	610	,,		2750	22,100	3410	635	No band	
XVII. 2 : 5-di-Cl	2700	22,100	3270	285	,,		2740	23,000	3300	295	,,	
XVIII. Tri-Cl	2700 2780	16,000 17,000	3560	500	,,		2815	19,900	3640	510	,,	
XIX. Tetra-Cl	2820 2910	20,500 26,200	3620	300			2820 2920	21,400 23,800	3720	280	,,	
XX. Br	2540	12,400	3290	1190	,,		2580	11,900	3380	1070	~4400	25·6
XXI. 2 : 6-di-Br	2820 2910	12,200 12,900	3520	805	,,		2820 2920	13,700 15,000	3620	810	No band	
XXII. 2 : 5-di-Br	2820 2880	12,300 12,100	3280 3370	270 270	,,		2820 2910	12,000 12,300	3510	240	,,	
XXIII. Tri-Br	2960	10,800	3750	580	,,		3010	12,500	3850	665	,,	
XXIV. Tetra-Br	3080	15,700	3780	280	,,		3140	17,500	3980	300	,,	
XXV. 2 : 5-di-NMe₂	2210 3530	26,800 24,300	4800	340	—		3680	24,300	5250	500	—	
XXVI. 2 : 5-di-NHPh	Insoluble						2640 3880	19,100 15,400	5200	885	—	

* Light, *loc. cit.*

TABLE III.

Substituent effects in the visible and ultra-violet light absorption of p-benzoquinones.

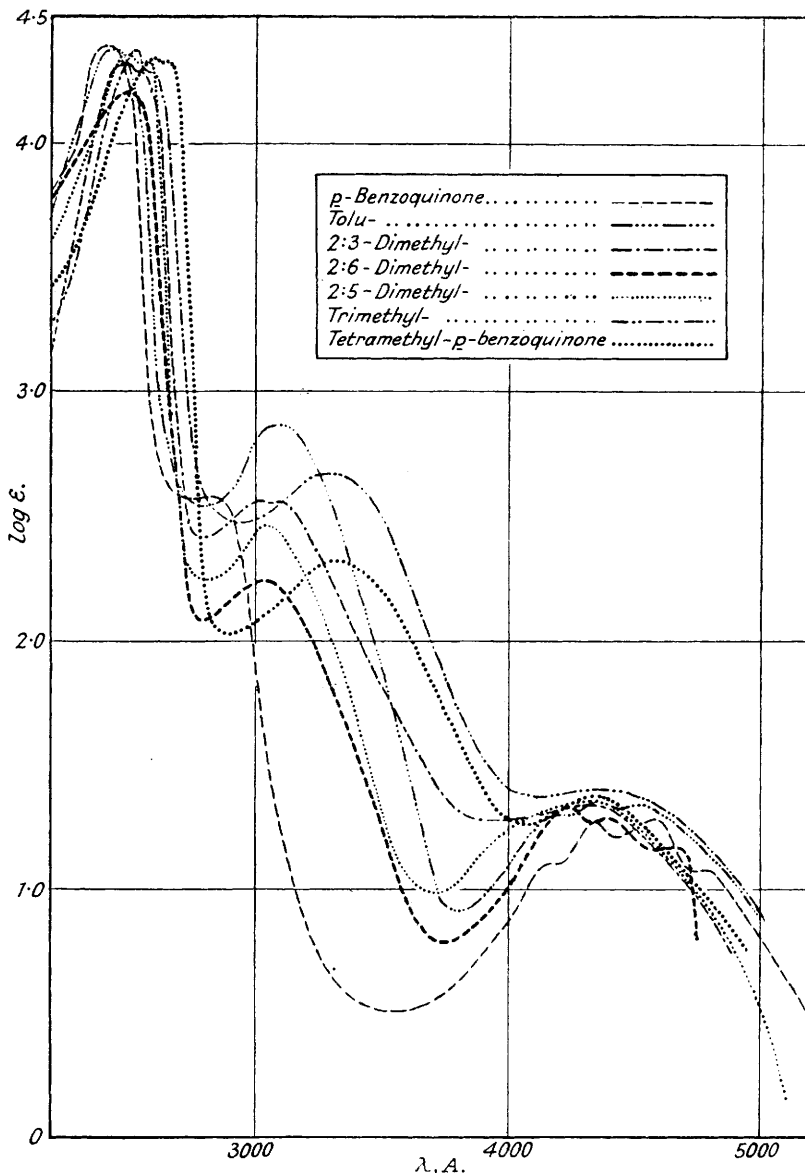(n = Number of substituents; BQ = p-benzoquinone; Δλ in A.)

Absorption band.		Alkyl.	Chloro.	Bromo.	Methoxy.	Amino.
A.	λ_{max}.	+Δλ = ~50 × n. Fine structure increases with n. λ_{max}. and fine structure also slightly increase with increasing size of alkyl group.	+Δλ = ~100, 300, 400, 500 for n = 1, 2, 3, 4.	+Δλ = ~100, 400, 550, 650 for n = 1, 2, 3, 4.	+Δλ = 100, 400 for n = 1, 2.	+Δλ = 1100 for n = 2, and new high-intensity band at shorter wavelength.
	ε	Decreases slightly with increasing n and size of alkyl group.	Small irregular variation with n.	Halved for n = 1, then slightly increases with n.	−Δε = ~4000 × n.	Unchanged.
B.	λ_{max}.	+Δλ = 300 for n = 1, 2; +Δλ = 500 for n = 3, 4. Fine structure increased.	+Δλ = ~350, 450, 750, 800 for n = 1, 2, 3, 4.	+Δλ = ~500, 600, 950, 1000 for n = 1, 2, 3, 4.	+Δλ = ~500 for n = 1, 2.	+Δλ = 2000 for n = 2.
	ε	Varies with n (Fig. 4).	Varies with n (Fig. 4).	Varies with n (Fig. 4).	Unchanged in 5-MeO-2Me-BQ. Four-fold increase in 2 : 6-di-MeO-BQ.	Unchanged.
C.	λ_{max}.	Unchanged. Fine structure decreases with n and size of alkyl group.	No band, except for n = 1.	No band except for n = 1.	No band.	—
	ε	Slightly increased by methyl groups; doubled by long-chain alkyl groups.	—	—	—	—

location of band C, but it increases the wave-length positions of band A by 30—60 A., and of band B by 100—200 A.

<div align="center">DISCUSSION.</div>

In discussing the selective light absorption due to a comparatively complex system such as *p*-benzoquinone, it is customary to attempt an assignment of the various electronic bands to the simpler constituent systems, or partial chromophores. Such attempts are based on the assumption that some or all of the partial chromo-

<div align="center">FIG. 1.

Light absorption in n-*hexane solution.*</div>

p-Benzoquinone........... —————
Tolu- .... ▬▬▬▬
2:3-Dimethyl- .... ▬·▬·▬·
2:6-Dimethyl- .... ▬▬ ▬▬
2:5-Dimethyl- ....
Trimethyl- .... ▬··▬··▬··
Tetramethyl-p-benzoquinone ....

phores are maintained as individual systems in the complex molecule, without being radically altered by interaction with the other systems present; or, if interaction does occur, that the bands characteristic of the partial chromophores are to some extent preserved in the presence of bands due to the more complex whole. Conversely, the degree of modification of the bands expected for the partial chromophores is regarded as an indication of the extent of electronic interaction. Apart from the values of $\lambda_{max.}$ and $\varepsilon_{max.}$ (or of the curve area $\int \varepsilon d\lambda$), a particular absorption band can often be related to an individual chromophore by the dependence of $\lambda_{max.}$ and $\varepsilon_{max.}$ on the solvent and on non-absorbing substituents. Such correlations are purely empirical

and do not depend on the precise theoretical interpretation of the light-absorbing properties of the individual chromophores.

The recognition of the fact that certain types of molecule are not satisfactorily represented by any one conventional structural formula, but that two or more " resonance " structures, differing in the distribution of the electron pairs about the atomic nuclei, make a contribution to the normal state of the molecule, necessitates the recognition of additional chromophore possibilities. Bands due to chromophores present in any

FIG. 2.
Light absorption in chloroform solution.
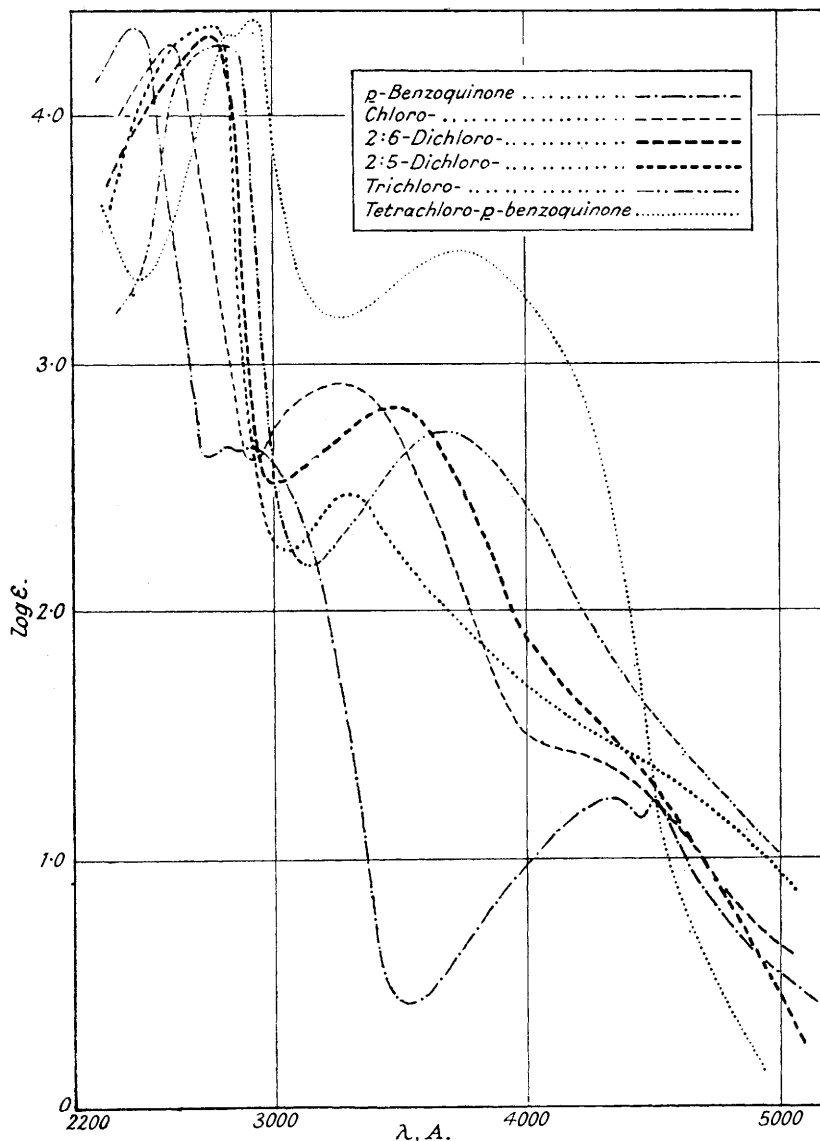
of the chief resonance forms may appear, but in addition, bands may arise from transitions between the " hybrid " ground state and the resonance forms.

In the case of *p*-benzoquinone, the structures which would be expected *a priori* to make the chief contributions to the ground state are shown in (I)—(V). The structures (I) and (II) have long been advocated on chemical grounds, which indicate that (I) predominates. The peroxide structure (II) has been completely eliminated, however, by Robertson's *X*-ray diffraction study (*Proc. Roy. Soc.*, 1935, *A*, **150**, 106). This result is supported by dipole-moment measurements (Hammick, Hampson, and Jenkins, J., 1938, 1277; Coop and Sutton, J., 1938, 1269); the evidence from magnetic moments is somewhat ambiguous (Mikhail and Baddar,

Light absorption of $\begin{cases} 1. & \text{p-benzoquinone} \\ 2. & 2:5\text{-dimethylamino-p-benzoquinone} \\ 3. & 2:5\text{-dianilino-p-benzoqvinone} \end{cases}$

in chloroform solution.

FIG. 3.

FIG. 4.
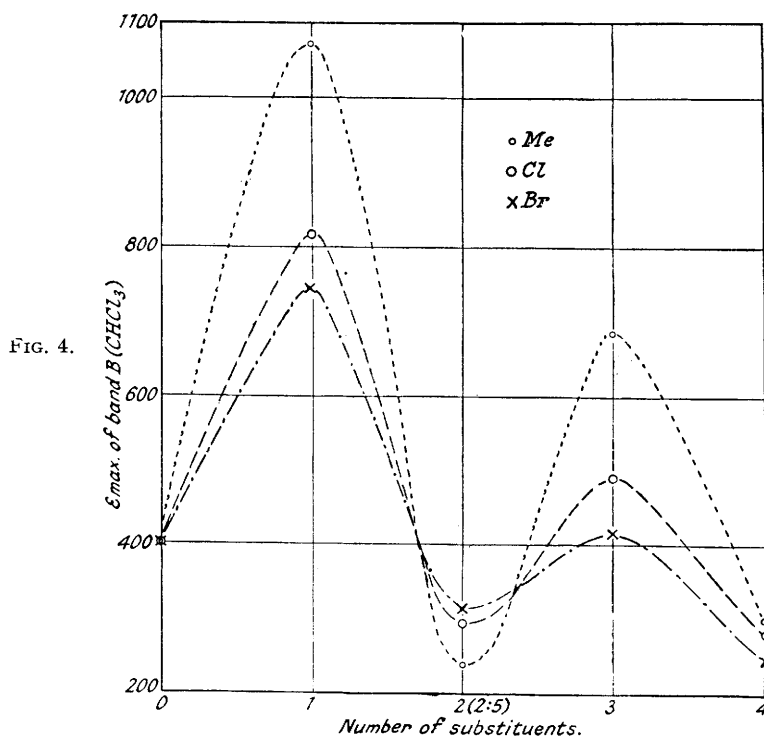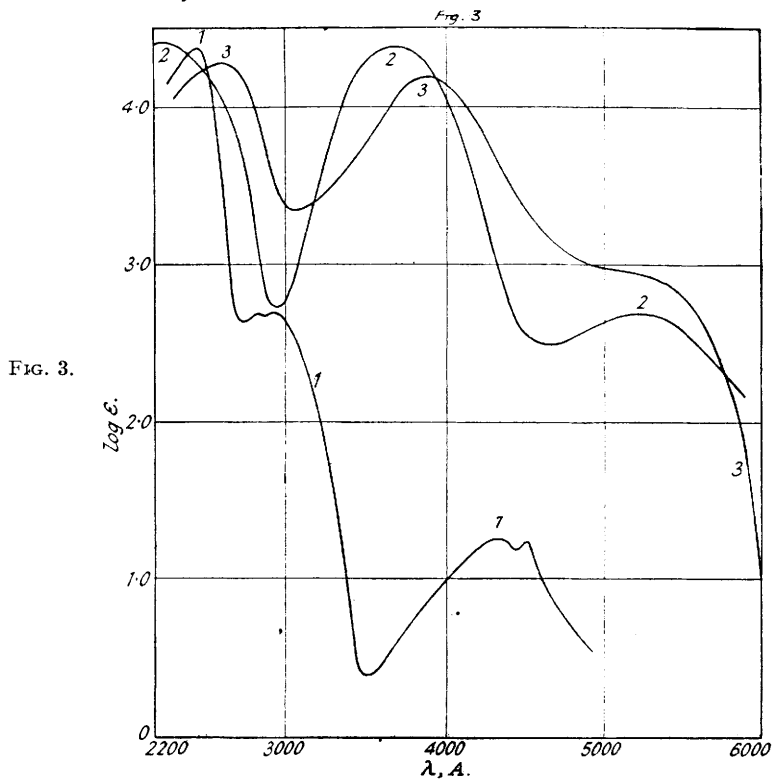
J., 1944, 590), but appears to indicate contributions from polar structures.   The empirical resonance energy is 13 kg.-cals./mol. (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606).
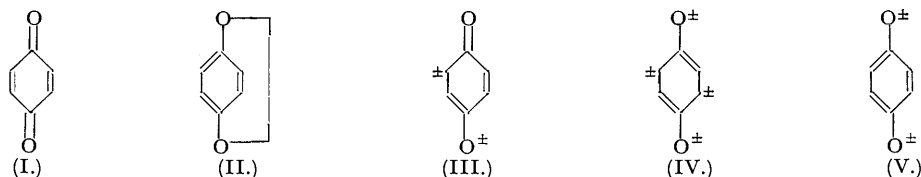
The partial chromophores of the resonance structures (I), (III), (IV), and (V) most likely to give rise to
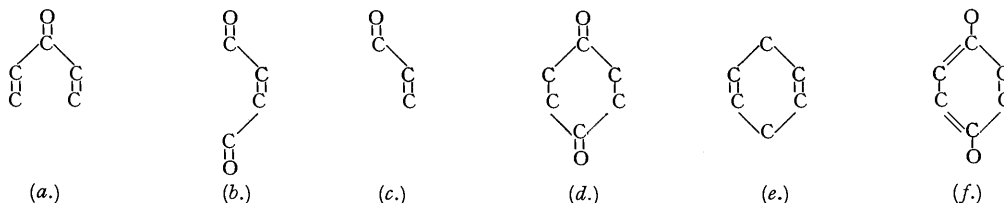
selective absorption in the 2100—6000 A. region can be represented by (*a*)—(*f*).   The light absorption in alcoholic solution of typical compounds containing these systems is as follows :

Type.	Compound.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	Type.	Compound.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
(*a*)	Phorone	2590	23,500 [1]	(*d*)	1 : 4-*cyclo*Hexanedione	2820	30 [4]
		3750	80	(*e*)	$\Delta^{1:4}$-*cyclo*Hexadiene	No high-intensity absorption $>\lambda = 2100$ [5]	
(*b*)	Diacetylethylene	2260	14,600 [2]	(*f*)	Quinol	2250	4400 [6]
		3380	70			2950	2400
(*c*)	Ethylideneacetone	2240	10,000 [3]				
		3135	40				

[1] Scheibe, *Ber.*, 1925, **58**, 587.   [2] Unpublished.   [3] Evans and Gillam, *J.*, 1941, 815.   [4] Unpublished.
[5] Measurements on 6-hydroxy-3 : 3 : 6-trimethyl*cyclo*hexadiene in ethereal solution, quoted by Dimroth, *Angew. Chem.*, 1939, **52**, 545.   [6] Klingstedt, *Compt. rend.*, 1922, **175**, 365.

On a purely numerical basis, band A ($\lambda_{max.}$ *ca.* 2500 A.) is intermediate between the high-intensity bands of (*a*), (*b*) and (*c*), and band B ($\lambda_{max.}$ *ca.* 3000 A.) is intermediate between the benzenoid band of (*f*) and the low-intensity bands of (*c*) and (*d*), while a band similar to band C ($\lambda_{max.}$ *ca.* 4400 A.) is not shown by any of the formal constituent systems.   An almost identical band is shown, however, by α-diketones, *e.g.*, diacetyl.   The last two relationships were appreciated by the early investigators (Hartley and Leonard, *loc. cit.*; Stewart and Baly, *loc. cit.*) and generally accepted by later workers.   Lifschitz (*loc. cit.*), on the other hand, considered that bands A and C originate in electrons belonging to carbon atoms, and band B in electrons belonging to oxygen atoms, and that the light absorption of quinones resembles that of " crossed " rather than " straight " conjugated systems (*e.g.*, phorone).   The three bands will be discussed in turn.

Band A shows wave-length position, intensity, and solvent and substituent effects very similar to the K (high-intensity) band of αβ-unsaturated ketones, $CHR_1{:}CR_2{\cdot}\overset{|}{C}{:}O$.   Table IV gives a formal comparison of substituent effects in the two systems (the quinone system is taken as the sum of two αβ-unsaturated ketone

TABLE IV.

Substituents	None	2 × Me	4 × Me	4 × Br	2 × NMe$_2$		2 × NHPh	
$\lambda_{max.}$, A band, *ca.*	2400	2500	2650	3100	2200	3500	2650	3900
Substituents	None	1 × Me	2 × Me	2 × Br	1 × NMe$_2$		1 × NHPh	
$\lambda_{max.}$, K band, *ca.*	2150 [1]	2250 [1]	2400 [1]	2600 [2]	2200	3100 [2]	2300	3400 [2]
Δλ	250	250	250	500	0	400	350	500

[1] Evans and Gillam, *J.*, 1941, 815.   [2] Unpublished data obtained in these laboratories.

systems for this purpose, so that two substituents in the former correspond to one in the latter).   The A bands are displaced to higher wave-lengths with respect to the corresponding K bands of αβ-unsaturated ketones by 250—500 A., and this displacement may be regarded as due to interaction between the two " half-systems " of the quinone molecule.   It is interesting that the high-intensity bands at shorter wave-lengths which appear on introduction of dimethylamino- and anilino-groups are also observed in aliphatic systems; these additional bands may be ascribed to the partial –C:C·NR$_2$ chromophore (forthcoming publication).

Band B is the most susceptible to changes of solvent and substituents.   It takes the form of a " step-out "

rather than a distinct maximum, and evidently arises from the superposition of a discrete maximum of lower intensity on the continuous absorption due to the falling branch of the high-intensity band A. In *p*-benzoquinone itself band B is very similar in position and intensity to that exhibited by quinol, and this similarity is confirmed by vibrational analysis of the vapour spectra (Seshan, *loc. cit.*). Data are not, however, available to establish whether the very marked solvent and substituent effects exhibited by band B are also shown by the corresponding quinols.

If the assignment of band A as corresponding to the K band of $\alpha\beta$-unsaturated ketones is correct, and possesses more than formal significance, then the low-intensity R band of the latter should also be exhibited by the quinone system. It would be masked, however, by the more intense band due to the partial chromophore (f) falling in the same wave-length region. The alternative possibility, *viz.*, that band B is itself an intensified R band, can certainly be discounted since the wave-length position of the latter is displaced in the opposite sense by different solvents and is almost independent of substituents. Also, there is no relationship between the very pronounced variations in intensity of the B band and the oxidation–reduction potentials (La Mer and Baker, *J. Amer. Chem. Soc.*, 1922, **44**, 1954; Conant and Fieser, *ibid.*, 1923, **45**, 2194) of the quinones. It may be possible, however, that these variations are due to the varying small contributions of the benzenoid resonance form (e) to the ground states of the various quinones.

Band C is almost identical both in shape and in vibrational fine structure with the long wave-length band of diacetyl and other α-diketones (Baly and Stewart, *loc. cit.*; Lardy, *Compt. rend.*, 1923, **176**, 1548; Klingstedt, *loc. cit.*; Lowry and Simpson, *J.*, 1936, 1156). The origin of this band is not clearly understood; steric juxtaposition of the two carbonyl groups is not sufficient for its appearance since it is not shown by 1 : 4-*cyclo*hexanedione or by diacetylethylene. The fact that band C originates in the carbonyl groups is confirmed by the observation (Hunter and Northey, *J. Physical Chem.*, 1933, **37**, 875) that the change in visible light absorption of quinones due to molecular compound formation increases regularly with increasing oxidation–reduction potential of the quinone. If band C is due to the partial chromophore (c), the retention of vibrational fine structure almost identical with that shown by α-diketones is not easily understood. It might be thought that band C originates in an α-diketone system simulated by orientation of the quinone molecules leading to superimposed rings and adjacent carbonyl groups, but both X-ray diffraction and magnetic susceptibility measurements (Robertson, *loc. cit.*; Mikhail and Baddar, *loc. cit.*) provide evidence against such orientation. Band C is hardly affected by alkyl substituents, but the long-chain alkyl quinones are almost colourless in the solid state, whereas in solution band C is intensified as compared with that in benzoquinone. When the number of halogen substituents exceeds one, band C disappears, possibly owing to interaction between the substituents and the carbonyl oxygen (cf. Hodgson, *J. Soc. Dyers Col.*, 1944, **60**, 65). The visible colour is maintained nevertheless in the more highly substituted quinones through the general absorption and because band B moves into the visible region.

EXPERIMENTAL.

Materials.—None of the compounds investigated is new. The highest degree of purity was essential, particularly in view of the strong absorption of the common impurities, such as quinhydrones, and the low intensities of the long wave-length bands. Hydroxylic solvents, though widely used, are unsuitable for the recrystallisation of quinones for the reasons already cited. Light petroleum (b. p. 40—60° or 60—80°) was invariably employed. Purification was also effected by sublimation in a high vacuum, but this often resulted in loss of material through the formation of dark, intractable residues. References to the methods of preparation and the m. p.'s given in the literature, preceded by the m. p.'s (sealed tube, uncorr.) found, are given below.

(I) 113° (Underwood and Walsh, *Org. Synth.*, 1932, **14**, 73, give 113°); (II) 67° (Nietzki, *Annalen*, 1882, **215**, 125, gives 67°); (III) 38° (prepared by the method of Cook, Heilbron, and Lewis, J., 1942, 659; Bayrac, *Ann. Chim.*, 1897, **10**, 18, gives 38°); (IV) 70° (Cook, Heilbron, and Lewis, *loc. cit.*, give 72°); (V) 77·5° (*idem, ibid.*, give 77·5°); (VI) 83° (*idem, ibid.*, give 83°); (VII) 76° (*idem, ibid.*, give 76°); (VIII) 55° (Noelting and Forel, *Ber.*, 1885, **18**, 2668, give 55°); (IX) 121° (Noelting and Baumann, *ibid.*, 1885, **18**, 1151, give 123°); (X) 45° (Kremers, Hixon, and Wakeman, *Org. Synth.*, 1926, **6**, 92, give 45·5°); (XI) 72° (Noelting and Baumann, *loc. cit.*, give 72°); (XII) 30° (Nietzki and Schneider, *Ber.*, 1894, **27**, 1429, give 32°); (XIII) 111° (Smith, *Org. Synth.*, 1930, **10**, 40, gives 110°); (XIV) 158° (Ashley, J., 1937, 1471, gives 173°); (XV) 236° (Graebe and Hess, *Annalen*, 1905, **340**, 232, give 255°, corr.); (XVI) 52° (Levy and Schultz, *ibid.*, 1881, **210**, 133, give 57°); (XVII) 159° (*idem, ibid.*, give 159°); (XVIII) 118° (Faust, *ibid.*, 1869, **149**, 149, gives 120°); (XIX) 162° (von Knapp and Schultz, *ibid.*, 1881, **210**, 164, give 165°); (XX) 286° (Graebe, *ibid.*, 1891, **263**, 16, gives 283—290°); (XXI) 56° (Sarauw, *ibid.*, 1881, **209**, 93, gives 56°); (XXII) 191° (*idem, ibid.*, gives 187°); (XXIII) 130° (Levy and Schultz, *loc. cit.*, give 131°); (XXIV) 155° (Sarauw, *loc. cit.*, gives 147°); (XXV) 296° (Ling, J., 1892, **61**, 558, gives 300°); (XXVI) 174° (Mylius, *Ber.*, 1885, **18**, 463, gives 173°); (XXVII) 343° (Willstätter and Majima, *Ber.*, 1910, **43**, 2558, give 345°).

The large discrepancies in m. p.'s cited in the literature have already been commented upon by Conant and Fieser (*loc. cit.*). Colour is often as good a criterion of purity as m. p. in this series.

Light-absorption Measurements.—These were carried out by standard methods using a Hilger E 498 quartz spectrograph fitted with a Spekker photometer and a 15,000-volt tungsten-steel spark as light source. Quinone solutions were kept in the dark, and exposures taken within half an hour of dissolution, cells 0·01—10 cm. long being used. ε is the molecular extinction coefficient defined by $\varepsilon = (\log_{10} I_0/I)/cl$, where I_0 and I = intensity of incident and of transmitted light. respectively, c = concentration in mols./l., and l = cell thickness in cm.