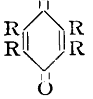
430. *Spectra of Anthraquinone Derivatives.*

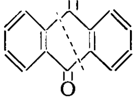
By R. H. Peters and H. H. Sumner.

The absorption spectra of a number of mono- and di-substituted anthraquinones have been measured, and the effect of the substituents on the visible colour of anthraquinone has been correlated with the electromeric possibilities of the groups. The wave-length of maximum absorption also depends on the ability of the substituents to take part in internal hydrogen bonds and on the presence of steric interactions in the molecule. Interaction between 1 : 4-substituents is demonstrated, the position of the absorption peak of 1-amino-4-R-anthraquinone depending on the nature of R. This effect is much less marked in the 1 : 5-compounds. Results showing the effect of chromophoric insulation in a series of derivatives containing two anthraquinone nuclei are included. It is found that methylene groups, and both *m*- and *p*-phenylene residues act as excellent chromophoric insulators in the compounds studied.

The relation between the colour and the constitution of anthraquinone derivatives has been studied by Morton and Earlam (*J.*, 1941, 159) and by Spruit (*Rec. Trav. chim.*, 1949, **68**, 325) for both the visible and the ultra-violet region of the spectrum. They concluded that for simple substituted anthraquinones the spectra may be obtained by summation from less complex series. For instance, Morton and Earlam constructed the spectrum of anthraquinone from twice that of acetophenone plus a contribution from a chromophore of the type (I), the weak visible band originating in the carbonyl groups of the latter. The spectrum was therefore regarded as arising from the two halves of the molecule divided diagonally as in (II). Spruit, on the other hand, derived the spectra of simple anthraquinone derivatives from the algebraic sum of those of the substituted naphthaquinones corresponding to the two halves of the molecules; *e.g.*, anthraquinone gave a spectrum which is double that of 1 : 4-naphthaquinone. He thus attributed the weak visible band to a " fundamental " electronic oscillation of naphthaquinone, and not of anthraquinone. This suggests that the visible spectrum of an anthraquinone derivative arises from a particular part of the molecule and, as such, the visible bands would be described in the terminology of G. N. Lewis as " partials " (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273). However, it is to be expected that strongly coloured substituted anthraquinones will show bands due to the molecule as a whole, *i.e.*, " fundamentals : " indeed, the intensity of the yellow colour of benzoquinone, naphthaquinone, and anthraquinone decreases in that order, which may be associated with the decreasing quinonoid character of the molecules, as suggested by Morton and Earlam (*loc. cit.*).



(I)



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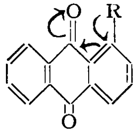

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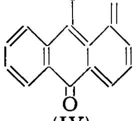


(IV)

In benzoquinone the molecule is mainly quinonoid, whilst in naphthaquinone the second ring has two Kekulé structures; the additional resonance will change the double-bond character of the bond common to both rings, thereby reducing the quinonoid character of the molecule. In anthraquinone, with two benzene rings capable of resonance, this effect is even more marked; and the visible band of this compound is very weak.

A substituent in these nuclei will affect the resonance, causing either a change in the existing bands associated with the quinonoid part of the molecule, or development of new absorption bands arising from new resonance possibilities. The groups normally regarded as auxochromes may be expected to act in the latter way. Change in the existing bands has been studied in detail by Morton and Earlam (*loc. cit.*); the work now reported is concerned in the main with the new bands. We append some observations on the spectra of anthraquinone compounds which show strong absorption bands in the visible region of the spectrum. These bands are attributed to " fundamental " oscillations in the molecule, and their positions are correlated with the electromeric properties of the substituents.

Mono-substituted Anthraquinones.—The above views are similar to those given by Spruit (*loc. cit.*) and Allen, Wilson, and Frame (*J. Org. Chem.*, **1942**, **7**, 169), who have postulated that the visible colour of substituted anthraquinones depends on the ability of the substituents to supply electrons by a " mesomeric shift " to the nucleus, and in particular to the carbonyl oxygen of the quinonoid grouping, as indicated in (III), thereby increasing the contribution from (IV). Such ionic states are considered to be the optically important resonance forms, and hence the substitution of any group which has an atom more capable of carrying a positive charge than the carbon atom of the unsubstituted molecule will lower the energy of these forms and increase their contribution to the system. Enhancement of these forms will give an increase in colour, which will be generally shown as a shift in absorption to longer wave-length or by development of a new band. However, before considering the visible colour of these compounds it is necessary to discuss the ultra-violet absorption.

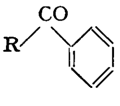
The ultra-violet absorption spectrum of anthraquinone can be considered to originate

TABLE 1. *Ultra-violet absorption peaks of monosubstituted anthraquinones in methanolic solution.*

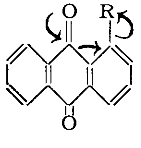
Substituent R	1-R-Anthraquinone				2-R-Anthraquinone			
	" Benzenoid " bands *		" Quinonoid " bands *		" Benzenoid " bands *		" Quinonoid " bands *	
NO_2	255 (37,000)	325 (4,300)	—	—	258 (39,700)	323 (5,200)	—	—
CN	257 (43,000)	325 (3,400)	—	~272 (ca. 12,000	255 (48,600)	325 (5,300)	—	~270 (ca. 18,000)
Cl	253 (42,800)	333 (5,000)	~266 (ca. 14,000)	~270 (ca. 13,000)	256 (49,400)	325 (3,900)	~265 (ca. 23,000)	274 (17,100)
H	252 (48,100)	323 (4,500)	~262 (ca. 20,000)	272 (18,400)	252 (48,100)	323 (4,500)	~262 (ca. 20,000)	272 (18,400)
Me	252 (45,200)	331 (4,800)	~263 (ca. 18,000)	272 (14,500)	—	—	—	—
OH	252 (29,000)	327 (3,300)	~266 (ca. 14,000)	~277 (ca. 12,000)	245 (20,500)	328 (4,400)	271 (33,600)	~279 (ca. 28,000)
OMe	254 (32,800)	328 (2,900)	~262 (ca. 23,000)	~270 (ca. 15,000)	246 (16,200)	329 (3,600)	267 (32,700)	~280 (ca. 24,000)
NH_2	236 (32,200)	298 (5,500)	261 (12,400)	~270 (ca. 11,000)	242 (31,300)	~327 (ca. 9,000)	~286 (ca. 21,000)	298 (23,500)
O^-	246 (35,000)	313 (5,000)	—	273 (11,400)	243 (31,900)	~338 (ca. 7,000)	~285 (ca. 17,000)	304 (23,100)
NHMe	243 (31,400)	312 (7,000)	—	272 (11,000)	243 (31,200)	~345 (ca. 8,000)	~287 (ca. 17,000)	303 (21,400)
NMe_2	246 (33,000)	317 (6,400)	—	~272 (ca. 11,000)	244 (31,800)	352 (8,900)	~290 (ca. 15,000)	307 (19,600)

~ denotes inflexion. * Wave-length, mμ (extinction coefficient).

in contributions from the chromophoric systems, (I) and (V) (Morton and Earlam, *loc. cit.*). The bands at 252 and 325 mμ are associated with the benzenoid character of the molecule, and those at 263 and 272 mμ are considered to originate in the C:C bond of the quinone (I). These bands are still evident, more or less modified, in substituted anthraquinones. Electron-attracting substituents do not much alter the absorption spectrum (see Table 1), owing mainly to the counteracting influence of the carbonyl oxygen which hinders transfer of electrons across the molecule as in (VI) and (VII). The most noticeable effect in the 1-position is the decrease in intensity of absorption, while for the 2-derivatives even this effect is absent, the changes occurring being merely small alterations in the position of the maxima.



(V)



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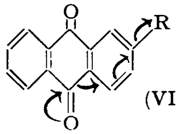


(VII)

Electron-donating substituents have more marked effects on the ultra-violet absorption spectra. For the 1-derivatives the band at 252 mμ shows in general a lower intensity and a trend towards shorter wave-lengths as one proceeds downwards from H in Table 1, while for the band at 325 mμ the changes are more random, being bathochromic with reduced intensity for Me, OH, and OMe, and hypsochromic with increased intensity for NH_2, O^-, NHMe, and NMe_2. For these derivatives there is little change in those bands associated with the quinonoid structure, except that again there appears to be a tendency for the intensity to be diminished by substitution. For the 2-derivatives a hypsochromic shift of the band at 252 mμ, and bathochromic shifts of the bands at 323, 262, and 272 mμ are observed. Associated with these changes is an increase in intensity of the band at 272 mμ, due to contributions of structures of type (VIII). This is particularly noticeable for 2-hydroxyanthraquinone where the bands at 271 and 279 are notably more intense. These results for electron-donating substituents accord with the observations of Morton and Earlam (*loc. cit.*) who suggest that substitution at position 1 decreases the importance of the quinonoid element, while substitution at position 2 increases it.

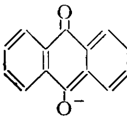
TABLE 2. *Visible absorption bands of monosubstituted anthraquinones.*

Substituent R	Band of longest wave-length			
	1-R-Anthraquinone *		2-R-Anthraquinone *	
	in MeOH	in o-$C_6H_4Cl{\cdot}OH$	in MeOH	in o-$C_6H_4Cl{\cdot}OH$
NO_2	—	—	∼420 (ca. 50)	—
CN	∼417 (ca. 70)	—	∼413 (ca. 100)	—
Cl	∼415 (ca. 100)	—	—	—
H	∼410 (ca. 60)	—	∼410 (ca. 60)	—
Me	∼415 (ca. 150)	—	—	—
OMe	378 (5,200)	—	363 (3,950)	—
OH	402 (5,500)	—	368 (3,900)	—
NH_2	475 (6,300)	488 (6,400)	440 (4,500)	445 (6,400)
NHMe	503 (7,100)	—	462 (5,700)	—
O^-	493 (5,000)	—	465 (5,400)	—
NMe_2	503 (4,900)	—	472 (5,900)	—
NHAc	400 (5,600)	414 (5,000)	367 (4,200)	—
NHBz	405 (6,400)	424 (6,200)	—	375 (6,900)
NMeAc	—	ca. 337 (ca. 5,000)	—	—
NMeBz	—	ca. 335	—	—

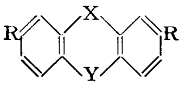
* See footnote to Table I.

However, the principal difference between electron-attracting and electron-donating substituents lies in the effect on the visible absorption spectrum. The former do not alter appreciably the small visible absorption of anthraquinone (Table 2), from which it may be concluded that they do not develop a new fundamental oscillation, but merely modify those already present. On the other hand, electron-donating substituents cause very marked changes which completely overshadow those in the ultra-violet region; the principal change is development of an absorption band in, or overlapping, the visible region of the spectrum, and this must be regarded as a fundamental band arising from electronic oscillations in the molecule as a whole.

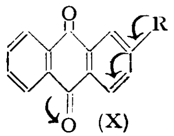
The wave-length of maximum visible absorption increases in the order OH, NH_2, O^-, NHMe (Table 2), which is also the order of increasing electromeric possibilities of these groups. Lewis (*J. Amer. Chem. Soc.*, 1945, **67**, 770) similarly showed that for dyes of the type (IX), when X and Y are constant, $\lambda_{max.}$ increased along the series R = OH, OR, NH_2, O^-, NR_2, owing to changes in the contributions of the optically important ionic structures; and Doub and Vandenbelt (*ibid.*, 1947, **69**, 2714) observed that the position of the primary band of benzene underwent an increasing bathochromic shift along the series H, OH, Me, NH_2, and associated this shift with the displacement of electrons to or from the benzene ring depending on the electron-attracting or -donating power of the group. For 2-substituted anthraquinones (Table 2) $\lambda_{max.}$ of the band of longest wave-length increases in the order of $OH < NH_2 < NHMe < O^- < NMe_2$, which can be connected with electron-donation into the anthraquinone nucleus as shown in (X). It follows that if the auxochrome is modified by a group which tends to attract electrons the absorption band will be moved to shorter wave-lengths. In the naphthaquinone series Spruit and Morton and Earlam (*locc. cit.*) demonstrated that acetylation of 1-hydroxy-naphtha- and -anthra-quinone entirely suppressed the visible band, the spectrum reverting to that of the unsubstituted quinone, but with more intense absorption. Similarly acetylation or benzoylation of 1- or 2-aminoanthraquinone causes a large hypsochromic shift in the visible band (Table 2). The electromeric effect may also be suppressed by immobilising the lone pair of electrons on the nitrogen atom as hydrochloride, the visible peaks in methanol solution being diminished and finally completely suppressed by the addition of increasing amounts of hydrogen chloride.



(VIII)



(IX)



(X)

One anomaly must, however, be mentioned. On the grounds of electromeric effects the wave-length associated with a methoxyl should be greater than that associated with a hydroxyl group, the methyl group increasing the effect. Doub and Vandenbelt showed that the change in wave-length of the primary band of benzene is greater for methoxyl than for hydroxyl; however, later work by Robertson, Seriff, and Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 1539) on the longer wave-length absorptions of these compounds shows that phenol absorbs at longer wave-lengths than anisole (approx. 273 and 271 mμ respectively), and they interpreted this as being due to the oxygen atom having a higher electron density when a hydrogen atom is attached to it than when an alkyl group is present, as is shown by the bond dipole moments of 1·5 D for hydroxyl and 0·8 D for methoxyl. Thus, it seems probable that the hydroxyl group would resonate more with the benzene nucleus than would the alkoxyl group, and absorption would then occur at longer wave-lengths. In a further paper Robertson and Matsen (*ibid.*, p. 1543) show that, for aniline, introduction of *N*-methyl groups has the reverse and, on the basis of electronic theory, the expected effect : *i.e.*, the absorption is moved towards the visible region and it is suggested that the lower electronegativity of nitrogen permits the alkyl groups to enter into resonance with the aniline nucleus to a greater extent than in anisole. Analogously, Dannenburg (*Z. Naturforsch.*, 1949, **4*b***, 327) showed that the wave-lengths of maximum absorption of *p*-hydroxybenzoic acid and *p*-hydroxyacetophenone are greater than for the corresponding methoxy-derivatives; and again for 2-substituted anthraquinones (Table 2) the bands of longest wave-length fall in the order OMe, OH, NH_2, NHMe, O^-, NMe_2.

1-Substituted anthraquinones show further anomalies, namely, that $\lambda_{max.}$ should be greater for NMe_2 than for NHMe, and greater for NMeAc than for NHAc. Here two explanations are possible, depending on the presence of intramolecular hydrogen bonding or steric interactions within the molecule.

Now there is, in a large number of cases, a hydrogen atom in the substituent which in the 1-substituted anthraquinones is able to form a hydrogen bond, as in (XI; R = H or acyl). The resultant possibilities of further resonance will alter the colour of the compound. Such mechanisms have been suggested by others for 1-hydroxy-naphtha- and -anthraquinones, and their effect may be shown most easily by a correlation of the Hixon–Johns type (*J. Amer. Chem. Soc.*, 1927, **49**, 1786). In Fig. 1 an arbitrary straight line *AB* is drawn whose ordinate scale represents the wave-length of maximum absorption, the absicssa being undefined. The points corresponding to the $\lambda_{max.}$ of the 2-R-anthraquinones, where R is an electron-donating substituent, are marked on this line, and an arbitrary scale of abscissae is then constructed labelled with the names of the substituents. Plots of the measured $\lambda_{max.}$ of *para*-substituted benzoic acids, acetophenones, and nitrobenzenes, respectively due to Dannenburg (*loc. cit.*), Doub and Vandenbelt (*loc. cit.*), and Kumler (*ibid.*, 1946, **68**, 1184), on the scale of substituents so defined, also show linear relations, confirming the validity of this abscissa scale. However, $\lambda_{max.}$ of the 1-R-anthraquinones, plotted against the same scale, do not approximate to a straight line. In this case if those substituents are chosen where interaction is unlikely, that is O^- and OMe, and a line is drawn through these points, all the derivatives which have internal-hydrogen-bonding possibilities lie above the line. This suggests that they have a $\lambda_{max.}$ greater than would be expected from their electron-donating capabilities, the excess being attributable to the resonance possibilities developed by the formation of the chelate structure.

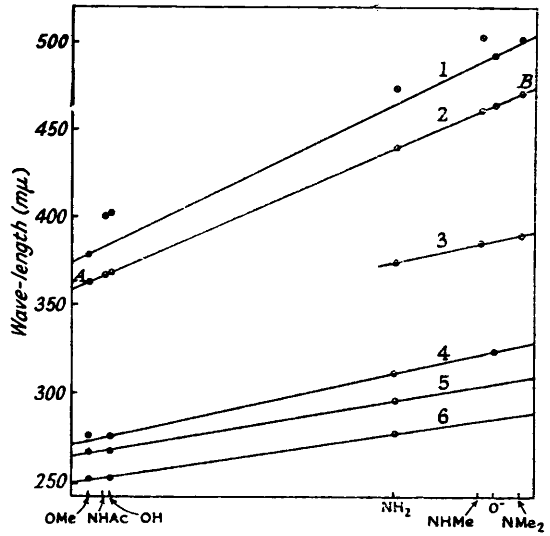
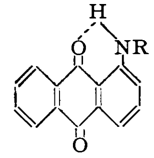


FIG. 1.

1, 1-R-*Anthraquinone in* MeOH.
2, 2-R-*Anthraquinone in* MeOH.
3, p-R-*Nitrobenzene in* EtOH.
4, p-R-*Acetophenone in* H_2O.
5, p-R-*Acetophenone in* Et_2O.
6, p-R-*Benzoic acid in* Et_2O.



(XI)

Further evidence for the presence of such intramolecular hydrogen bonds is found in calorimetric data of Doherty, Grimshaw, Longster, and Nicholson (personal communication), to the effect that, for the 1-hydroxy-, 1-amino-, and 1-methylamino-anthraquinone, the heats of sublimation and resonance energies suggest the presence of such bonds, whereas in 2-aminoanthraquinone the bonds are intermolecular. Chaplin and Hunter (*J.*, 1938, 375) similarly found that 1-acetamidoanthraquinone did not aggregate in solution, this being attributed to the presence of the chelate structure, whilst the 2-derivatives formed aggregates. The basic dissociation constants of amino- and *N*-substituted amino-anthraquinones in methanol (Peters and Sumner, unpublished work; Table 3) show a markedly higher basic strength for the 2- than for the corresponding 1-derivatives, which can again be correlated with intramolecular hydrogen bonding. Hydroxyanthraquinones show a similar effect (Huttig, *Z. physikal. Chem.*, 1914, **87**, 129), the dissociation constant being $3{\cdot}2 \times 10^{-12}$ and $2{\cdot}4 \times 10^{-8}$ for the 1- and 2-derivative respectively.

If hydrogen bonding is eliminated by methylation, $\lambda_{max.}$ should fall into line with the electron-donating powers of the group, and this is found to be so for the 1-dimethylamino-anthraquinone (Fig. 1). By a similar mechanism the acetyl and benzoyl derivatives of 1-methylaminoanthraquinone absorb at shorter wave-lengths than the corresponding derivatives of 1-aminoanthraquinone, but it also appears likely that here the second possibility of steric hindrance must be considered.

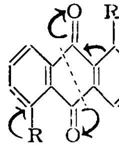
Molecular models show that there is marked steric hindrance between these substituents and the rest of the molecule for the 1-substituted anthraquinones, which will reduce the mesomeric effect by preventing the molecule from taking up a planar configuration. Classical examples are in the diphenyl series (Ferguson, *Chem. Reviews*, 1948, **43**, 421; Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854). Similarly, steric hindrance may occur between large 1-substituents and the keto-oxygen atom, the result being to twist the group out of the position relative to the anthraquinone nucleus in which the maximum mesomeric possibilities can occur. Such is the case for 1-dimethylaminoanthraquinone where, although the wave-length of maximum absorption accords with the mesomeric capabilities of the group, the extinction coefficient is considerably reduced (Table 2). Again, it is of interest that the basic strength of 1-dimethylaminoanthraquinone is markedly higher than those of the amino- and methylamino-derivatives (Table 3), as follows from consideration of the resonance of the amino-group with the nucleus. *E.g.*, aniline is a much weaker base than methylamine, a fact which is attributed to the mesomeric shift of electrons from the amino-group to the benzene ring in the former compound. If the amino-group is out of the plane of the aromatic nucleus, as is the case for 1-dimethylaminoanthraquinone, the conjugation is reduced and the group tends to exert its normal basicity.

TABLE 3. *Basic dissociation of aminoanthraquinones in methanol.*

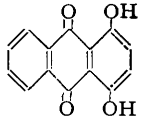
Substituent	Basic dissoc. const.	Substituent	Basic dissoc. const.	Substituent	Basic dissoc. const.
1-NH_2	$8{\cdot}1 \times 10^{-17}$	2-NH_2	$7{\cdot}4 \times 10^{-16}$	1 : 5-$(NH_2)_2$ (1st dissoc.)	ca. 2×10^{-16}
1-NHMe	$2{\cdot}9 \times 10^{-17}$	2-NHMe	$1{\cdot}1 \times 10^{-16}$	1 : 4-$(NH_2)_2$ (1st dissoc.)	$4{\cdot}9 \times 10^{-15}$
1-NMe_2	ca. 5×10^{-13}	2-NMe_2	$6{\cdot}1 \times 10^{-17}$		

Summarising, it has been shown that the visible colour of the simple monosubstituted anthraquinones can be attributed to the mesomeric drift of electrons from the substituent to the nucleus. The effect of this drift in producing visible colour is assisted by the formation of new resonance possibilities due to intramolecular hydrogen bonding, and suppressed by steric hindrance which prevents the full electron-donating properties of the substituent from being effective.

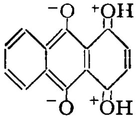
Disubstituted Anthraquinones.—Although the absorption band in the visible region of the spectrum has been attributed to resonance between the nucleus and the substituent, in some of the disubstituted anthraquinones there is evidence that this band does not necessarily arise from the molecule as a whole, but only from a part of it. Thus the intensities at any wave-length for 1 : 8- and 1 : 5-dihydroxyanthraquinone are approximately twice those for the 1-hydroxy-compound (Spruit, *loc. cit.*). This would arise if, as suggested previously, the band was associated with the conjugation of the substituent with the keto-group, that is, the molecule would than be divided diagonally, as in (XII). The 1 : 4-derivatives show no such simple additivity, owing, no doubt, to interaction between the two chromophoric systems, probably producing a new one. Thus, in 1 : 4-dihydroxyanthraquinone, interaction may occur giving resonance, the extreme structures being (XIII)



(XII)



(XIII)



(XIV)

and (XIV). Similar considerations apply to the 1 : 4-diamino-compound. This difference in behaviour of the 1 : 4-diamino-compounds has been discussed by Allen, Wilson, and Frame (*loc. cit.*) who point out that the simple 1 : 4-disubstituted anthraquinones have a "double-headed" peak which is not shown by the 1- or 1 : 5-compounds. They attribute this to a two-fold mesomeric shift of electrons from the substituents.

These effects are evident in the spectra of 1-amino-, 1-acetamido-, and 1-benzamido-anthraquinone, and the corresponding 1 : 5-derivatives. In all cases, the 1 : 5-compound has a spectrum which is approximately double that of the monosubstituted derivative, whereas the 1 : 4-disubstituted anthraquinones show a marked shift in peak absorption to longer wave-lengths (Fig. 2, and Table 4). Further, the basic dissociation constants of substituted 1-aminoanthraquinones fall into line with the concept of the separation of the chromophoric system of 1 : 5- but not of 1 : 4-disubstituted anthraquinones. Introduction of substituents in the 5-position causes changes in the dissociation constant which are much less marked than with the same substituent in the 4-position; compare the results for the 1-amino-, 1 : 5-diamino-, and 1 : 4-diamino-anthraquinone quoted in Table 3.

FIG. 2.

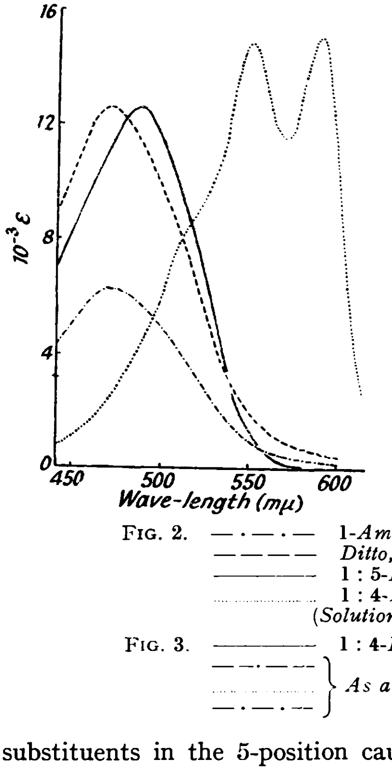


FIG. 3. *Effect of acid on* 1 : *4-diaminoanthraquinone.*

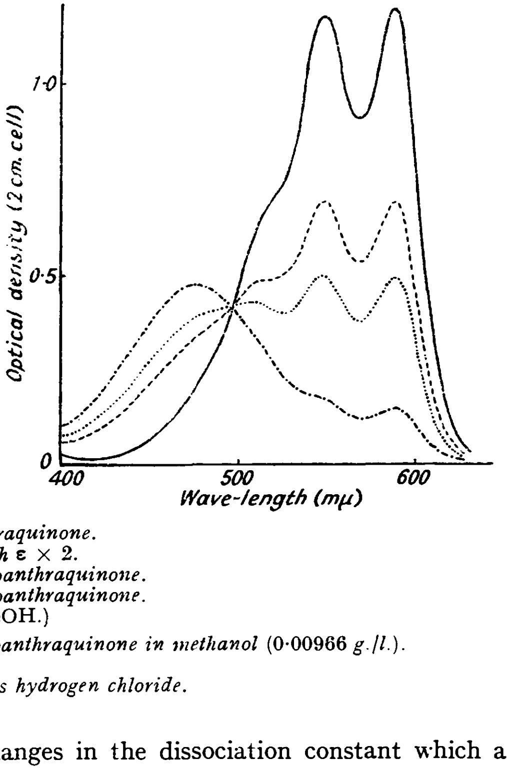


FIG. 2. — · — · — 1-*Aminoanthraquinone.*
— — — — *Ditto, but with* ε × 2.
———— 1 : 5-*Diaminoanthraquinone.*
.... 1 : 4-*Diaminoanthraquinone.*
(*Solutions in* MeOH.)

FIG. 3. ———— 1 : 4-*Diaminoanthraquinone in methanol* (0·00966 *g./l.*).
— — · — — · ; .... ; — · — · — *As above plus hydrogen chloride.*

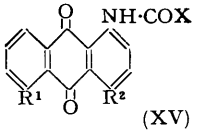
Again, as for the monosubstituted derivatives, if electron-attracting groups are introduced by acetylation or benzoylation of the amino-compounds, a shift of $\lambda_{max.}$ to shorter wave-lengths occurs (Table 4). It is worthy of note that, in these instances, the usual

TABLE 4. *Solutions in* o-*chlorophenol.*

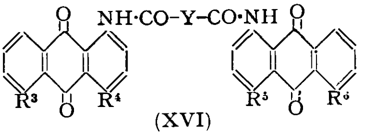
Anthraquinone derivative	Peak wave-length ($\lambda_{max.}$, mμ)	ε	2 × ε	Anthraquinone derivative	Peak wave-length ($\lambda_{max.}$, mμ)	ε	2 × ε
1-NH_2	488	6,400	12,800	1-NHBz	424	6,100	12,200
1 : 5-$(NH_2)_2$ ...	500	11,900	—	1 : 5-$(NHBz)_2$	445	11,500	—
1 : 4-$(NH_2)_2$ ...	596	13,800	—	1 : 4-$(NHBz)_2$	488	7,100	—
	554	13,400	—				
1-NHAc	414	5,000	10,000				
1 : 5-$(NHAc)_2$ ...	435	9,700	—				
1 : 4-$(NHAc)_2$ ...	474	6,700	—				

double-headed peak of the 1 : 4-derivatives does not appear. The effect of *N*-methylation is the same as in the monobenzamido-derivative, 1 : 4-bis-*N*-methylbenzamidoanthraquinone having no peak in the visible region. Again, addition of acid to a methanolic solution of 1 : 4-diaminoanthraquinone results in development of an absorption band at the wave-length of 1-aminoanthraquinone owing to formation of the monohydrochloride and suppression of the effect of one of the amino-groups (Fig. 3).

Chromophoric Insulation.—The absorption spectra of a series of acylated aminoanthraquinones of types (XV) and (XVI) are given in Table 5 and Figs. 4, 5, and 6, where the molar extinction coefficients are plotted against wave-length. In these compounds Y may be (*a*) $-[CH_2]_n-$, or a phenyl group linked (*b*) in the *meta*- or (*c*) in the *para*-positions.



(XV)



(XVI)

In type (*a*), the absorption spectra of compounds (XVI) are double those of the corresponding derivatives (XV) when $R^1 = R^3 = R^6$, $R^2 = R^4 = R^5$, and X = Me (in some cases values of *n* from 1 to 8 have been considered) (see Fig. 4 and Table 5). Such a series of compounds is analogous to those given by Piper and Brode (*J. Amer. Chem. Soc.*, 1935, **57**, 135), showing again that methylene groups behave as excellent chromophoric insulators. Comparable sets of type (*b*) give similar results. For example, the spectrum of the *iso*phthaloyl compound (XVI; $Y = m\text{-}C_6H_4$, $R^4 = R^5 = H$, $R^3 = R^6 = NHBz$) is twice that of 1 : 5-dibenzamidoanthraquinone (XV; X = Ph, $R^1 = NHBz$, $R^2 = H$). Two examples of this series are given in Figs. 5 and 6, and show that the *m*-phenylene group acts as a chromophoric insulator.

FIG. 4.

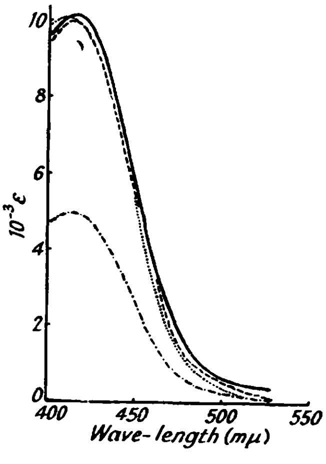


FIG. 5.

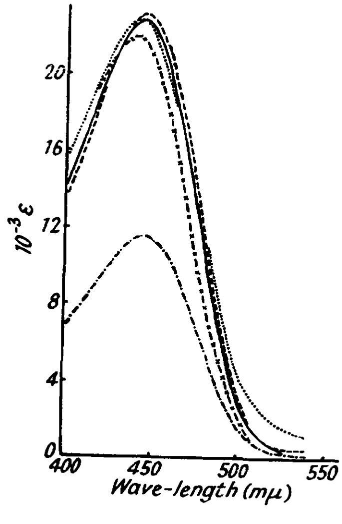


FIG. 4. — · — · — 1-*Acetamidoanthraquinone.*
— — — — *Ditto, but with* ε × 2.
———— (XVI; $R^3 = R^4 = R^5 = R^6 = H$, $Y = [CH_2]_2$).
……… (XVI; $R^3 = R^4 = R^5 = R^6 = H$, $Y = [CH_2]_4$).
(*Solutions in o*-$C_6H_4Cl{\cdot}OH$.)

FIG. 5. — · — · — 1 : 5-*Dibenzamidoanthraquinone.*
— — — — *Ditto, but with* ε × 2.
———— (XVI; $R^4 = R^5 = H$, $R^3 = R^6 = NHBz$, $Y = m\text{-}C_6H_4$).
……… (XVI; $R^4 = R^5 = H$, $R^3 = R^6 = NHBz$, $Y = p\text{-}C_6H_4$).
— × — × — (XVI; $R^4 = R^5 = H$, $R^3 = R^6 = NHBz$, Y = —).
(*Solutions in o*-$C_6H_4Cl{\cdot}OH$.)

If the group Y is a *p*-phenylene residue the additivity still occurs, though it is possible to form a conjugated system of double bonds across the benzene ring (Fig. 5). Similarly, joining the two anthraquinone nuclei by means of the oxalyl group does not influence the additivity (Fig. 5). The insulating effect of the *p*-phenylene group is readily explained. In a compound *p*-X·C_6H_4·CHO, conjugation of the benzene ring with the carbonyl group is restrained by the presence of an electron-attracting (+*E*) substituent in the *para*-position. In the case under consideration therefore, the benzene residue between the two strongly electron-attracting carbonyl groups takes little or no part in the conjugation. Similarly, in the oxalyl derivative, the bond between the carbonyl groups will be stabilised, and as such will prevent conjugation between the two halves of the molecule.

TABLE 5. *Solutions in* o-*chlorophenol.*

Compound (XV)			Compound (XVI)			Max. absorption,		
R^1	R^2	X	$R^3 = R^6$	$R^4 = R^5$	Y	$\lambda_{max.}$, mμ	ε	2 × ε
H	H	Me				414	5,000	10,000
			H	H	$[CH_2]_2$	415	10,100	—
			H	H	$[CH_2]_4$	411	10,100	—
H	NHBz	Me				480	7,000	14,000
			H	NHBz	$[CH_2]_4$	484	14,400	—
NHBz	H	Me				440	10,600	21,200
			NHBz	H	$[CH_2]_2$	441	21,200	—
			NHBz	H	—	440	21,900	—
H	H	Ph				424	6,100	12,200
			H	H	*m*-C_6H_4	419	11,600	—
			H	H	*p*-C_6H_4	420	12,600	—
H	NHBz	Ph				488	7,100	14,200
			H	NHBz	*m*-C_6H_4	485	13,000	—
			H	NHBz	*p*-C_6H_4	485	13,000	—
NHBz	H	Ph				445	11,500	23,000
			NHBz	H	*m*-C_6H_4	444	22,800	—
			NHBz	H	*p*-C_6H_4	442	22,800	—
			$R^3 = R^5 = H$, $R^4 = R^6 = NHBz$		*m*-C_6H_4	451	14,800	—

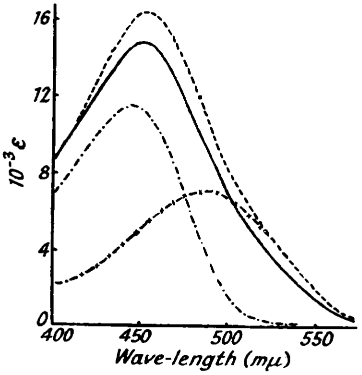


FIG. 6.

— · — · — · — 1 : 5-*Dibenzamidoanthraquinone* (*A*).
— × — × — 1 : 4-*Dibenzamidoanthraquinone* (*B*).
— — — — — *Algebraic sum of* (*A*) *and* (*B*).
———— (XVI; $R^3 = R^5 = H$, $R^4 = R^6 = NHBz$, Y = *m*-C_6H_4).

It is possible to cause small changes in the wave-lengths of maximum absorption of the benzamidoanthraquinones by substitution in the benzoyl group (Table 6). Electron-

TABLE 6. *Anthraquinone derivatives.*

Substituent in NHBz	1-NHBz in pyridine		1 : 4-$(NHBz)_2$ in *o*-C_6H_4Cl·OH		1 : 5-$(NHBz)_2$ in *o*-C_6H_4Cl·OH	
	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
p-NO_2	407	6500	—	—	—	—
m-NO_2	408	6050	—	—	—	—
p-Cl	417	6400	487	7300	445	11,800
m-Cl	415	6100	483	6700	444	10,700
H	415	6350	488	7100	445	11,500
p-Me	420	6500	493	6980	449	11,200
m-Me	419	6250	490	7020	446	11,200
p-OMe	424	6200	498	6940	454	11,600
m-OMe	—	—	—	—	446	11,600

attracting substituents, which decrease the amount of conjugation, cause a greater mesomeric drift of electrons from the nitrogen atom to the carbonyl group, and thus less to the nucleus. This is shown in a hypsochromic shift in $\lambda_{max.}$. The reverse is found to be true for electron-donating substituents. It is of interest, however, that the hypsochromic changes due to electron-attracting groups are relatively small. This suggests that an unsubstituted benzene ring is already partaking to the minimum possible extent in the conjugation within the molecule.

Experimental.—The compounds used were recrystallised several times from suitable solvents. The absorption spectra in solution were measured in the visible region (400—700 mμ) by means of a General Electric, and in the ultra-violet by a Cary, Recording Spectrophotometer. The solvents were dried and distilled to spectroscopic quality.

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