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Fungus Pigments

X.* The Ultra-violet Absorption of Some Substituted 2,5-Diphenylbenzoquinones and their Leucoacetates

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The ultra-violet absorption spectra of a number of substituted 2,5-diphenylbenzoquinones and their leucoacetates have been determined. These spectra and their significance in structure determination are discussed.

During the investigation of aurantiacin, the most recently isolated member of the diphenylbenzoquinone pigments found in fungi, the ultra-violet absorption spectrum was of considerable help in the structure determination [1].

It was felt that a knowledge of the spectra of other substituted diphenylbenzoquinones might be of value in future work. The spectra of a number of such compounds were therefore measured in dioxan solution and the results are given in Table 1.

Dioxan was selected because it is the only suitable solvent which is not too polar in which all the compounds are sufficiently soluble. The spectrum of 2,5-diphenylbenzoquinone (I) in carbon tetrachloride has been published by Flaig *et al.*[2] and it agrees well with that obtained here. Murray [3] reported maxima at 388 and 494 mμ for polyporic acid (II) in pyridine; in this solvent, however, polyporic acid is present at least partly as an anion, and the absorption is therefore not comparable with the data given here.

All the spectra have two maxima, that at shorter wave-length being always the stronger. The spectra are divided clearly into two distinct groups by the position of the second maximum. In the first, substances I—VIII, this maximum lies between 330 and 350 mμ. In substances IX—XVI forming the second group, this maximum is at 380—405 mμ. On inspecting the structural features of the compounds in the two groups, it is obvious, that in all those belonging to the first group, R is either hydrogen or an acylated hydroxyl, while in the second group R is hydroxyl or methoxyl. The nature of the substituent

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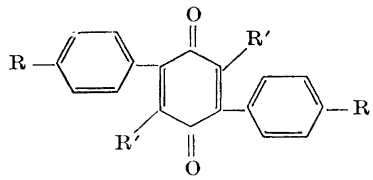
Table 1.



			max$_1$		max$_2$	
			mμ	log ε	mμ	log ε
I	R = H;	R′ = H	240	4.37	338	3.94
II	R = H;	R′ = OH	261	4.45	332	3.86
III	R = H;	R′ = $OCOCH_3$	240	4.33	336	3.78
IV	R = $OCOCH_3$;	R′ = H	246	4.49	346	4.02
V	R = $OCOCH_3$;	R′ = $OCOCH_3$	247	4.46	347	3.82
VI	R = $OCOCH_3$;	R′ = $OCOC_6H_5$	244	4.67	350	3.81
VII	R = $OCOC_6H_5$;	R′ = $OCOC_6H_5$	244	4.82	351	3.89
VIII	R = $OCOC_6H_5$;	R′ = OCH_3	242 *	4.66	337	3.82
IX	R = OH;	R′ = H	252	4.48	393	4.03
X	R = OCH_3;	R′ = H	251	4.43	390	3.98
XI	R = OH;	R′ = OH	268	4.55	385	3.66
XII	R = OH;	R′ = OCH_3	256	4.34	386	3.64
XIII	R = OCH_3	R′ = OH	268	4.55	382	3.66
XIV	R = OCH_3;	R′ = OCH_3	257	4.45	385	3.70
XV	R = OH;	R′ = $OCOC_6H_5$	240	4.63	405	3.82
XVI	R = OCH_3;	R′ = $OCOC_6H_5$	242	4.65	404	3.80

* In addition an inflexion at 260 mμ (4.45)

R′, on the other hand, seems to be much less important because both types of substituents occur in both groups.

A hydroxyl or methoxyl group in the *p*-position of the aromatic ring thus has a bathochromic effect, which disappears on acylation. A hydroxyl or methoxyl group attached directly to the quinone ring has no such effect and in fact a slight hypsochromic effect can be observed (Compare: II with I; VIII with VII; XI, XII, XIII and XIV with IX and X).

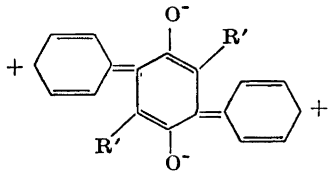
The effect of different substituents on the short wave maximum is more difficult to determine because in the substances with a benzoyl group the absorption of this group will appear in the same region and may thus mask the absorption of the parent substance. The contribution of the benzoyl group to the absorption is seen clearly in the higher extinction coefficient for the benzoates. The substance VIII forms a special case. In addition to the maximum at 242 mμ there is an inflexion at ~ 260 mμ (The complete absorption curve of this substance is reproduced in Part IV [1]). It is assumed that the maximum at 242 mμ is due to the benzoyl group and that the absorption of the other part of the molecule is responsible for the inflexion.

Hydroxyl or methoxyl groups in the *p*-positions have a bathochromic effect as is shown by comparison of IX and X with I and of XI and XIII with II. An apparent exception is formed by XV and XVI which show no bathochromic shift in the short-wave band in spite of a hydroxyl or methoxyl group in

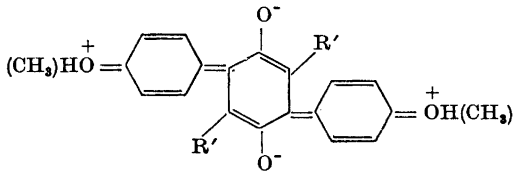
the *p*-position. This is probably the result of overlapping of the absorption referred to above.

Hydroxyl groups and to a lesser extent methoxyl groups in the quinone ring have a definite bathochromic affect on the short-wave band as is readily seen by a comparison of II with I, and of XI, XII, XIII and XIV with IX and X. The inflexion in VIII will also be due to such an effect. This bathochromic effect is at least partly removed by acylation (see III, XV and XVI).

The effect of the substituents in the *p*-positions on the long wave absorption maximum is readily understood, on the assumption that this absorption is the result of an electronic transition leading to excited forms such as A and B



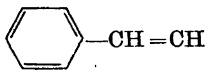
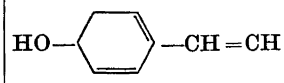
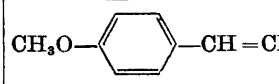
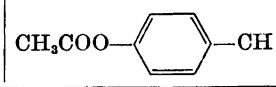
A



B

that is, that the chromophore is composed of two benzylideneketone systems.

Table 2.

	max_1		max_2	
	mμ	log ε	mμ	log ε
	220.5	4.08	286	4.37
	234	4.01	323	4.37
	232	4.02	318	4.39
	223	4.06	290	4.36

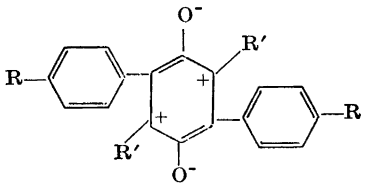
As can be seen from the figures reported in Table 2, which are taken from the work of Wilds *et al.*[4], the effect of a substituent in the aromatic ring in benzylideneacetone on the second maximum is of the same relative magnitude as in the diphenylbenzoquinones. The fact that the maximum in the diphenylbenzoquinones is at much longer waver-lengths than in similarly substituted benzylideneacetones shows clearly that the two benzylideneketone systems

which formally exist in the diphenylbenzoquinones are not independent of another, although they are neither conjugated nor cross-conjugated in the ordinary sense [5]. They are, however, both cross-conjugated with the same vinylketone system forming a kind of double cross-conjugated system, similar to that found for instance in benzil and vinylogous benzils [6,7].

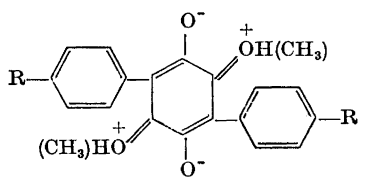
A possible explanation for the slight hypsochromic shift of the long-wave maximum observed when R′ is hydroxyl or methoxyl is given below.

For the maximum at shorter wavelenghts there are two obvious explanations: it may correspond either to the shortwave absorption of the benzylideneketone system or to that of the quinone ring. As can be seen from Table 2, the effect of the substitutes in the *p*-position on this band in the benzylideneacetones is the same as on the long-wave band, just as is observed in the diphenylbenzoquinones. It should, however, be noted that the shortwave maximum in the benzylideneacetones is weaker than the long-wave maximum, while the opposite is true for the diphenylbenzoquinones. Further the observed bathochromic effect of the hydroxyl or methoxyl groups in the quinone ring finds no obvious explanation in this way.

The second possibility referred to above, however, offer a ready explanation of this. According to Braude [8] the short-wave band of benzoquinone has its origin in an electronic transition leading to an excited state, which in the present cases would be C and D with a consequent bathochromic shift



C



D

when R′ is hydroxyl or methoxyl. Actually the bathochromic shift is smaller than expected on this assumption. For instance 2,5-dihydroxybenzoquinone has maxima at ~277 and 285 mμ and 2,5-dihydroxythymoquinone has a maximum at ~295 mμ [2]. One explanation for this would be that the electronic transition leading to D is in the opposite direction to that leading to A and B and may thus require more energy than in 2,5-dihydroxybenzoquinone and its homologues.

The bathochromic shift when R is hydroxyl or methoxyl is not readily explained in this way; the opposite effect, due to the counteraction of the two systems, would have been expected.

This counteraction of the two systems could, however, explain the hypsochromic effect on the second maximum, which is observed when R′ is hydroxyl or methoxyl.

It is obvious that neither of the two alternative explanations alone is quite satisfactory, and it may well be that both contribute to the formation of the short-wave band.

Brockmann and Budde [9] have devised a method by which the parent ring system of a polycyclic quinone is fixed by comparison of the UV-spectrum of the acetylated hydroquinone with that of the corresponding hydrocarbon. These usually differ only by a small bathochromic shift caused by the acetoxyl groups. It was of interest to see whether this method was applicable also to the diphenylbenzoquinones.

Table 3.

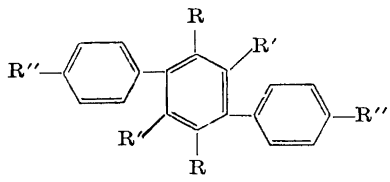
		max	
		mμ	log ε
XVII	R = $OCOCH_3$; R′ = R″ = H	260	4.40
XVIII	R = $OCOCH_3$; R′ = H; R″ = $OCOCH_3$	263	4.40
XIX	R = R′ = $OCOCH_3$; R″ = H	245	4.27
XX	R = R′ = R″ = $OCOCH_3$	249	4.35

Table 3 gives absorption maxima of the leuco-acetates of some of the diphenylbenzoquinones listed in Table 1. They are all at shorter wavelengths than that of terphenyl [10] (276 mμ). This hypsochromic shift instead of the expected bathochromic shift is by no means surprising. It is well known that substituents *ortho* to the central bond in diphenyl have a hypsochromic effect which has been attributed to non-coplanarity of the two rings due to steric hindrance [11]. Even a single methyl group is enough to produce this effect [12]. The same should also apply to derivatives of terphenyl, although very little is known about their spectra. Erdtman *et al.*[13] have shown that the spectrum of 2,5,2′,5′,2″,5″-hexa-acetoxy-*p*-terphenyl, an isomer of (XX), has a strong inflexion at ~250 mμ, and is thus in good agreement with that of XX, although this has a definite maximum.

The difference between those substances having only a single substituent adjacent to the connecting bonds between the aromatic rings and those having two substituents is also clerly revealed by the figures of Table 3.

In the spectra of aurantiacin leuco-acetate and the acetate of dihydroaurantiacin dibenzoate, recorded in a previous paper [14], the maximum due to the terphenyl system is covered by the strong absorption of the benzoyl group and occurs only as a weak inflexion at 260—270 mμ.

When allowance is made for this hypsochromic effect due to restricted rotation, it should be possible to identify diphenylbenzoquinones by the spectra of their leuco-acetates, and it is definitely possible to distinguish them from quinones derived from condensed hydrocarbons.

EXPERIMENTAL

All the quinones used in this investigation have been described before. The compounds V, VI, VII, VIII, XI, XV and XVI were obtained during work on the structure of aurantiacin [1]. XII, XIII and XIV were obtained from atromentin (XI) according to Kögl and Becker[15]. I, IX and X were synthesised according to the method of Pummerer and Prell[16] and II according to Frank and coworkers [17]. III and IV were obtained by acetylation of II and IX, respectively. All substances prepared in the present work had m. p. s in agreement with those given in the literature, except 3,6-dibromo-2,5-diphenylbenzoquinone, used as an intermediate in the synthesis of polyporic acid (II). Our sample had m. p. 232–233°, whereas Frank *et al.*[17] as well as Schildneck and Adams [18] report 223–224°. Dr. Frank has kindly informed us that the m. p. of his sample, determined now, is 233–234° and that he regards the earlier statement as a misprint.

The leuco-acetates were prepared by reductive acetylation of the corresponding quinones in the presence of pyridine. XVIII and XX have been described before [1,16]. XVII had m. p. 193–194°. (Found: C 76.28; H 5.24. $C_{22}H_{18}O_4$ requires C 75.85; H 5.29 %) and XIX m. p. 266–267°. (Found: C 66.60; H 4.72. $C_{26}H_{22}O_8$ requires C 67.52; H 4.80 %.) Both substances were recrystallised from acetic acid.

The spectra were measured with a Beckman Model DU Spectrophotometer. The dioxan, used as solvent, was purified by distillation over sodium.

The author wishes to thank Prof. R. Adams and Dr. R. L. Frank for their help in settling the reason for the differences in m. p. referred to above.

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