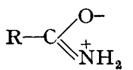
294. *The Application of Infra-red Spectroscopy to Structural Problems in the Anthraquinone Field.*

By M. St.C. Flett.

Some possible applications of infra-red spectroscopy in the anthraquinone field have been examined. In most cases the compounds were examined as solids, on account of their limited solubility and the possibility of molecular rearrangements in solution. Although complete interpretations of the spectra are not possible, information has been gained about the finer details of the structures of various quinones of known constitution, from measurements of the frequencies of bands associated with carbonyl, hydroxyl, amino-, and other groups. The hydrogen bonding in hydroxyquinones has been examined. An interesting resonance phenomena is observed in aminoanthraquinone derivatives. The spectra of certain benzamido- and acetamido-quinones in the solid state show anomalies. The use of infra-red spectroscopy in identifying reduction products of unknown constitution has been assessed, by examining various authentic anthrones, oxanthrones, etc. This application shows promise. Leucoquinizarin and the stable leuco-compound of 1 : 4-diaminoanthraquinone have been examined.

A complete assignment of the bands in the infra-red absorption spectrum of a molecule to particular modes of vibration of its atoms is possible only in the case of very simple or highly symmetrical molecules. Accordingly, only a partial interpretation of the spectra of anthraquinone derivatives is possible. It is, however, well established that certain atomic groupings such as CO, CN, OH, NH_2, CH_3, give rise to infra-red bands at characteristic frequencies even when they occur in complicated molecules. These characteristic frequencies are determined largely by the strengths of the bonds and masses of the atoms in the group in question. It has been shown that in suitable series of compounds containing a common group, the precise value of the characteristic frequency in each member of the series provides a measure of the strength in that member of the bonds associated with the frequency. In a series of substituted benzoic acids, for example, as the electron-attracting character of the substituent increases, the carbonyl frequency rises, corresponding to strengthening of the $>C=O$ bond, whereas the OH frequency falls, the OH bond becoming weaker. Hydrogen bonding has been studied by infra-red methods. Resonance effects can also be detected. The carbonyl frequency in amides, for example, is considerably lower than in aldehydes and ketones, indicating that in amides the $C=O$ bond is weakened, probably by resonance involving the form (I).



(I.)

In the present work attempts have been made to apply the above methods in the anthraquinone field. For the above reasons, attention has been directed mainly to the study of characteristic frequencies rather than to considerations of the spectra as a whole. The carbonyl frequencies of the quinone group are of particular interest, since the ease of reduction and other chemical properties are connected with the group. In the case of hydroxy-, amino-, and substituted amino-anthraquinones, the ^-NH and ^-OH frequencies have also been studied.

The constitutional formulæ of most of the compounds studied were known. Information was sought in such cases about bond strength, hydrogen bonding, and similar " fine details " of structure. Some substances of doubtful constitution were, however, examined. Attempts were then made to detect characteristic frequencies, which could be associated with atomic groups. Various reduction products of anthraquinones were examined since in some cases the determination of their structures by chemical methods has proved difficult. Recent work on chemical aspects of this problem by colleagues in this Department will be published later.

Experimental.

(a) *Determination of Spectra.*—The spectrum of a solid is perhaps most satisfactorily determined in solution. Unfortunately, few solvents are transparent over considerable regions of the infra-red wave-length range. Anthraquinone derivatives are not usually sufficiently soluble for their spectra to be determined in these, though it proved possible to use carbon tetrachloride for some purposes. Most of the spectra were, therefore, obtained from the solid materials, as powders suspended in " Nujol ", a medicinal paraffin which does not itself absorb except at the frequencies characteristic of CH_3 and CH_2 groups. Spectra of solids suffer from the disadvantage that they may be affected by intermolecular forces, which do not occur in dilute solution in non-polar solvents. Against this, substances in solution may undergo keto-enol or similar transformations. As far as possible, comparisons are drawn only between substances examined in the same state of aggregation.

The spectra were measured (in most cases from 2 to 15 μ) by a Hilger D.209 infra-red spectrometer, with rock-salt prism. The resolution appeared adequate for this type of work since the natural width of the bands of solids is considerable. Some difficulty was caused by water-vapour absorption, since carbonyl frequencies fall in the 6 μ water-vapour band. The carbonyl frequencies were obtained from the automatic records by interpolation between bands of known wave-length in the water-vapour spectrum. The wave-lengths of NH and OH bands were similarly determined by interpolation between a peak in the 2·7 μ water band and the $-CH_2$ frequency in " Nujol ".

(b) *Materials.*—Samples of quinones were supplied by various colleagues. They were all purified by recrystallisation or chromatography. Some of the anthrones, oxanthrones, and anthraquinols referred to were recently prepared for the first time in this Department. Details will be published later. The solvents used were of " AnalaR " quality.

RESULTS AND DISCUSSION.

This section is in two parts, the first dealing with quinones, and the second with their reduction products.

(I) *Quinones.*—(a) *General.* The vibration of the two carbonyl groups in a quinone appear not to be closely coupled. Thus anthraquinone itself and symmetrically substituted derivatives give a single $C{=}O$ frequency. In certain unsymmetrically substituted quinones, two carbonyl bands arise, since the strengths of the two $>C{=}O$ bonds are now unequal. This is very marked with amino- and hydroxy-derivatives, but with many substituents the dissymmetry is insufficient for two separate bands to be observed. The single band then probably provides a rough measure of the mean strength of the two carbonyl bonds. With the exception of amino- and hydroxy-compounds, the carbonyl frequencies of anthraquinones were found to be close to 1680 cm.$^{-1}$. A number were found to be sufficiently soluble in carbon tetrachloride for their carbonyl frequencies in it to be determined. The bands in solution were sharper than in the solid, and these wave-lengths could, therefore, be more accurately measured. Table I lists the frequencies.

TABLE I.

$C{=}O$ *frequencies of anthraquinones in carbon tetrachloride.*

Substituent(s).	Frequency (cm.$^{-1}$).	Substituent(s).	Frequency (cm.$^{-1}$).
None	1678	1-Nitro-2-methyl	1685
1-Methyl	1676	2-Nitro	1684
2-Methyl	1676	1-Cyano	1684
1-Chloro	1680	1-Methoxy	1675
2-Chloro	1680	2-Methoxy	1675
1 : 5-Dichloro	1686	1 : 4-Dimethoxy	1675
1 : 8-Dichloro	1691	1-Acetoxy	1679
1-Chloro-2-methyl	1679	2-Acetoxy	1679

It will be observed that in all cases electron-attracting substituents, such as Cl, CN, NO_2, shift the $C{=}O$ frequency to higher values, strengthening the bond, whereas the electron-donating methyl and methoxy-groups have the reverse effect. The $C{=}O$ frequency appears to provide some measure of electronic shifts in the ring system.

In Table II the carbonyl frequency of anthraquinone derivatives is compared with various other carbonyl bonds.

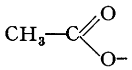
TABLE II.

$C{=}O$ *frequencies of various compounds.*

Compound.	Frequency (cm.$^{-1}$).	Compound.	Frequency (cm.$^{-1}$).
In dilute solution.		In the solid state.	
Benzoyl chloride	1778 1744	*p*-Benzoquinone	1660
		Thioindigo	1650
Benzoic acid (monomer)	1743	Benzanilide	1655
Methyl benzoate	1725	1 : 4-Dihydroxyanthraquinone	1627
Benzaldehyde	1705	1 : 4-Diaminoanthraquinone	1610
Acetophenone	1690	Urea	1600
Most anthraquinone derivs.*	1675—1690	Sodium acetate	1575

* As solid or in solution.

Although the above figures are not strictly comparable since all the materials cannot be measured in the same state, it is likely that variations in strength of the various carbonyl bonds are roughly parallel to the frequency changes. In sodium acetate the carbonyl bond has only about one half double-bond character, since there will be complete resonance between (II) and (III). Accordingly, the bond is weak and the frequency low. Similarly in urea the bond is weakened by resonance with such forms as (IV). At the other end of the scale, groups such as Cl which exert a powerful inductive effect in their immediate vicinity stiffen the C=O bond. The value of 1675—1690 for most anthraquinone derivatives therefore indicates that their C=O bond is weaker than in most esters, ketones, aldehydes, etc., but stronger than in anilides or amides.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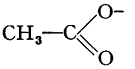
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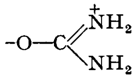

(IV.)

(b) *Hydroxy-derivatives of anthraquinone.* Table III lists the observed carbonyl and hydroxyl frequencies of hydroxyquinones.

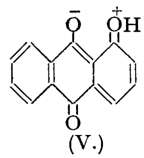
TABLE III.

OH *and* C=O *frequencies of hydroxyanthraquinones.*

Quinone.	Frequency (cm.$^{-1}$). OH.	C=O. (*a*).	C=O. (*b*).	Δ.
Anthraquinone	—	1676	—	—
1-Hydroxy	—	1673	1636	40
2-Hydroxy	3320	1673	—	—
1 : 2-Dihydroxy	3380	1660	1636	40
1 : 3-Dihydroxy	3380	1675	1635	41
1 : 4-Dihydroxy (quinizarin)	—	—	1627	49
1 : 5-Dihydroxy	—	—	1639	37
1 : 8-Dihydroxy	—	1675	1622	54
1 : 3 : 4-Trihydroxy (purpurin)	3330	—	1623	53
1 : 4 : 5 : 8-Tetrahydroxy	—	—	*ca.* 1595	81

It is apparent that in every case where a hydroxyl group *not* adjacent to a carbonyl group is present, a band is observed at about 3350 cm.$^{-1}$, which may be associated with the –OH vibration. A hydroxyl in the 1-position gives rise to no such band, but causes a second carbonyl band at lower frequencies. Clearly, hydrogen bonding is responsible. The apparent absence of a hydroxyl frequency is interesting, since no case seems previously to have been reported where hydrogen bonding has this effect on the OH fundamental. Normally bonded hydroxyl groups absorb strongly though at longer wave-lengths. Cases are, however, known (Pauling, " Nature of the Chemical Bond ", Chapter IX) where the first overtone disappears because of hydrogen bonding.

The absence of the hydroxyl band and shifting to 1630—1640 cm.$^{-1}$ of the C=O frequency indicates very marked weakening of the OH and C=O bonds. Causes of this may include resonance with forms such as (V) and (VI), in addition to (VII). The position of the hydrogen atom is, of course, the same in (VI) and (VII); (V) is probably unimportant, since the carbonyl frequency in 1 : 4-dimethoxyanthraquinone where a similar phenomenon could occur is nearly normal. A considerable contribution from (VI) would, however, explain the weakening of the C=O bond, and the apparent absence of a hydroxyl band, since the hydrogen atom is in effect shared by two oxygen atoms.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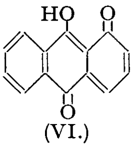
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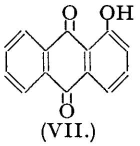

(VII.)

It has been observed (Badger, *J. Chem. Physics*, 1940, **8**, 288) that in many cases the shift of a hydroxyl frequency increases with the heat of formation of the resulting hydrogen bond. Unfortunately, this cannot be applied in the case of the hydroxyquinones, since no definite band can be assigned to the hydroxyl group. There is, however, some evidence that in cases of

$>C{=}O\cdots H{-}O^-$ bonding shifts in the OH frequency roughly parallel shifts in the carbonyl frequency. Table IV shows some such cases, together with data on 1 : 4- and 1 : 8-dihydroxyanthraquinone, which were sufficiently soluble respectively in chloroform and carbon tetrachloride for their carbonyl frequencies in dilute solution to be measured.

TABLE IV.

Effect of hydrogen bonding on OH *and* C=O *frequencies.*

Compound.	OH frequency (cm.$^{-1}$).	Shift of OH from normal value (cm.$^{-1}$).	C=O frequency (cm.$^{-1}$).	Shift (cm.$^{-1}$).
Benzoic acid (monomer)	3600		1743	—
Benzoic acid (dimer)	*ca.* 3000	*ca.* 600	1697	46
Benzaldehyde	—	—	1705	—
Salicylaldehyde	3100	*ca.* 550	1670	35
Methyl benzoate	—	—	1725	—
Methyl salicylate	3230	*ca.* 450	1687	38
Anthraquinone	—	—	1678	—
1 : 4-Dihydroxyanthraquinone	—	—	1623	55
1 : 8-Dihydroxyanthraquinone	—	—	1680 1628	50

Large carbonyl shifts appear to be accompanied by large hydroxyl shifts, but more examples are required to establish this generalisation. Therefore carbonyl shifts probably also provide some measure of the heat of formation of the hydrogen bond. Hence, we conclude that the energy of the hydrogen bond in quinizarin is somewhat greater than the value 7350 cals. per $>C{=}O\cdots H{-}O^-$ bond (Davies, *Trans. Faraday Soc.*, 1938, **34**, 410) for benzoic acid. Hydrogen bonding therefore probably stabilises quinizarin by about 15,000 cals. per mol. Similarly 1 : 8-dihydroxyanthraquinone is stabilised by 7000—8000 cals. Judging from the shifts recorded in Table III, the hydrogen bonds in quinizarin and purpurin are rather stronger than in 1-hydroxy- and the 1 : 2-, 1 : 3-, and 1 : 5-dihydroxy-compounds. Similarly, they are much stronger in the 1 : 4 : 5 : 8-tetrahydroxy- than in the 1 : 8-dihydroxy-compound. The measurements on 1 : 8-dihydroxy- and 1 : 4 : 5 : 8-tetrahydroxyanthraquinone show that one C=O group can bond strongly to two hydroxyl groups. As might be expected, the shift in the C=O frequency is greater when the group is doubly bonded.

In the above series the hydroxyl groups not internally bonded absorb at about 3300 cm.$^{-1}$. This suggests that they are involved in intermolecular hydrogen bonding. This explains why, for example, 1-hydroxyanthraquinone (m. p. 190°) melts much lower than the 2-hydroxy-derivative (m. p. 302°). In the former case the hydroxyl groups are too tightly bonded to the carbonyl groups to be available for intermolecular bonding. Similarly, quinizarin (m. p. 194—195°) and 1 : 8-dihydroxyanthraquinone (m. p. 193°) melt lower than 1 : 2-dihydroxy- (m. p. 290°), 1 : 3-dihydroxy- (m. p. 262°), and 1 : 2 : 4-trihydroxy-anthraquinone (m. p. 256°). 1 : 5-Dihydroxyanthraquinone (m. p. 280°) is anomalous, showing that hydrogen bonding is not the only factor involved. Possibly the molecules of 1 : 5-dihydroxyanthraquinone, being highly symmetrical, pack more closely than those of quinizarin.

(c) *Amino- and methylamino-derivatives.* Table V lists the carbonyl and amino-frequencies of such derivatives, with a few amines for comparison. There is an element of uncertainty in assigning frequencies below about 1620 cm.$^{-1}$, since ring vibrations are known to give bands at about 1600 cm.$^{-1}$. However, the 1610 band in aminoquinones is much stronger than any band observed in this region with the anthraquinones previously examined, so is almost certainly a carbonyl frequency.

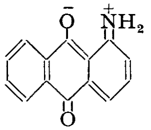
The results show that in every case the amino-group gives rise to a lowered carbonyl frequency. There appear to be two possible explanations. Powerful hydrogen bonding may occur between the C=O and NH groups, analogous to the phenomenon in the hydroxyquinones. This seems unlikely, since, though a shift of 40—50 cm.$^{-1}$ in the carbonyl frequency of the hydroxyquinones corresponded to a profound effect on the OH frequency, the NH_2 frequencies in 1-amino- and 1 : 4-diamino-anthraquinones are not much different from the values in α-naphthylamine where such bonding is, of course, impossible. Similarly, the NH frequencies of 1-methylamino- and 1 : 4-bismethylamino-anthraquinones are only about 100 cm.$^{-1}$ lower than in secondary amines. Therefore, though weak hydrogen bonding cannot be ruled out, it is probably not the main cause of the very great weakening of the carbonyl bonds, indicated by the frequency 1610 cm.$^{-1}$. This is confirmed by the fact that 2-aminoanthraquinone exhibits the same phenomenon. More

TABLE V.

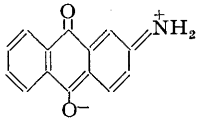
$C=O$ *and* NH *frequencies of aminoanthraquinones.*

Quinone.	Frequency (cm.$^{-1}$). C=O. (*a*).	(*b*).	NH or NH_2.	Quinone.	Frequency (cm.$^{-1}$). C=O. (*a*).	(*b*).	NH or NH_2.
Anthraquinone	1676	—	—	1 : 4-Diamino	—	1610	3370 3250
1-Amino	1665	1612	3420 3300	1 : 4-Bismethylamino	—	1610	3240
2-Amino	1676	1625	3470 3330 3220	α-Naphthylamine	—	—	3330 3230
1-Methylamino	1675	1635	3300	β-Naphthylamine	—	—	3400 3310 3230
1-Dimethylamino	1650	1645	—	*N*-Methylaniline	—	—	3390 (liq.)
2-Dimethylamino	1667	1650	—	Diphenylamine	—	—	3420

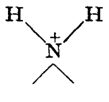
probably a large resonance contribution from the forms (VIII) and (IX) in the case of 2-aminoanthraquinone, giving the $>C=O$ bond much single-bond character is responsible. Comparison of the series 1-amino-, 1-methylamino-, and 1-dimethylamino-anthraquinone shows that the extent of this resonance is reduced by methyl groups. The 1-dimethylamino-compound has, however, an unusually large effect on the second carbonyl group. Possibly the reduction is partly due to steric hindrance, since in the form (X) the N–H bonds tend to be pulled into the plane of the ring. The resonance is more marked with 1 : 4-bismethylamino- than with 1-methylamino-anthraquinone.



(VIII.)



(IX.)



(X.)

It is interesting that 2-aminoanthraquinone should show a triple NH_2 band, since all primary amines in dilute solution, and most of them in the solid state, give two frequencies, corresponding to symmetrical and antisymmetrical combination of the two separate N–H vibrations. A similar phenomenon is observed with solid β-naphthylamine. Accordingly the $C=O$ groups are probably not responsible. Intermolecular interactions between NH_2 groups may be responsible.

Reference to Table II shows that the carbonyl bonds in 1 : 4-diaminoanthraquinone are similar to those in amides. This is in accord with the fact that the compound has little basic character.

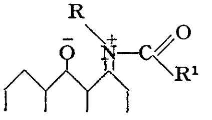
(d) *Benzamido- and acetamido-anthraquinones.* It must be stated at the outset that the interpretations here are less certain than in the classes previously studied. There is an additional complication in that both quinone and benzoyl carbonyl groups give bands. Also the possibility of molecular interactions in the solid is increased, and the acylamido-group can tautomerise.

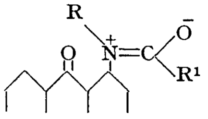
TABLE VI.

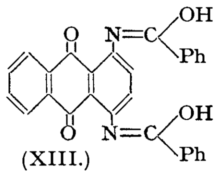
$C=O$ *and* NH *frequencies of solid benzamidoanthraquinones.*

Quinone.	? C=O frequencies (cm.$^{-1}$).	?NH frequencies (cm.$^{-1}$).
1-Benzamidoanthraquinone	1677, 1670, 1637	3250
1-Methylbenzamidoanthraquinone	1676, 1641	—
1 : 4-Bisbenzamidoanthraquinone	1679, 1633	3130
1 : 4-Bismethylbenzamidoanthraquinone	1663, 1648	—
1-Acetamidoanthraquinone	1705, 1676, 1645	3225
1 : 4-Bisacetamidoanthraquinone	1705, 1642	3215
Benzanilide	1658	3330
p-Chlorobenzanilide	1657	3340
Benz-*p*-chloroanilide	1656	3340

It might be expected that the nitrogen atoms in these compounds donate electrons to both carbonyl groups through the resonance forms (XI) and (XII). One would thus expect both the quinone and the other carbonyl bond to be weaker, with lowered characteristic frequencies.

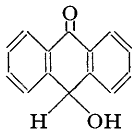

(XI.)


(XII.)


(XIII.)

The results in the first three compounds in Table VI can be interpreted on this basis, the three bands in 1-benzamidoanthraquinone, for example, being attributed to a normal quinone group (1677 cm.$^{-1}$), a weakened quinone group (1670 cm.$^{-1}$), and a benzoyl carbonyl group (1637 cm.$^{-1}$). This explanation does not, however, cover the data on 1 : 4-bisbenzamido- or the acetamido-quinones, where the quinone frequency is raised rather than lowered. It is possible that these quinones may tautomerise, 1 : 4-bisbenzamidoanthraquinone having, for example, the structure (XIII). This explains why the quinone frequency is not lowered, since resonance from (XI) would now require two double bonds attached to the same nitrogen atom, which seems unlikely. Also the band at 3130 cm.$^{-1}$ is at a somewhat longer wave-length than the N–H band in compounds previously examined and may in fact be a hydroxyl band. It is now necessary to suppose that the 1633 cm.$^{-1}$ band is associated with $-C{=}N$ bonds. There does not, however, appear to be chemical evidence for tautomerisation, and the postulate seems unlikely to account for the spectra of the acetamidoquinones.

(II) *Reduction Products.*—The object of this work was to devise methods of characterising anthrones, oxanthrones, anthraquinols, and similar derivatives which are difficult to identify by chemical means. For this reason a number of authentic compounds have been examined. It should, in principle, be easy to distinguish between oxanthrones, *e.g.*, (XIV), anthrones, *e.g.*, (XV), and anthraquinols, *e.g.*, (XVI). The first should show both OH and C=O bands, the second C=O only, and the third OH only. However, complications arise with amino- and hydroxy-quinones since the NH and OH bands are at similar wave-lengths and with benzoyl and acetyl derivatives where the substituent also contains a carbonyl group.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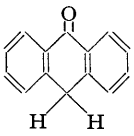
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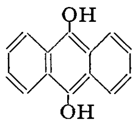

(XVI.)

(a) *Anthrones.* Table VII lists the characteristic frequencies of various solid anthrones, with, for comparison, the carbonyl frequencies of the corresponding quinones; Δ is the shift in carbonyl frequency from the quinone.

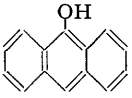
TABLE VII.

Characteristic frequencies of anthrones (solids) [CH_2 = 10, CO = 9].

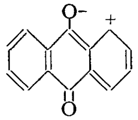
Anthrone.	C=O frequency (cm.$^{-1}$).	C=O frequency of corresponding quinone (cm.$^{-1}$).	Δ (cm.$^{-1}$).	NH or OH frequencies (cm.$^{-1}$).
Unsubstituted	1654	1676	22	—
4-Chloro	1654	1678	24	—
4-Methoxy	1658	1675	17	Weak absorption probably due to trace impurity
1-Amino	1614	1665, 1612	−2	3440, 3320
4-Amino	1645	1665, 1612	20	3320, 3230
1-Hydroxy	1633	1673, 1636	3	—
4-Hydroxy	1645	1673, 1636	28	—
1 : 4-Bisbenzamido	1648, 1635	1679, 1633	31	3200 3200 (weak)
1-Acetamido	1679, 1637	1705, 1676	26	3130
4-Acetamido	1660, 1652	1705, 1676	16	3310

There is no evidence that these anthrones exist in the enol forms such as (XVII) : a band at about 2950 cm.$^{-1}$ in the spectra of anthrone solution confirms the presence of CH_2 groups.

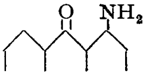
The carbonyl group in an anthrone gives rise to bands at a lower frequency than in the parent quinone. The degree of lowering falls with the original quinone frequency, from about 30 to zero. The reason for the lowering is not clear. If the quinone carbonyl bonds are weakened by resonance with forms such as (XVIII), one might expect the effect to be more marked in anthrone where one carbonyl group is free to utilise all the capacity of the rings for assuming a positive charge. The effect is smaller in solution, since the carbonyl band of anthrone in carbon tetrachloride is at 1670 cm.$^{-1}$. The spectra of the hydroxy- and the amino-anthrones confirm the structures assigned to them; 1-hydroxyanthrone shows no hydroxyl band, since the same hydrogen bonding as in the quinone is present. The resonance postulated for the aminoquinones persists in 1-aminoanthrone. It has been shown that whereas 1-chloro- and 1-methoxy-anthraquinone on reduction under special conditions give 100% 4-anthrone, yet 1-hydroxy- and 1-amino-anthraquinone give respectively 70% and 85% of 1-anthrone. This is to be expected, since in the last two cases formation of the 4-anthrone involves destruction of a powerful hydrogen bond, or the resonance of the system (XIX).



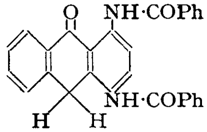
(XVII.)



(XVIII.)



(XIX.)



(XX.)

The anthrone of 1 : 4-dibenzamidoanthraquinone is probably correctly formulated as (XX), the anomaly of the quinone spectrum having disappeared and the 3320 band being the NH frequency. Of the acetamidoanthrones, the 4-compound is normal, but neither the C=O nor the NH frequency of the 1-anthrone is quite as expected.

In general, infra-red methods should be adequate in identifying anthrones.

(b) *Oxanthrones.* The measurements on oxanthrones, *e.g.*, (XIV), are given below. The first three oxanthrones behave similarly in dilute solution, giving a C=O frequency at about the same wave-length as the quinone, and hydroxyl bands at the expected wave-lengths. Oxanthrone itself is anomalous in that the solid shows a double carbonyl frequency of which there is no obvious explanation. It is unlikely that the 1673 cm.$^{-1}$ band is due to anthraquinone present as an impurity. Most probably the doubling is caused by some type of intermolecular bonding in the crystal. The characteristic frequencies of 1 : 4-bisbenzamido-oxanthrone differ from those of the quinone only in that a band at 3250 cm.$^{-1}$ is developed, which may well be a hydroxyl band. The anomalies of the quinone spectrum persist in this compound.

Characteristic frequencies of oxanthrones (cm.$^{-1}$).*

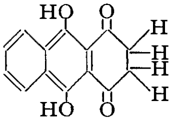
Compound.	C=O frequency. (*a*).	C=O frequency. (*b*).	C=O frequency of quinone. (*a*).	C=O frequency of quinone. (*b*).	OH frequency. (*a*).	OH frequency. (*b*).
Oxanthrone	1673 1653	1676	1676	1678	?3510 3450	3650 3370 (w)
4-Chloro-oxanthrone	1652	1678	1678	1679	3460	3650 3370 (w)
4-Methoxyoxanthrone	1653	1678	1675	1676	3480	3650 3370 (w)
1 : 4-Bisbenzamido-oxanthrone	1678 1637	— —	1679 1633	— —	3250 3100	— —

* (*a*) = solid; (*b*) = in carbon tetrachloride solution.

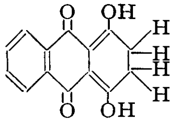
Infra-red spectra should in general be useful in identifying oxanthrones.

(c) *Anthraquinols.* Unsubstituted anthraquinol and the 1-chloro-derivative were sufficiently stable for the infra-red spectra of the solids to be measured. No strong bands were observed in the carbonyl region, and strong –OH bands were present respectively at 3300 and at 3380 and 3480 cm.$^{-1}$. Such compounds can therefore readily be identified spectroscopically.

(d) *Compounds of uncertain constitutions.* (i) Leucoquinizarin. It was suggested (Zohn and Ochwatt, *Annalen*, 1928, **462**, 72) that this compound has the structure (XXI). The infra-red spectrum confirms that this is essentially correct. No OH frequency is observed, and there is a carbonyl frequency at 1633 cm.$^{-1}$. Accordingly, the hydrogen-bond system of quinizarin is unaffected on reduction. Also leucoquinizarin shows a band at about 2950 cm.$^{-1}$ characteristic of CH_2 groups, which is not shown by quinizarin. The actual structure may be regarded as a resonance hybrid involving (XXI) and (XXII), the hydrogen atom being partially bonded to both oxygen atoms, but it is not possible to say from the spectrum which, if either, form predominates.

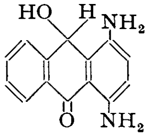


(XXI.)

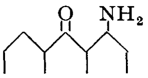


(XXII.)

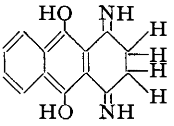
(ii) The stable leuco-derivative of 1 : 4-diaminoanthraquinone. This compound shows two bands in the $3\ \mu$ region, a strong, broad band at 3150 cm.$^{-1}$ which is almost certainly a hydroxyl band, and a sharp peak at 3420 cm.$^{-1}$, probably associated with an N–H vibration. This band cannot be assigned unambiguously either to $>$N–H or to $-NH_2$, since, though normally an amino-group gives rise to a double peak, it is clearly possible for one peak of the doublet in this case to be overlapped by the strong OH band. Comparison with the value 1610 cm.$^{-1}$ for the carbonyl frequency of 1 : 4-diaminoanthraquinone suggests that the 1615 cm.$^{-1}$ band is due to a carbonyl group as in the oxanthrone (XXIII). The formation of an oxanthrone rather than an anthraquinol is not surprising since the former would involve loss of only half the energy associated with the resonance within the system (XXIV). Chemical evidence, however, favours (XXV) in view of the chemical similarity to leucoquinizarin. If this formulation is correct, the 1615 cm.$^{-1}$ band must be attributed to the $-C{=}N$ bonds. It is possible that this apparent anomaly may be due to some difference between the structures of the molecule in solution and in the solid state.



(XXIII.)



(XXIV.)



(XXV.)

An examination of the leuco-derivative of 1 : 4-bismethylaminoanthraquinone might settle this point.

I am indebted to many colleagues for advice and helpful discussions, for purified samples, and for permission to quote certain results of chemical work before their publication.

Research Laboratories, Imperial Chemical Industries Ltd.,
Hexagon House, Manchester, 9.

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