939. *The Infrared Absorption Spectra of the Carbonyl Group in Methoxyanthraquinones, and in the Hydrochlorides of 1-Methoxyanthraquinones.*

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The carbonyl stretching frequency in anthraquinones is lowered by a methoxyl group *para* to a carbonyl group. The hydrochlorides of 1-methoxyanthraquinones have not a chelate ring structure as hitherto supposed. The polyhydrochlorides show an *increase* in the carbonyl frequency, and their structure is considered.

The main purpose of this work was to investigate the structure of the hydrochlorides formed by 1-methoxyanthraquinones, but as a large number of methoxyanthraquinones were available the infrared absorption of their carbonyl groups was first examined, and the results are recorded since they extend the earlier information.

Methoxyanthraquinones.—Flett,[1] in a study of the effect of electron-donating and electron-attracting substituents on the carbonyl stretching frequency of anthraquinones, measured the infrared absorption spectra of 1- and 2-methoxy- and 1 : 4-dimethoxyanthraquinones. The carbonyl frequencies showed in each case a small change to a value 3 cm.$^{-1}$ lower than in anthraquinone. For our wider range of compounds the methoxyl group causes a marked diminution in the carbonyl frequency in some cases, while in others there is little significant difference. Dilute solutions, generally in carbon tetrachloride, were employed, but, when the solubility in this solvent was too low, chloroform was used : an examination of several methoxyanthraquinones showed that this change of solvent did not affect the position of the carbonyl band. The Nujol mull technique gave anomalous results which must be ascribed to intermolecular forces. It is significant in this connection that isomeric methoxyanthraquinones often differ considerably in melting point.

Table 1. *Methoxyanthraquinones.*

	Position of OMe	Shift of CO frequency (cm.$^{-1}$)
1.	1-	− 3 s
2.	2-	− 3 s
3.	1 : 2-	0 b
4.	1 : 3-	− 8 s
5.	1 : 4-	− 6 s
6.	1 : 5-	− 6 b
7.	1 : 8-	− 3 s
8.	2 : 3-	−14 b
9.	2 : 6-	−15 sc
10.	2 : 7-	−15 sc
11.	1 : 2 : 3-	−11 b
12.	1 ; 2 : 4-	−11 b
13.	1 : 2 : 7-	−11 b
14.	1 : 4 : 5-	0 s
15.	1 : 2 : 5 : 8-	− 8 b
16.	1 : 4 : 5 : 8-	0 c
17.	2 : 3 : 6 : 7-	−20 s

s = sharp band; b = broad band (shift measured to mean frequency at half-band width); c = in chloroform.

Table 1 gives the results for methoxyanthraquinones. The chief points of interest are :

(*a*) Methoxy-substituents only in the 1-positions cause little or no change in the carbonyl frequency. This supports Flett's contention [1] that the resonance contribution of the high energy *o*-quinonoid form (I) is small. Moreover it is in these α-positions that the oppositely directed inductive effect of methoxyl will be strongest.

(*b*) (i) With a single 2-methoxy-group there is only a small frequency change. The carbonyl group at the 9-position will be unaffected by the methoxy-group, while that in the 10-position can be conjugated with a *para*-quinonoid resonance form (II). A similar contribution is evident in 1 : 3-dimethoxyanthraquinone. (ii) When *both* carbonyl groups can be influenced by *para*-quinonoid resonance the carbonyl shift is considerable (Nos. 8, 9, 11, 17). (iii) When *one* carbonyl group only can be influenced from β-positions in *different* rings the shift is again considerable (Nos. 10, 13). Shaw and Simpson [2] found recently that suitably substituted methoxy-flavanones and -flavones also show a diminution in carbonyl frequency when *para*-quinonoid resonance is possible.

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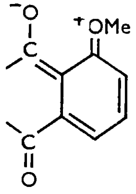
[1] Flett, *J.*, 1948, 1441.

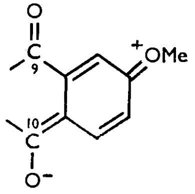
[2] Shaw and Simpson, *J.*, 1955, 655.

The spectra of unsymmetrically substituted methoxyanthraquinones gave evidence of a splitting of the carbonyl band. Yates, Ardao, and Fieser,[3] from an infrared study of substituted *p*-benzoquinones, did not consider that the presence of two different conjugated systems necessarily led to splitting of the carbonyl band. In agreement with our results, Josien and Deschamps,[4] using a higher degree of resolution than Yates *et al.*, found that the carbonyl band is always split in unsymmetrical *p*-benzoquinones.

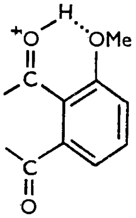
Hydrochlorides of 1-*Methoxyanthraquinones.*—Many polycyclic ketones (*e.g.*, xanthones, thioxanthones, and anthraquinones) which have a carbonyl in the *peri*-position to a methoxyl group are markedly basic. These halochromic compounds were extensively studied by Smiles and his co-workers, and have recently been further examined.[5, 6]



(I)



(II)



(III)

Roberts and Smiles [7] suggested that the cations of these compounds have a hydrogen bond linked to methoxyl in a chelate 6-membered ring (cf. III). Before the electrostatic nature of the bond was realised it was thought that the salts owed their stability to resonance stabilization.

The methoxyl group is capable of forming chelate rings. Thus the infrared spectra of *o*-methoxyphenol [8] and *o*-methoxybenzoic acid [9] show marked shifts in the position of the hydroxyl bands.

Mesomeric structures such as (I) which have a positive ether-oxygen atom and an increased negative charge on the carbonyl-oxygen atom suggested the possibility that protonation might occur to the carbonyl oxygen (as in IV) but with no chelate ring. It was

$$>C=\overset{+}{O}H \longleftrightarrow >\overset{+}{C}-O-H \quad (IV)$$

of interest, therefore, to study the result of hydrochloride formation on the infrared absorption of the carbonyl group in 1-methoxyanthraquinones. If formulation (III) were correct a marked diminution (or suppression) of the carbonyl frequency is to be expected, while structure (IV) would cause only a small effect.

The dihydrochlorides of the methoxyanthraquinones (methoxyl at 1 : 4-, 1 : 5-, 1 : 4 : 5-, and 1 : 4 : 5 : 8-) were prepared by passing dry hydrogen chloride over the solid anthraquinone cooled by solid carbon dioxide. Under these conditions a considerable number of mols. of hydrogen chloride were absorbed, but warming to room temperature in a stream of hydrogen chloride gave the dihydrochloride as residue. The hydrochlorides dissolved unchanged in chloroform, and the infrared spectrum of each solution so obtained was superimposed on that of the parent methoxyanthraquinone. For each hydrochloride there was a very small decrease (1—3 cm.$^{-1}$) of the carbonyl frequency.

Structure (III) is therefore incorrect. Moreover, structure (IV) in which the carbonyl group is protonated is also incorrect since there was no hydroxyl bond absorption around 3 μ. Furthermore the carbonyl frequency was only slightly perturbed, there was no marked change in the intensity of the absorption on hydrochloride formation, and the

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[3] Yates, Ardao, and Fieser, *J. Amer. Chem. Soc.*, 1956, **78**, 650.
[4] Josien and Deschamps, *Compt. rend.*, 1956, **242**, 3067.
[5] Wiles, *J.*, 1952, 1358.
[6] Wiles and Baughan, *J.*, 1953, 933.
[7] Roberts and Smiles, *J.*, 1929, 1322.
[8] Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287.
[9] Fox and Martin, *Nature*, 1939, **143**, 199.

ultraviolet spectra of the methoxyanthraquinones and of their hydrochlorides showed no conspicuous differences.

The above-mentioned facts, and the marked instability of the hydrochlorides, is explained by weak hydrogen bonding of the carbonyl oxygen with hydrogen chloride, $>$C=O • • • H–Cl (V). An attempt was made to locate an H–Cl stretching frequency between 2000 and 2800 cm.$^{-1}$, but at the concentrations permissible none was found.

Recently the infrared carbonyl frequency of the polynuclear quinone, hypericin pentamethyl ether, and of its hydrochloride have been measured as dispersions in potassium bromide.[10] The parent compound absorbed at 1640 cm.$^{-1}$ and the hydrochloride at 1610 cm.$^{-1}$. The considerable difference is attributed to hydrogen bridges between the carbonyl and methoxyl groups of the type given in (III). This ether is much more basic than the methoxyanthraquinones, but it is our experience that infrared measurements of carbonyl compounds in the solid phase may be unreliable.

At low temperatures, ketones add a considerable number of molecules of hydrogen chloride in non-stoicheiometric proportions[6] and the effect on the carbonyl frequency of such addition was also examined. Dry hydrogen chloride was passed for several hours over a thin layer of the solid anthraquinone cooled by solid carbon dioxide. The highly coloured product was then rapidly transferred into chloroform and the solution stored at a low temperature until its spectrum was recorded. The results given in Table 2 were unexpected. The outstanding feature is the *increase* in carbonyl frequency, in some instances considerable. The mesomeric effect which operated in the parent compound to weaken very slightly the carbonyl link has now been suppressed, the electronic changes are reversed in direction, and the carbonyl bond is strengthened.

TABLE 2.

Position of OMe	1 : 4-	1 : 5-	1 : 4 : 5-	1 : 4 : 5 : 8-
Shift (cm.$^{-1}$) of CO frequency	+34 s	0 s	+28 s	+8 b

Cf. footnotes to Table 1.

The literature has a few isolated examples of the strengthening of a bond on protonation. Bernstein and Martin[11] found an increase of the N–O frequency in the Raman spectra of hydroxylamine hydrochloride. Witkop[12] has shown that the infrared absorption of the $>$C=N– group in aromatic Schiff bases and in pyridines invariably moves to shorter wavelengths on salt formation, while Hammick and Roe[13] have found that in the formation of the hydrochloride of Besthorn's Red the protonation of a nitrogen atom results in a considerable frequency increase in a neighbouring carbonyl group.

It is difficult to provide a reason for the strengthening of the carbonyl bond in the anthraquinone polyhydrochlorides. Protonation of the methoxy-group instead of the carbonyl group would have this effect, but it would then have been expected to occur in hydrochloride formation at room temperature. A possible explanation is that the additional molecules of hydrogen chloride are associated with the π-electrons of the aromatic nuclei, thereby reducing the polar nature of the carbonyl group. Brown and Brady[14] found that the solubility of hydrogen chloride in dilute solutions of aromatic compounds at $-78°$ is a measure of the basic properties of the aromatic nuclei, and they suggest that a weak interaction between the π-electrons of the ring and the polar hydrogen chloride molecule is involved.

EXPERIMENTAL

Materials.—The methoxyanthraquinones have been described,[5] but 1 : 4 : 5-*trimethoxyanthraquinone* is new. Complete methylation of the 1 : 4 : 5-trihydroxy-compound was unsuccessful, and the trimethyl ether was prepared from 1 : 4 : 5-trichloroanthraquinone. 1 : 4 : 5-Trichloroanthraquinone (1 mol.) was heated with sodium methoxide (12 mols.) in methanol for 9 hr. at 165°. The product, recrystallised twice from butan-2-ol, had m. p. 209° (corr.) (Found : C, 68·3; H, 5·0; OMe, 30·5. $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7; OMe, 31·2%).

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[10] Brockmann and Franck, *Naturwiss.*, 1955, **42**, 70.
[11] Bernstein and Martin, *Trans. Roy. Soc. Canada*, 1937 (III), **31**, 95.
[12] Witkop, *Experientia*, 1954, **10**, 420; *J. Amer. Chem. Soc.*, 1954, **76**, 5597.
[13] Hammick and Roe, *Chem. and Ind.*, 1953, 900.
[14] Brown and Brady, *J. Amer. Chem. Soc.*, 1952, **74**, 3570.

Absorption Spectra.—The infrared absorption spectra were obtained by means of a Perkin-Elmer Model 21, double-beam spectrophotometer fitted with a sodium chloride prism. The compounds were examined in 1% solutions in carbon tetrachloride or chloroform, in 0·2 mm. cells. The spectrum of each anthraquinone was superimposed on that of its parent compound and only the frequency shift was measured. The spectra were recorded by running the sample spectrum, reversing the instrument, and running the reference spectrum without disengaging the drum from the wavelength drive.

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