33. *Physical Properties of Anthraquinone and its Derivatives. Part I. Infrared Spectra.*

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The infrared spectra between 2 and 15 μ of anthraquinone and fifty-nine derivatives of it are reported, and correlations to assist the identification of unlisted anthraquinones are discussed.

In a survey by Briggs *et al.*[1] of the colouring matters of the *Coprosma* genus, various new hydroxyanthraquinones were isolated. To aid the elucidation of their structure, an investigation of the physical properties of hydroxy- and other substituted anthraquinones is being made. In this paper the infrared absorption spectra of anthraquinone and fifty-nine of its derivatives are reported and, where possible, correlations are made between the structure and observed absorption pattern. It is hoped to submit later reports on ultraviolet absorption spectra, half-wave potentials, and chromatographic properties of this series.

Experimental.—The anthraquinones were mostly natural products but some were of commercial origin. Derivatives without hydroxyl groups were purified by crystallization, but hydroxyanthraquinones were also purified by previous chromatography on columns of magnesia or magnesium carbonate. The spectra were recorded between 2 and 15 μ on a Beckman IR-2 spectrophotometer with rock-salt monochromator, the samples being prepared as paraffin mulls because of the low solubility of hydroxyanthraquinones in any suitable solvent.

Results and Discussion.—The sixty anthraquinones with their observed absorption bands are listed in Table 1. Spectra of anthraquinone derivatives having the same substitution pattern were found to be similar, regardless of the substituents, provided these compounds contained no hydroxyl groups. Hence compounds without hydroxyl groups are arranged first in the Table. β-Hydroxy-derivatives which show, in addition, absorption in the O–H stretching region are listed next; α-hydroxy-derivatives, in which the substitution pattern of the spectra is strongly modified, are given last. Bands arising in the regions of the C–H stretching and bending vibrations at around 3000 cm.$^{-1}$ and between 1480 and 1360 cm.$^{-1}$ are omitted because of the difficulty of measuring these in the presence of the paraffin mulling agent.

The hydroxyl and carbonyl stretching regions of absorption have been most often investigated by other workers, and a correlation between spectra in these regions and constitution has enabled certain limited groupings of anthraquinones to be made, thus assisting in their identification. The results in Table 1 extend the value of their correlations considerably. In the hydroxyl region they show that anthraquinones with one hydroxyl group in the β-position on the nucleus, or attached to a substituent group, all have one hydroxyl stretching band. The appearance of more than one hydroxyl band between 3600 and 3150 cm.$^{-1}$ indicates more than one such hydroxyl group attached to the anthraquinone nucleus, although the reverse does not always hold. More than one hydroxyl band appears only when two β-hydroxyl groups are adjacent or when β-hydroxyl groups are in a different environment, one in the normal position on the anthraquinone ring, and the other attached through a side chain or adjacent to some other α- or β-hydroxyl group.

α-Hydroxyl groups attached to the nucleus apparently show no hydroxyl absorption in a spectrum of a mulled sample. This was noted first in the overtone region by Hilbert, Wulf, Hendricks, and Liddel [2] and later by Flett,[3] working with the rock-salt region. The same effect was found by Johnson, Quayle, Robinson, Sheppard, and Todd [4] for hydroxy-derivatives of the extended quinones, but their investigation of a few simple α-hydroxyanthraquinones revealed a weak, broad absorption band with its centre near 2700 cm.$^{-1}$ which they assigned to the O–H stretching vibration. Hadži and Sheppard,[5] working with perfluorokerosene mulls, assigned a broad strong peak at 2900 cm.$^{-1}$, usually hidden by the paraffin mulling agent,

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[1] Briggs and his co-workers, " Chemistry of the *Coprosma* Genus," Parts I—X, Part X (*J.*, 1955, 3298 and earlier papers).

[2] Hilbert, Wulf, Hendricks, and Liddel, *J. Amer. Chem. Soc.*, 1936, **58**, 548.

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

[4] Johnson, Quayle, Robinson, Sheppard, and Todd, *J.*, 1951, 2633.

[5] Hadži and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 911.

TABLE 1. *Spectra of paraffin mulls of anthraquinones.*

No.	Anthraquinone	Frequency of infrared bands													
1	Unsubst.			1675s		1572m				1333s	1305w	1284s		1209w	
				Monosubstituted anthraquinones											
2	1-Cl			1678s		1572m				1319s		1267s		1236m	
3	1-OAc		1764s	1678s		1585s				1325s		1279s		1241m	1185s
4	1-OH			1667s	1631s	1582s			1357s	1290s		1266s		1230s	
5	2-Cl			1678s		1575s				1325s		1287s			
6	2-Me			1675s		1592s				1330s		1297s	1269w	1221w	
7	2-OH	3344s		1667s		1587s				1339s	1304s	1282s	1239s	1224s	
				Disubstituted anthraquinones											
8	2-OH, 3-Me	3311s		1658s		1575s		1504m		1342s	1307s	1284w	1250s		1186s
9	2 : 3-$(OH)_2$	3472s	3268s	1675s		1585s		1520s		1340s		1289w	1245w		1193m
10	2 : 6-$(OH)_2$	3300s		1656s		1587s				1323s	1297m		1239s	1218w	
11	2 : 7-$(OMe)_2$			1672s		1590s					1305w	1284s	1241m		
12	2 : 7-$(OH)_2$		3195m	1653s		1597s					1314s	1264w			1206s
13	1-OMe, 2-Me			1669s		1572s			1325s			1277s			1198m
14	1-OH, 2-Me			1669s	1634s	1587s			1359s		1292s	1267s			1200s
15	1 : 2-$(OH)_2$	3367m		1658s	1634s	1587s			1351m	1333w		1289s			1195s
16	1 : 3-$(OH)_2$	3413s		1675m	1637s	1590s			1340s	1319s			1266m		1195w
17	1 : 4-$(OH)_2$				1626s	1582s			1355s	1314s			1256s	1220s	
18	1 : 5-$(OH)_2$				1634s	1600s	1572s				1305s		1245s	1218w	1174m
19	1 : 6-$(OH)_2$	3390m		1664s	1634s	1592s				1328w	1290w	1277m	1245m	1218w	
20	1 : 8-$(OH)_2$			1678s	1621s	1600w			1348m		1300w	1269s		1205m	

No.																			
1	1163m		1098w				971m	936s						812s					693w
							Monosubstituted anthraquinones												
2	1166s	1136m					964s		920w			831w		805s	786w	750m		702s	
3	1164m			1041m		1020m	996m				900s	862s		810s	776w	733m		708s	689m
4	1159s	1101w	1066m	1042w		1013s			927w		881s	838s		815w	775s	737m		708s	
5	1164s	1112w	1078m				965m		929s	913s	899s	857s		816m	792m			707s	
6	1164s	1147w	1083w	1043m		1008w	970s		933s		895m	850s		816w	789w			710s	
7	1175m	1145w	1088s				986s		932s	911w	883s	854s		811w	795m	749m	719s	711s	
							Disubstituted anthraquinones												
8	1163m	1106s	1082s	1047m		1019w	963s		917m	904m	888m				797s	776s	736s	716s	693m
9	1167m	1116s	1088w	1048w	1033w	1015w	970m			903s	880w	853w	833w		794s		741w	713s	
10	1149s		1082s			1001w		934w			885s		841m			750s	732s	709m	
11		1116m	1092w		1025s		976s	930s		911s	889s	847s	822w	802m	775m		744s	712m	
12			1086m		1017w			923m		901m		855s		796s		750w	735m		
13	1164s			1055s		1017m	975s	958s			882w	858s	824w		798m	755m		715s	
14	1156m			1052s		1010s					896m	850s	817w		778s	748m		710s	
15	1178s			1048m	1034w	1011s					897m	854s	829s		770s	752s		714s	
16	1163s		1098w	1063 w	1030w	1006m			923w		879w	863w		801m	778s		728m	714s	
17	1151s		1072w		1027m		981w	962s		903w	876w		838w		789s	574w			699s
18	1157s	1101w	1086s	1050s		1018w	989w				868s		824m	787s	775m			713s	
19	1156w			1065w	1037w					910w	877m	856w	827m	796m	770s	755m		713m	
20	1159m		1080m	1058m	1032m		972s		922w			846s		816s	779s	741m			

TABLE 1. (*Continued.*)

Frequencies of infrared bands

No.	Anthraquinone															
					Trisubstituted anthraquinones											
21	1 : 2 : 3-$(OMe)_3$				1664s		1570s			1344s	1323w	1285s	1276s	1244w	1215s	1190s
22	1 : 3-$(OMe)_2$, 2-Me				1664s		1570s			1323s		1287s			1230s	1190s
23	1 : 3-$(OMe)_2$, 2-$CH_2{\cdot}OH$		3300m		1669s		1570s			1318s		1280s			1225s	1189m
24	1-OMe, 2-Me, 3-OH		3311m		1669s		1570s			1337s	1300s	1282s			1222m	1198m
25	1-OH, 2-$CH_2{\cdot}OH$, 3-OMe	3521m			1658s	1629s	1572s		1504w	1339s	1300s				1230s	1188s
26	1 : 3-$(OH)_2$, 2-$CH_2{\cdot}OH$	3448m	3367m		1656s	1621s	1587s	1575s		1339s	1304s	1287s		1242w	1212m	1196w
27	1 : 3-$(OH)_2$, 2-OMe		3378s		1664s	1634s	1587w	1575s		1359s		1284s	1264s		1203s	1163s
28	1 : 3-$(OH)_2$, 2-Me	3413s			1658s	1623s	1582s			1339s	1312s	1277w			1233m	1196s
29	1 : 2 : 3-$(OH)_3$		3378m		1650s	1626s	1575s			1340m	1309s	1280m	1264w		1221m	
30	1 : 2 : 4-$(OH)_3$		3226m			1621s	1580s			1337s	1309s		1264s			1183s
31	1 : 2 : 5-$(OH)_3$		3333m			1626s	1577s			1353m	1304s		1264s	1238m		1200m
32	1 : 2 : 6-$(OH)_3$		3356s	3279w	1650s		1580s				1294s			1229s		1196s
33	1 : 2 : 7-$(OH)_3$		3390w	3311s	1647s		1582s				1314s	1302s	1258w	1233w	1214w	1198s
34	1 : 2 : 8-$(OH)_3$		3378m		1661m	1621s	1570s		1506w			1290s	1266s		1209m	
35	1 : 8-$(OH)_2$, 3-Me				1675s	1621s		1558m		1350s		1287m	1271s		1208s	
36	1 : 3 : 8-$(OH)_3$		3367s		1664m	1616s	1570s			1353m		1265s		1225s		
37	1 : 4 : 8-$(OH)_3$					1605s	1575w				1321s	1282s	1259s	1221s		
					Tetrasubstituted anthraquinones											
38	1 : 2 : 5-$(OH)_3$, 6-Me	3460m				1623s	1605m			1355m	1311w	1293s	1261w	1225s		1174m
39	1 : 2 : 5 : 8-$(OMe)_4$		3344s			1616s	1575s				1321s		1267s	1238s	1203w	
40	1 : 3 : 5 : 7-$(OMe)_4$				1653s		1595s	1555s				1304s	1256s		1214s	1193m
41	1 : 5-$(OH)_2$, 3 : 7-$(OMe)_2$					1616s	1575s			1340s		1287s	1259w		1206s	

									Trisubstituted anthraquinones										
21	1170w	1130s	1100w	1065s	1045s	1030w	988s	962s	911s		873s	824m	802m	789s		760s		716s	
22		1134s		1068m	1021m	1006m	977s			898m	876s	826w		796m		760s		717s	686w
23	1161m	1135s		1067s	1041m	1002s	974s			897s	873s	826m		796w		763s		717s	
24		1120s	1094w	1067m	1019m		978s		907m	887m	871w	824w		794w		762m		713s	687m
25		1134s	1101w	1076m	1043m	1011s			924m		864s	831w		795m		756m		718s	
26	1168m	1127s		1086m	1045w	1007s	984s	955w	934w	894m	875m	824s	812s	792m		754w	738w	717s	
27		1134s	1093m	1066w	1040m	1007s	965s			896w	873s			789s		762s	735m	712s	699m
28		1124s	1098m	1076m	1044m	1015s	973m	943m			868s	831s		804s	772w	746s	734s	713s	
29		1122s	1091w	1063w	1032s		989s				869m	834m		796m		752w		716m	
30				1064s	1029m		964s		904w		867s	831w				751s	732s	704s	
31	1160s		1087s		1032m	1013w		938m		895m	854m	834m	810m		777s	751w	735w		687s
32			1103s		1035s	1009w	976w	959w	941w	897m	858w	847s	818w	797m	775m	752s	720s		681s
33	1172w	1148m	1104m	1045m	1024s				942m	890m	859s		819w	800m	769w	751s	742s		
34	1160m			1073m	1029m						858s	838m	813m	792w		758w	736m		686m
35	1160s		1086s	1052w	1024s		996w			903m	870s	841s	818w	806m		752s	733s		
36	1153s		1089m	1053m	1017s				912w	880w	864s	840s	818m	807w	774s	753s	737m		690m
37	1157s		1093s	1057m			983s	970s		895w	853w	839m		800m	773s	745w		703m	
									Tetrasubstituted anthraquinones										
38	1156m			1078s	1016s		968m			870w	848w			800s			734s		
39	1166s		1095s		1034w		982w	940m			845s			807m	782s	769m		711m	
40	1157s		1083m	1056s			988s	935s		869w	855s	833s		795w		761s	720s		
41	1139s		1086w	1025m			964s		903s	865m	840s						722s		

TABLE 1. (*Continued.*)

Frequencies of infrared bands.

No.	Anthraquinone															
	Tetrasubstituted anthraquinones															
42	1 : 3 : 5 : 7-$(OH)_4$		3344s	3077m		1608s	1580s		1497s	1326s		1282s	1242s		1199m	
43	1 : 8-$(OH)_2$, 3-OMe, 6-Me				1678m	1623s		1562s		1326s	1299s	1276s	1256m	1230s	1205w	1189w
44	1 : 3 : 8-$(OH)_3$, 6-Me		3390s		1672m	1621s		1562s		1340s	1300m	1276s	1252w	1220s		
45	1 : 3 : 8-$(OH)_3$, 6-CH_2·OH	3521m	3448s	2667m	1678m	1626s	1600s	1562s		1311s	1300s	1258s		1217s		
46	1 : 3 : 8$(OH)_3$, 6-CO_2H		3390m	3185m	1706s	1623s		1560s				1271m		1209m		
47	1 : 4 : 5-$(OH)_3$, 7-Me						1603s	1575s			1302s		1261s	1239s		1181s
48	1 : 4 : 5-$(OH)_3$, 2-Me						1592s				1312m		1245s			
49	1 : 4 : 5 : 8-$(OH)_4$						1592s	1577s					1264s		1200w	1182w
	Pentasubstituted anthraquinones															
50	1 : 2 : 3 : 5-$(OMe)_4$, 6-Me				1669s		1570s		1490m		1337s	1289s	1264s		1200s	1185s
51	1 : 3-$(OH)_2$, 2 : 5-$(OMe)_2$, 6-Me		3300m		1653s	1629s	1562s				1340m	1284s			1198m	1174m
52	1 : 5-$(OH)_2$, 2 : 3-$(OMe)_2$, 6-Me					1623s	1575s					1304s	1248s		1198m	1182m
53	1 : 3 : 5-$(OH)_3$, 2-OMe, 6-Me		3413s			1618s	1575s				1314m	1282w	1250s		1200w	1167m
54	1 : 2 : 3 : 5-$(OH)_4$, 6-Me		3472m	3195w		1621s	1590s			1350m	1299s	1284s		1233w	1220s	1170s
55	1 : 2 : 3 : 7-$(OH)_4$, 6-Me	3584m 3509w	3367s	3165s		1631s	1595s		1504m	1339s	1321w		1256s	1238m		1175w
56	1 : 4 : 5 : 8-$(OH)_4$, 2-Me						1572s		1486m			1272s	1255s			1171s
57	1 : 4 : 5-$(OH)_3$, 2-Me, 7-OMe						1592s		1490m		1305s		1255s		1206w	1179s
58	1 : 4 : 5 : 7-$(OH)_4$, 2-Me	3571s					1603s	1558s	1504m		1325s		1264s			1190s
59	1 : 4 : 5 : 7-$(OH)_4$, 2-CH_2·OH		3378m			1613m	1595m	1560m					1250m			1171m
	Hexasubstituted anthraquinone															
60	1 : 2 : 3 : 5 : 6 : 7-$(OH)_6$		3367w			1645m	1582s						1263s		1198m	1183m

No.																			
	Tetrasubstituted anthraquinones																		
42	1148s		1085m	1014s					902s	861m	841s			806w		756m	719s	705s	
43	1163s	1139w	1105s		1035s		979s	928m	903m	875s	851s					759s[a]			
44	1170s		1100s		1032s		979w	943w	907s	875s	860s	829s				762s[a]			
45	1172s	1131w	1100s	1050s	1026s		982s	938m	914m	876s	865m	835m				759s[a]			
46	1170s		1104m		1025m	1000w			914w	887s						755s			
47	1164s		1105m		1033m	1002m	975w	951m	913w	879s	843s			805m	776w		739s		
48	1172s	1136w		1076s	1012s		977w		915m	890s	840m			806s	789s	752m	728s		
49	1155s						973m				838s				780s		737m		
	Pentasubstituted anthraquinones																		
50	1140s		1099m	1081w	1034s	1017w	980s		936m	918s		866s	822w	802w	786w	764m	730s	709m	686w
51	1125s		1098m	1054m	1035m		988m	968m	943m	891m		853m		816s	798s	766w	744s	728m	
52	1136s		1103m	1078m	1035m		990s		957m	876w		856w		799w	784s		741m		
53	1139m		1103w	1060w	1025m		981m		949m	902w	881w	855w	833m	814m	786m	773m	738w		
54	1124s		1092m	1043m		1010s		966w		900m		854m		810m		776s			
55	1139w			1085s	1058m	1008m		972m		911w	872m	845w		812m	777w	761s	741s		
56	1134w			1079s	1026s			972s	923w	891m		849m			787s	757m	736m		
57	1159s	1136w	1089s		1021s		991m	945m	920m	909w	876s	858w	835w	823w	803s	769m	750s[a]		
58		1138m	1091s		1024s				921s	882s	858s				805s	771s	736s	693m	
59			1092s	1038w	1021w	1005w			923w			855w				775m		703m	
	Hexasubstituted anthraquinone																		
60	1152s							972s					838s		781s		737s		

[a] Spectrum recorded from 2 to 14 μ only.

to the α-hydroxyl stretching frequency. To clarify the position, the spectrum of α-hydroxyanthraquinone has been re-investigated, using potassium bromide pressed discs and mulls in hexachlorobutadiene. A broad, weak absorption band with centre at approximately 2700 cm.$^{-1}$ was obtained in both cases, corresponding to the stretching frequency of chelated hydroxyl bonds.[4] In addition, there was a broad peak of medium strength at 3039 cm.$^{-1}$, assignable to the normal aryl C–H stretching frequency.

The absence in paraffin mulls of the usual hydroxyl stretching vibration is accompanied by a profound change in frequency and intensity of the stretching vibration of the carbonyl group adjacent to the α-hydroxyl group, so that a second, more intense band at lower frequency results. From his work in the hydroxyl and carbonyl regions of some hydroxy-derivatives Flett [3] suggested a useful grouping according to the arrangement of the α-hydroxyl groups in hydroxyanthraquinones, and this was extended by Howard and Raistrick [6] to include hydroxyanthraquinones with other substituted groups. With the large number of complex anthraquinones available for this study it has been possible to extend still further the usefulness of the spectra in this region. In Table 2 are set out the carbonyl frequencies of anthraquinones grouped according to the arrangement of α-hydroxy-groups on the nucleus. (The numbers in parentheses indicate the number of compounds measured.)

TABLE 2.

		C=O frequencies		
Group no.	Type of anthraquinone	*a*	*b*	Δ
1	No α-OH (18)	1678—1653	—	—
2	1-OH (14)	1675—1647	1637—1621	24—38
3	1 : 4- and 1 : 5-(OH)$_2$ (11)	1645—1608	—	—
4	1 : 8-(OH)$_2$ (8)	1678—1661	1626—1616	40—57
5	1 : 4 : 5-(OH)$_3$ (7)	1616—1592	—	—
6	1 : 4 : 5 : 8-(OH)$_4$ (2)	1592—1572	—	—

Depending on the number of carbonyl peaks and their frequency range, it is possible, with the minimum overlapping, to place an anthraquinone in one of the six groups of Table 2.

In group 3, the lone carbonyl frequency of the 1 : 3 : 5 : 7-tetrahydroxy-derivative has an exceptionally low value (1608 cm.$^{-1}$), falling below 1616 cm.$^{-1}$ which is the upper limit for the single peak of compounds in group 5. Exceptions are 1 : 2 : 6- and 1 : 2 : 7-trihydroxyanthraquinone, which, instead of the expected two carbonyl peaks, have only one, at 1650 and 1647 cm.$^{-1}$ respectively. Both 2 : 6- and 2 : 7-dihydroxyanthraquinone have very low carbonyl frequencies (1656 and 1653 cm.$^{-1}$ respectively), and it is possible that in the case of 1 : 2 : 6- and 1 : 2 : 7-trihydroxyanthraquinone, the vibrations of the two carbonyl groups, now that they are closer in frequency and linked through a conjugated system, have become indistinguishable. In the case of 1 : 2 : 3 : 7-tetrahydroxy-6-methylanthraquinone (compound 55), the weaker of the two carbonyl absorptions (normally expected to appear at about 1675 cm.$^{-1}$) is masked by the strong, very broad peak at 1595 cm.$^{-1}$, while the stronger carbonyl absorption appears only as a band on the side of the 1595 cm.$^{-1}$ peak. Another apparent exception is 1 : 3 : 8-trihydroxyanthraquinone-6-carboxylic acid (compound 46) where the high-frequency carbonyl band is masked by the absorption of the carboxyl group at 1706 cm.$^{-1}$.

In anthraquinones with no α-hydroxyl groups, the single carbonyl frequency occurs between 1678 and 1653 cm.$^{-1}$ and, except in cases of strongly electrophilic substituent groups which raise the frequency a few cm.$^{-1}$, the position and nature of the substituent groups have no noticeable effect on the carbonyl frequency. This is in contrast with the benzoquinones, where the effect of substituent groups can be predicted.[7]

The lowered frequency of the α-hydroxyl group and the accompanying changes of intensity and frequency in the carbonyl region have been ascribed by Hilbert, Wulf, Hendricks, and Liddel [2] to what was later called " conjugated-chelation " [8] where the strength of hydrogen-bonding between the hydroxyl and the carbonyl group (I) and (II) is enhanced by resonance with an ionic form (III) having a conjugated system in which the donor-acceptor properties of the chelating centres are increased. A conjugated-chelate system always results in the disappearance or lowering of the hydroxyl stretching frequency, and at the same time the

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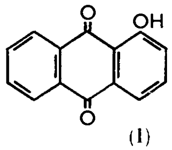
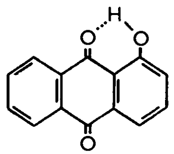
[6] Howard and Raistrick, *Biochem. J.*, 1955, **59**, 478.
[7] Yates, Ardao, and Fieser, *J. Amer. Chem. Soc.*, 1956, **78**, 650.
[8] Rasmussen, Tunnicliff, and Brattain, *ibid.*, 1949, **71**, 1068.

carbonyl band is lowered in frequency and increased in intensity owing to the weakened force constant and increased moment of the bond. Flett[3] considers an ionic form unimportant, but considers that form (IV) makes a considerable contribution. Josien, Fuson, Lebas, and Gregory[9] consider the hydrogen to be equally bonded to the two oxygen atoms in a similar way, but Hadži and Sheppard[5] reject these suggestions since too great a lowering of the hydroxyl frequency would result. They also suggest considerable resonance through the conjugated system (II) and (III). Further consideration, however, as, for example, a comparison of α- and β-hydroxy- and α- and β-amino-anthraquinone, suggests that the primary cause of the lowering of the carbonyl frequency of α-hydroxyanthraquinones is, not chelation, but altered electron-distribution as in forms (V)–(VI) and (VII)–(VIII), chelation serving only to stabilize the resulting ionic forms.


(I)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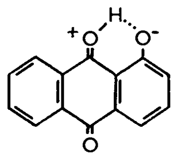
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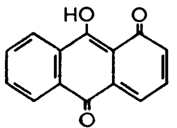
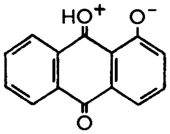
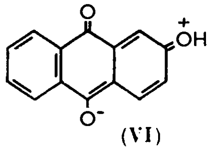

(IV)

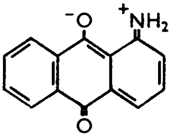
Electron re-distribution to give an ionic form $=OH^+$ takes place less readily than that giving $=NH_2^+$ in the amino-derivatives, and this is reflected in the frequencies of the perturbed carbonyl vibrations of α- and β-aminoanthraquinone[3] compared with the frequencies of the corresponding hydroxyanthraquinones set out in Table 3. Chelation is not important for aminoanthraquinones, hydrogen stretching frequencies in the α- and β-substituted compounds being hardly different. That the single carbonyl frequency of β-hydroxyanthraquinone is lower than that of anthraquinone itself suggests a small contribution from the mesomeric effect, as in (VI).

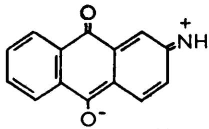
TABLE 3.

Anthraquinone	C=O frequencies *a*	*b*	Hydrogen-stretching frequencies
Anthraquinone	1675	—	——
α-Amino	1665	1612	3420, 3300
β-Amino	1676	1625	3470, 3330, 3220
α-Hydroxy	1667	1631	—
β-Hydroxy	1667	—	3344


(V)


(VI)


(VII)


(VIII)

In the same way the carbonyl frequency of α-hydroxyanthraquinone is initially lowered by resonance with an ionic form (V), which is stabilised by chelation because of the greater donor-acceptor properties of the ionic forms of the carbonyl and hydroxyl groups (III). That chelation, of itself, does not lower the carbonyl frequency is shown by the extended quinones, 2 : 11- (IX) and 4 : 9-dihydroxyperylene-3 : 10-quinone (XI), where the carbonyl vibrations absorb at 1621 cm.$^{-1}$ and 1631 cm.$^{-1}$ respectively,[10, 11] even though hydrogen bonding is so strong in the second compound that it has no hydroxyl absorption peak. In spite of the fact that chelation through a five-membered ring, of either the ionic (X) or the non-ionic form (IX) of the first compound, is less likely than chelation of the two forms (XI) and (XII) of the second compound, the carbonyl frequency of the first compound is the lower. This suggests, as in the case with the aminoanthraquinones, that altered electron distribution, rather than chelation, is primarily responsible for the lowering of the carbonyl frequency of hydroxy-quinones.

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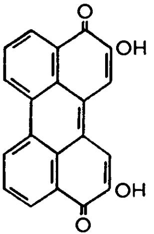
[9] Josien, Fuson, Lebas, and Gregory, *J. Chem. Phys.*, 1953, **21**, 331.

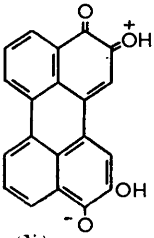
[10] Brown and Todd, *J.*, 1954, 1280.

[11] Calderbank, Johnson, and Todd, *J.*, 1954, 1285.

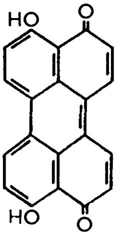
All the compounds examined have a further strong band in the double-bond region characteristic of C=C frequency. The position of this varies, but is most often around 1575 cm.$^{-1}$. In a few cases where the carbonyl frequency is very low, the two bands are indistinguishable. A similar band in the spectra of the *p*-benzoquinones at a slightly higher frequency [7] is attributed to the C=C stretching frequency of the quinone. For anthraquinones the double bonds that are conjugated directly with a carbonyl vibration have a more aromatic nature and occur at a lower frequency than normal. Further aromatic absorption occurs less regularly throughout the series, but is often masked by peaks of the mulling agent. The band around 1575 cm.$^{-1}$ is useful in distinguishing anthraquinones of the 1 : 4- and the 1 : 5-dihydroxy-group from those of the 1 : 4 : 5-trihydroxy-group. Both groups have only one carbonyl absorption band, and the frequency range in the two cases overlaps. The C=C peak has a frequency greater than 1575 cm.$^{-1}$ characteristic of the 1 : 4- and 1 : 5-dihydroxy-group of anthraquinones, but less than 1575 cm.$^{-1}$ of the 1 : 4 : 5-trihydroxy-group. If there appears to be more than one such peak, the average frequency of peaks higher than 1500 cm.$^{-1}$ is taken for classification. For anthraquinones in the 1 : 4 : 5 : 8-tetrahydroxy-group the C=O and C=C frequencies are indistinguishable. For anthraquinones having no α-hydroxyl groups the C=C band generally has a higher frequency and is less variable than in the other groups.



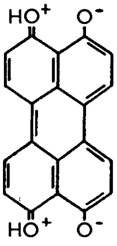
(IX)



(X)



(XI)



(XII)

It is not possible to assign further peaks to particular vibrations. Hadži and Sheppard [5] assigned some bands in the spectra of four hydroxyanthraquinones to hydroxyl deformation vibrations, but similar bands are found in most anthraquinones, whether containing hydroxyl groups or not. The out-of-plane C–H deformation bands are expected to be found in the region 900—650 cm.$^{-1}$. Absorption bands of methyl and methylene substituent groups are obscured by the mulling agent.

Apart from the regions of their characteristic absorption the effect of substituent groups on the rest of the spectrum is small, the position of a group on the anthraquinone nucleus being of more importance in determining the overall spectrum than the nature of the group. This is so, not only in the region of the C–H out-of-plane deformation vibrations of the anthraquinone nucleus where substitution of another group for a hydrogen atom must change the vibration spectrum, but also from the double-bond stretching region down through the C–H deformation vibrations beginning around 900 cm.$^{-1}$.

It may be seen from Table 1, that derivatives listed under the same heading of substitution pattern have many common bands within a narrow range of frequency and intensity. There are eleven groups of anthraquinones with different characteristic substitution patterns. Perusal of the Table shows that the common bands in each group can be distinguished from those of other groups, thus enabling an unknown anthraquinone to be classified within a definite group and therefore assisting in its identification (with the help of other available chemical, physical, and biosynthetic evidence).

Summary of Diagnostic Features.—(1) The infrared absorption spectrum of each of the 60 anthraquinones is unique and can be used to " fingerprint " each compound.

(2) β-Hydroxyl groups can be detected by the appearance of a sharp band in the region 3600—3150 cm.$^{-1}$. If there is more than one such band, two or more hydroxyl groups are attached to the anthraquinone nucleus in β-positions, each having a different environment.

(3) Derivatives with no α-hydroxyl group have one strong carbonyl band in the region 1678—1653 cm.$^{-1}$.

(4) Derivatives with one α-hydroxyl group have two carbonyl frequencies, one in the region

1675—1647 cm.$^{-1}$, and an even stronger band between 1637 and 1621 cm.$^{-1}$, the frequency separation between the bands lying in the range 24—38 cm.$^{-1}$.

(5) Substitution by two α-hydroxyl groups in the 1 : 4- and 1 : 5-positions yields spectra with a single carbonyl band between 1645 and 1608 cm.$^{-1}$.

(6) Derivatives with two α-hydroxyl groups in the 1 : 8-positions have two bands, one between 1678 and 1661 cm.$^{-1}$ and the other, stronger one between 1626 and 1616 cm.$^{-1}$, the frequency separation between the peaks lying between 40 and 57 cm.$^{-1}$.

(7) Substitution of α-hydroxyl groups in the 1 : 4 : 5-positions yields a single carbonyl band between 1616 and 1592 cm.$^{-1}$.

(8) Derivatives with four α-hydroxyl groups, *i.e.*, in the 1 : 4 : 5 : 8-positions, have a single carbonyl band, in the region 1592—1572 cm.$^{-1}$.

(9) The average C=C stretching band in anthraquinones of the 1 : 4- and the 1 : 5-dihydroxy-group has a frequency greater than 1575 cm.$^{-1}$, while in the case of the 1 : 4 : 5-trihydroxy-group, it is less than 1575 cm.$^{-1}$. For anthraquinones of the 1 : 4 : 5 : 8-tetrahydroxy-group, the C=O and C=C bands are indistinguishable.

(10) It is possible to group the spectra of anthraquinones of the same substitution pattern according to the frequency and intensity of the absorption bands.

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