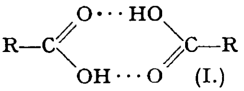
216. *The Characteristic Infra-red Frequencies of the Carboxylic Acid Group.*

By M. St. C. Flett.

The infra-red spectra of 60 carboxylic acids, with widely varying structures, have been measured between 700 and 4000 cm.$^{-1}$, to improve the certainty with which a carboxylic acid group can be distinguished from other acidic groups by infra-red spectroscopy. The reliability of five bands as tests for the presence of the carboxy-group has been assessed. For three of these bands it has proved possible to determine the effect of structural changes, such as the introduction of substituents and conjugation with double bonds and ring systems, on the precise frequency of the band. No general relationship between the spectra of acids and their dissociation constants was discovered.

In recent years infra-red spectroscopy has been used extensively for the detection of chemical groups in materials of unknown structure by observation of characteristic frequencies (Thompson, *J.*, 1948, 328; Williams, *Rev. Sci. Inst.*, 1948, **19**, 135). Deductions may, however, be uncertain if the correlation between the characteristic frequencies and the molecular environment of a group has not been established by measurements on a sufficiently wide variety of compounds. In the case of the carboxylic acid group, many investigators have studied particular acids but no comprehensive investigation of the effect of structure on its characteristic bands seems to have been undertaken, except by Lecomte (" Structure des Molecules " in

" Traité de Chimie Organique," Vol. 2, Masson et Cie, Paris, 1936) who considered only ten acids, in some cases over limited spectral ranges. Sixty carboxylic acids with widely varying structures were therefore examined. The problem is complicated by the dimerisation normally shown by acids in the solid and liquid states giving hydrogen-bonded structures of type (I). The monomers are formed only in dilute solution or in the vapour phase at high temperatures. It was at first thought that the extent of dimerisation in the condensed states might be influenced by bulky substituents close to the carboxy-group, and that it would, therefore, be necessary first to study the effect of structural changes on the bands by examining a series of acids in some solvent in which they were monomeric. Few such solvents are, however, available which are sufficiently transparent at the wave-lengths of the carboxyl group bands. In non-polar solvents, such as carbon tetrachloride (which are spectroscopically most suitable), acids exist as a mixture of monomer and dimer (Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755). Dioxan seemed suitable as it is a good solvent for carboxylic acids, and freezing-point measurements indicate (Lassettre, *Chem. Reviews*, 1937, **20**, 277) that benzoic acid is monomeric in it. This was confirmed by spectroscopic measurement, a single C=O stretching band being observed, whereas two are shown in carbon tetrachloride, corresponding to monomer and dimer. Dioxan was, however, transparent at the wave-lengths of only two of the five bands ultimately associated with the carboxyl group, and acetic acid showed signs of dimerisation in it and also in acetonitrile and chloroform. The idea of examining the frequencies and intensities of the bands of all the acids in the same solvent had, therefore, to be abandoned, though the C=O stretching bands of a number were examined in dioxan. It was decided to examine the liquid acids as thin films and the solids as solid films made by melting or, if the melting points were high, as powders moistened with Nujol to minimise scatter. This procedure has the advantage that the results obtained are more directly applicable to unknown materials, when frequently only a small amount of solid material is available. The spectra of a few low-melting acids were measured as solids and liquids; there were no striking differences, indicating that little would be gained by studying all the liquid acids as solids.



(I.)

EXPERIMENTAL.

The spectra were determined with a Hilger D.209 spectrometer, single-beam photographic recording being used. At those wave-lengths where atmospheric water-vapour absorption interferes, it was necessary to locate the band heads by point-by-point plotting of the " sample " and " background " traces. The wave-lengths were determined either by interpolation among atmospheric water-vapour and carbon dioxide bands where these appeared on the same record, or from calibration charts. Most of the wave-number values listed are believed to be accurate to ±3 cm.$^{-1}$. Some of the C=O stretching bands near 1700 cm.$^{-1}$ were, however, so broad that the uncertainty is greater, as indicated in the table, and the bands between 2500 and 2700 cm.$^{-1}$ are accurate only to ±10 cm.$^{-1}$. In the case of the 1700 cm^{-1}. bands studied in dioxan solution, the spectrum of dioxan in the same cell was recorded immediately after each solution was measured. From the two records a graph of optical density against wave number was drawn and the strength of the band determined from this graph (*a*) by calculating the molecular extinction coefficient, ε, and (*b*) by measuring the area under the band with a planimeter. This second procedure did not prove to have any advantage over simple measurement of the peak density.

The acids were mostly commercial samples. If of good appearance with melting point (or boiling point) near the literature values, they were normally used without further purification, since the present work was concerned with strong bands, and small amounts of impurity were unlikely to interfere. Some less common acids had been prepared by colleagues in the Research Department; they were recrystallised and their melting points checked, if low enough to be reliable. The two anhydrous crystalline forms of oxalic acid (Hendricks, *Z. Krist.*, 1935, **91**, 48) were made from the dihydrate; the rhombic form made by recrystallisation from acetic acid (Beilstein, Band 2, p. 505) melted at 180°, and the needle form (Hendricks, *loc. cit.*) was obtained from it by sublimation.

RESULTS.

The table lists the wave numbers of five bands thought to be characteristic of the carboxy-group in each acid examined in the condensed state. The value for the C=O stretching mode in dioxan is also included, with the molecular extinction coefficient, ε, and the dissociation constants of the acids in water.

DISCUSSION.

The acids were chosen to cover as wide a range of structures as possible. Mono- and di-basic aliphatic acids, unsaturated acids, and benzenoid and other aromatic acids were included, but not aliphatic amino-acids, whose zwitterion structure makes their infra-red spectra quite different from that of normal acids. From the band positions it appears that in all cases the solid and liquid acids exist as dimers (or possibly higher polymers) so complications due to monomer–dimer equilibria do not arise.

Previous work made it possible to predict the approximate positions of certain $-CO_2H$

Acid.	Between 2500 and 2700 cm.$^{-1}$.	Near 1700 cm.$^{-1}$.			Near 1400 cm.$^{-1}$.	Near 1250 cm.$^{-1}$.	Near 900 cm.$^{-1}$.	*K*.*
		Solid or liquid.	In dioxan.	10^{-2} ε.				
Acetic	2570(w), 2660(s)	1712±5	—	—	1415	1293	930(m)	1·86 × 10^{-5}
Propionic	2580, 2680(s), 2760	1715±5	1735	4·12	1418	1240	930(m)	1·4 × 10^{-5}
Hexanoic	2500(w), 2680(s)	1710±5	1733	5·53	1417	1286, 1245	937(s)	1·43 × 10^{-5}
Lauric	2570, 2650(s)	1700±5	—	—	1428	1300	937(s)	—
Chloroacetic	2590, 2700, 2540	1735 (in CCl_4)	—	—	1420±5	1213	933(w)	1·5 × 10^{-3}
Cyanoacetic	2530, 2610	1730±5	—	—	1395	1182	935(w)	3·6 × 10^{-3}
Phenylacetic	2570, 2650(s), 2740	1697±3	1730	3·21	1409	1230	928, 904(m)	4·88 × 10^{-5}
Diphenylacetic	2540, 2640(w), 2720	1695±5	—	—	1410	1225, 1312	937(s)	1·15 × 10^{-4}
Phenoxyacetic	2580(s), 2680	1735±5, 1703±5	—	—	1439	1234	915(w)	—
Glycollic	2580, 2640	1730±5, 1710±5	—	—	—	1213	—	1·5 × 10^{-4}
Thiolacetic	2590	1710±5	—	—	1420±5	—	—	—
α-Chloropropionic	2570, 2680	1730±10	1745	—	1420	1215	920(w)	1·4 × 10^{-3}
β-Chloropropionic	2690, 2590	1710±5	1735	—	1440(w), 1400	1245	932(m)	1·0 × 10^{-4}
Lactic	2520, 2630, 2700	1725±5	—	—	—	1225	920(w)	1·38 × 10^{-4}
Oxalic (dihydrate)	—	1690—1710	—	—	—	1250	—	—
Oxalic, anhydrous, needle or rhombs	—	1690—1710	—	—	—	1250	—	—
Malonic	2600, 2700	1740±5, 1710±5	—	—	1422	1311, 1224	920(s)	1·5 × 10^{-3} 2·1 × 10^{-6}
Succinic	—	1780(w), 1700±5	—	—	1420	1313	923(w)	6·6 × 10^{-5} 2·8 × 10^{-6}
Adipic	2620	1700±5	—	—	1425	1280	926(s)	3·8 × 10^{-5} 3·9 × 10^{-6}
Acrylic	2540, 2660	1705±3	—	—	†	1295, 1243	—	5·6 × 10^{-5}
Methacrylic	2530, 2610(s), 2700	1700±2	—	—	†	1320	—	—
α-Crotonic	2500, 2680	1700±5	1718	4·34	1438	1312	912(s)	2·03 × 10^{-5}
Maleic	2510, 2600	1705±2	—	—	1437	1272	930(w)	1·42 × 10^{-2} 8·57 × 10^{-7}
Fumaric	2540(s), 2700(w)	1680±5	—	—	1423	1280	932(m)	1·0 × 10^{-3} 4·8 × 10^{-5}
Benzoic	2580, 2700	1685±5	1720	5·58	1417	1290	935(s)	6·3 × 10^{-5}
o-Chlorobenzoic	2540, 2640	1690±2	1733	3·31	1410	1312	917(s)	1·2 × 10^{-3}
o-Cyanobenzoic	2530, 2640	1690±5	—	—	1418	1293	910(w)	—
o-Nitrobenzoic	†	1700±3	1730	—	1420	1308	907(w)	6·1 × 10^{-3}
Salicylic	2570, 2700	1665±5	1680	—	1440(w)	—	—	1·06 × 10^{-3}
Anthranilic (high-temp. form)	2550, 2640, 2710	1670±5	—	—	1420	1240	915(s)	1·05 × 10^{-5}
Anthranilic (normal)	2550	1660±5	1697	—	—	—	—	1·05 × 10^{-5}
m-Nitrobenzoic	2520, 2580	1690±5	1731	5·65	1412	1288	930(m)	3·44 × 10^{-4}

Acid.	Between 2500 and 2700 cm.$^{-1}$.	Near 1700 cm.$^{-1}$.			Near 1400 cm.$^{-1}$.	Near 1250 cm.$^{-1}$.	Near 900 cm.$^{-1}$.	K.*
		Solid or liquid.	In dioxan.	$10^{-2}\,\varepsilon$.				
p-Nitrobenzoic	†	1690±5	—	—	1430	1308, 1288	935(s)	$4 \cdot 0 \times 10^{-4}$
p-Chlorobenzoic	2550(s), 2640(w)	1685±5	1723	5·52	1425	1322, 1280	928(m)	$1 \cdot 04 \times 10^{-4}$
Anisic	2520, 2630	1685±3	1718	5·05	1428	1300, 1265	935(m)	$3 \cdot 38 \times 10^{-5}$
p-Hydroxybenzoic	2540, 2680	1680±5	1716	4·62	1420	1316, 1240, 1245	930(m)	$2 \cdot 88 \times 10^{-5}$
p-Aminobenzoic	2530, 2650	1670±10	1709	6·22	1420	1314, 1295	926(w)	$1 \cdot 15 \times 10^{-5}$
Mandelic	2530	1715±5	—	—	—	1249	940(w)	$4 \cdot 3 \times 10^{-4}$
Cinnamic	2530, 2660	1680±5	1713	4·62	1420	1311, 1285	940(m)	$3 \cdot 8 \times 10^{-5}$
o-Coumaric	2710(w), 2590, 2530	1665±3	—	—	1430	1220	907(m)	$2 \cdot 10 \times 10^{-5}$
Phthalic	2680, 2540	1695±5	—	—	1403	1282	904(s)	$1 \cdot 26 \times 10^{-3}$ $5 \cdot 4 \times 10^{-6}$
*tere*Phthalic	2550, 2680	1690±5	—	—	1425	1289	930(s)	—
2 : 4 : 6-Trinitrobenzoic	2540, 2670	1728±3	—	—	1412	1265	928(s)	—
Diphenic	2550, 2640	1685±5	1727	3·77 (per CO_2H)	1407	1284, 1258	920(m)	—
o-Naphthoylbenzoic	2550, 2680	1655–85 ‡	—	—	—	1271	918(m)	—
1-Naphthoic	2520, 2610	1678±3	1717	3·79	—	1284, 1258	—	$2 \cdot 0 \times 10^{-4}$
2-Naphthoic	2570(s), 2660	1690±3	—	—	1423	1307	935(s)	—
3-Hydroxy-2-naphthoic	2550, 2580	1655±5	—	—	1440(w)	1275	905(m)	—
3-Amino-2-naphthoic	—	1665±5	—	—	—	1300, 1270	—	—
Pyromucic	2570, 2680	1690±5	—	—	1428	1301	935(m)	$7 \cdot 1 \times 10^{-4}$
Nicotinic	2490	1700±5	1728	—	1420(w)	1322, 1300	—	$1 \cdot 4 \times 10^{-5}$
Quinaldinic	2510	v. weak	—	—	—	1316	—	—
2-Aminofluorene-9-carboxylic	2620	1700±2	—	—	—	1198	—	—
2-Amino-3-carboxyphenyl 2-hydroxy-4-sulphophenyl sulphone	2610	1660±5	—	—	—	1208	926(w)	—
o-(3-Amino-4-hydroxybenzoyl)benzoic	2560, 2680	1675–95 ‡	—	—	1435	1292	—	—
2-Carboxydiphenylamine	2570, 2650, 2750	1660±5	1690	—	1440, 1412(w)	1260	—	—
Acenaphthene-3-carboxylic	2540, 2590(s)	1665±5	—	—	1440, 1420	1285, 1265, 1245	—	—
3-Hydroxy carbazole-2-carboxylic	2600	1660±5	—	—	—	1315, 1207	902(m)	—
1-Anilinoanthraquinone-2-carboxylic	2570	1660–90 ‡	—	—	1418(w)	1260	935(w)	—
4-Bromo-1-chloroanthraquinone-2-carboxylic	weak	1710 ? ‡	—	—	—	1301	—	—

* The values quoted for the dissociation constant, K, were in nearly all cases those given at 25° in the various volumes of Landolt–Börnstein's "Tabellen." Where more than one value was quoted the most recent was normally chosen.

† Not measured in this region.

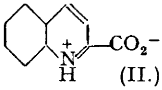
‡ Value uncertain owing to other C=O group in molecule.

bands. Formic, acetic, propionic, and other aliphatic acids have been studied as gases at various temperatures (*e.g.*, Bonner and Hofstatter, *J. Chem. Phys.*, 1938, **6**, 531; Herman and Hofstatter, *ibid.*, p. 534), and in carbon tetrachloride solution (Davies and Sutherland, *loc. cit.*; Buswell, Rodebush, and Roy, *J. Amer. Chem. Soc.*, 1938, **60**, 2239). This work shows that whereas the OH stretching mode of the monomers lies near 3600 cm.$^{-1}$, the dimeric form gives rise to a broad absorption region with many sub-maxima, at 2500—3000 cm.$^{-1}$. The reason for its great breadth has been discussed by Davies and Sutherland (*loc. cit.*). Similarly band pairs at 1768 and 1719 cm.$^{-1}$ and at 1378 and 1442 cm.$^{-1}$, observed in carbon tetrachloride solutions, are associated, respectively (Davies and Sutherland, *loc. cit.*), with the C=O stretching and C–O– stretching vibrations in the monomeric and dimeric forms. Lecomte (" Structure des Molecules " in " Traité de Chimie Organique," Vol. 2, Masson et Cie, Paris, 1936) mentions a band between 945 and 930 cm.$^{-1}$.

In agreement with the above, bands were observed in most of the acids at 2500—3000 cm.$^{-1}$, near 1700 cm.$^{-1}$, and near 1400 cm.$^{-1}$. Also most of the spectra had their strongest band in the 700—1600-cm.$^{-1}$ range between 1200 and 1300 cm.$^{-1}$. This band and another near 900 cm.$^{-1}$ are listed in the table.

The 2500—3000-cm.$^{-1}$ band is often modified by the C–H stretching bands which occur at 2800—3100 cm.$^{-1}$. A sub-group of one to three bands, however, appears between 2500 and 2700 cm.$^{-1}$ (with the resolution achieved by a rock-salt prism), as in the table. These are not overlaid by C–H bands, and accordingly show up well even in " Nujol " mulls of solid acids. The only acids studied which did not show these sub-bands were oxalic, succinic, and 3-amino-2-naphthoic acid. The first two did, however, show the broad absorption region between 2500 and 3000 cm.$^{-1}$. Oxalic acid was also unique in that its hydrate and both anhydrous forms showed a peak near 3400 cm.$^{-1}$. The two anhydrous forms did not show any spectral difference which could be interpreted in terms of their different crystal structures (Pauling, " Nature of the Chemical Bond," p. 309). The sample of 3-amino-2-naphthoic acid melted at 215—216° (literature 214°). Since 2500—2700 cm.$^{-1}$ is a range where bands due to other groups seldom occur, the bands in the range provide perhaps the surest way of detecting a carboxy-group. The absolute intensity of the band is not, however, very great, and the band might be too weak for detection in acids of very high molecular weight ($>$ 300—400). No conclusions could be reached regarding the effect of structure on the number and exact frequencies of the peaks in this region.

A strong band occurs near 1700 cm.$^{-1}$ in the spectrum of every acid examined, except quinaldinic acid, which possibly occurs in the solid state as the zwitterion (II), though this would apparently lead to a loss of resonance energy. Although this is the strongest of the carboxy-group bands, its usefulness in diagnosis is limited, since aldehydes, ketones, and possibly esters may absorb at this wave-length. The influence of structure is clearly reflected in the exact position of this band. Normally, it is higher than 1700 cm.$^{-1}$ for aliphatic and lower for aromatic acids. In only two acids where the carboxy-group is directly attached to an aromatic nucleus (*o*-nitrobenzoic and 2 : 4 : 6-trinitrobenzoic acid) is the value greater than 1700 cm.$^{-1}$; both contain the powerfully electron-attracting nitro-group. Only three acids (phenylacetic, diphenylacetic, and cinnamic), which might be regarded as aliphatic, have the band below 1700 cm.$^{-1}$. Of the five acids having unusually high values ($>$1725 cm.$^{-1}$), three (chloroacetic, α-chloropropionic, and 2 : 4 : 6-trinitrobenzoic) have electron-attracting substitutents. Of the nine in which the band is below 1680 cm.$^{-1}$, seven (salicylic, anthranilic, *o*-coumaric, 3-hydroxy-2-naphthoic, 3-amino-2-naphthoic, 3-hydroxy-carbazole-2-carboxylic acid, and 2-carboxydiphenylamine) are capable of internal hydrogen bonding. Phenoxyacetic, glycollic, succinic, and malonic acids show two bands in this region; two of these acids are dibasic, but there is no evidence that this is a general property of dibasic acids. It is clear that once the presence of the carboxy-group is established, further information about the structure of the acid is obtainable from the precise value of the C=O stretching frequency.


(II.)

This band was also studied in dioxan solutions of some acids. The possibility of correlating both the frequency and the intensity of the band in the monomeric acid with the structure and dissociation constant of the acid was considered. Provided that the structural changes are not very great (*e.g.*, the introduction of substituents into benzoic acid), a reasonably good correlation is observed between frequency, dissociation constant, and the electron-attracting or -donating power of the substituent (Flett, *Trans. Faraday Soc.*, 1948, **44**, 767). A similar correlation was observed by Gilette (*J. Amer. Chem. Soc.*, 1936, **58**, 1143) for various methyl- and halogen-substituted acetic acids. There is, however, no evidence for a comprehensive relationship between frequencies and dissociation constants; presumably the entropies of ionisation vary if the structural changes are considerable.

No regular effect of substitution on the extinction coefficient was deduced. The average value of ε for 18 acids was 464, but individual values are considerably spread around this figure.

Examination of the table shows that the 1400-cm.$^{-1}$ band is less useful for diagnosis than the two already discussed. It has not been observed in 15 acids. This is partly because it is intrinsically weaker, and is at a wave-length where it is likely to be overlaid by other strong bands. Though the evidence is not very strong, it appears that structural changes affect this band in the opposite direction to changes in the C=O stretching band. Thus, of six acids in which it is unusually high ($>$1430 cm.$^{-1}$), four are unsaturated or internally hydrogen-bonded (salicylic acid, 2-carboxydiphenylamine, maleic acid, crotonic acid), whereas of the eight in which it is below 1415 cm.$^{-1}$, four (*m*-nitrobenzoic, *o*-chlorobenzoic, 2 : 4 : 6-trinitrobenzoic, and β-chloropropionic) have electron-attracting substituents. A similar observation was made previously in the case of substituted benzoic acids (Flett, *Trans. Faraday Soc.*, 1948, **44**, 767).

The position of the 1250-cm.$^{-1}$ band varies widely from compound to compound, but the general influence of structure on it can be discerned. Of 18 acids where it is above 1280 cm.$^{-1}$, fourteen are aromatic and two more are unsaturated. Of the ten in which it is below 1240 cm.$^{-1}$ (lactic, phenoxyacetic, phenylacetic, cyanoacetic, glycollic, chloroacetic, α-chloropropionic, *o*-coumaric, 2-aminofluorene-9-carboxylic acid, and 2-amino-3-carboxyphenyl 2-hydroxy-4-sulphophenyl sulphone) six are substituted acetic acids. Esters and ketones (Thompson and Torkington, *J.*, 1945, 640) have bands near 1250 cm.$^{-1}$; this limits the usefulness of the band in diagnosis.

The band between 900 and 940 cm.$^{-1}$ was observed in the spectra of 43 acids, and its appearance is unlikely to be coincidental. There is no apparent correlation of its appearance and non-appearance, or of its precise frequency, with structural factors. The band might, on occasion, provide some confirmation of a carboxy-group detected by its other bands.

There are thus five bands to be considered in detecting a carboxy-group. The peak optical densities of the bands at 2500—2700 cm.$^{-1}$, near 1700 cm.$^{-1}$, near 1420 cm.$^{-1}$, near 1250 cm.$^{-1}$, and near 900 cm.$^{-1}$ were estimated to be very roughly in the ratio 1 : 5 : 2 : 3 : 1. The first two are the most highly characteristic and if neither can be detected, the substance is unlikely to be an acid. In doubtful cases the other three bands provide confirmatory evidence, though the absence of any of them does not imply the absence of a carboxy-group. Some information about the structure of the acid can be deduced from the precise frequencies of these bands. Conjugation with aromatic nuclei, internal hydrogen bonding with hydroxy- or amino-groups, and to a lesser extent conjugation with ethylenic double bonds lower the C=O stretching frequency, whereas electron-attracting substituents raise it. These influences seem to have the opposite effect on the bands near 1420 cm.$^{-1}$ and 1250 cm.$^{-1}$.

There appears not to be any sure means of distinguishing between monobasic and dibasic acids. Even in cases such as phthalic, maleic, and malonic acids, where the two carboxy-groups are in close proximity and would be expected to bond internally, the band positions are fairly normal.

The carboxy-group does not normally interfere with the characteristic frequencies of other groups. Of the unsaturated acids examined, maleic, acrylic, methacrylic, crotonic, cinnamic, and *o*-coumaric show respectively bands at 1635, 1640, 1640, 1630, 1635, and 1620 cm.$^{-1}$, which may plausibly be associated with the C=C stretching vibrations. Fumaric acid shows no outstanding band in this region. This may be connected with the centre of symmetry in the molecule which would render the C=C stretching band weak in the infra-red. Crotonic, cinnamic, and *o*-coumaric acids show bands respectively at 974 cm.$^{-1}$, 980 cm.$^{-1}$, and 990 cm.$^{-1}$ which are associated with bending of the C–H bond in *trans*-symmetrically disubstituted ethylenes (Sheppard and Sutherland, *Proc. Roy. Soc.*, 1949, *A*, **196**, 195). The band at 982 cm.$^{-1}$ in acrylic acid may be similarly explained. Hydroxy- and amino-groups in acids can readily be detected, since the 2500—3100-cm.$^{-1}$ acid absorption does not overlie the highly characteristic OH and NH bands. All the acids with an imino- or amino-group (except 1-anilinoanthraquinone-2-carboxylic acid) had bands between 3500 and 3250 cm.$^{-1}$, and all the hydroxy-acids (except glycollic) had a discrete band between 3500 and 3200 cm.$^{-1}$. The benzoic acids examined do not show bands in the region 700—850 cm.$^{-1}$ characteristic of *o*-, *m*-, and *p*-substitution. The nitro-acids showed the characteristic nitro-group bands near 1350 and 1550 cm.$^{-1}$.

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