41. *Infra-red Studies of the Salicylides and Cresotides.*

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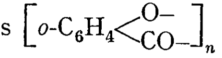
The infra-red spectra of the salicylides and cresotides have been measured. The variations in the carbonyl-bond stretching frequency are used to obtain information about the configurations adopted by these compounds. The frequencies found support the structures proposed by Edgerley and Sutton on the basis of dipole-moment measurements. The carbonyl frequencies for a number of substituted phenyl esters are also presented and discussed.

As an elaboration of the chemical investigation of the salicylides and cresotides (Baker, Ollis, and Zealley, *J.*, 1951, 202; Baker, Gilbert, Ollis, and Zealley, *J.*, 1951, 210) and the measurement of their dipole moments (Edgerley and Sutton, *J.*, 1951, 1069), the infra-red spectra of the salicylides  $\left[o\text{-}C_6H_4{<}^{O-}_{CO-}\right]_n$ and the corresponding cresotides derived from *o*-, *m*-, and *p*-cresotic acids (2-hydroxy-3-, 2-hydroxy-4-, and 2-hydroxy-5-methylbenzoic acids) have been measured.

Experimental

The spectra of the compounds listed in Tables 1, 2, and 3 were measured in the region of the carbonyl-bond stretching vibration (1700—1800 cm.$^{-1}$) with a Perkin–Elmer Model 12C spectrometer with a rock-salt prism. The substances were examined as suspensions in paraffin (Nujol), and as dilute solutions in carbon tetrachloride with a cell thickness of approx. 0·5 mm. Tetra-*p*-cresotide, hexasalicylide, and hexa-*m*-cresotide were not sufficiently soluble for their spectra to be measured in carbon tetrachloride solution.

Results and Discussion

The carbonyl-bond frequencies of the salicylides and cresotides are given in Table 1 (for solutions) and in Table 2 (for solids). In Table 3 are given the corresponding frequencies for several esters of related interest.

Table 1. *Carbonyl-bond stretching frequencies (in cm.$^{-1}$) for solutions in carbon tetrachloride (values in parentheses are for weak bands).*

	Di-	Tri-	Tetra-
Salicylides	1773	1749	1740
o-Cresotides	1777 (1769)	1764 (1748)	1736
m-Cresotides	1767	1739 (1749)	1736
p-Cresotides	1768	1742	—

Table 2. *Carbonyl-bond stretching frequencies (in cm.$^{-1}$) for solids.*

	Di-	Tri-	Tetra-	Hexa-
Salicylides	1751 (1764)	1730 (1743)	1730	1729
o-Cresotides	1751 (1762)	1746 (1729)	1729	—
m-Cresotides	1753 (1761)	1731	1730	1722
p-Cresotides	1753 (1768)	1724 (1746)	1725	—

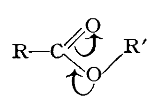
Table 3. *Carbonyl-bond stretching frequencies (in cm.$^{-1}$) for some esters in carbon tetrachloride solution.*

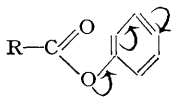
Ethyl acetate	1735	*p*-Dimethylaminophenyl acetate	1751
Phenyl acetate	1764	Phenyl benzoate	1738
p-Nitrophenyl acetate	1771		

Models show that compounds of the salicylide type can take up a number of interconvertible, strainless configurations. In order to obtain information from their infra-red spectra regarding the actual structure adopted it is necessary to consider bands which can be assigned to particular vibrations, variations in the frequency of which can be correlated with steric effects. The only such bands are those produced by the carbonyl-bond stretching vibration with a frequency of 1720—1780 cm $^{-1}$. The normal frequency for the carbonyl stretching vibration of an aliphatic ester in solution (*e.g.*, ethyl acetate, Table 3) is about 1735 cm.$^{-1}$ (Thompson and Torkington, *J.*, 1945, 640); this may be modified by the influence of the groups to which the ester group is attached. In an ester, $R{\cdot}CO_2R'$, when R is a group which can conjugate with the carbonyl group, as in methyl benzoate, the frequency is reduced by about 10—20 cm.$^{-1}$ (Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073). When R′ is unsaturated, as in phenyl acetate, the carbonyl frequency is raised to about 1765 cm.$^{-1}$ (Table 3). When both these effects are operative, as in phenyl benzoate, the carbonyl frequency might be expected to be somewhat above the normal value, and for phenyl benzoate it is found to be 1738 cm.$^{-1}$. This seems to be the normal value to be expected for the salicylide sand cresotides if the benzene rings exert their maximum effect.

The question arises why the carbonyl-bond stretching frequency for phenyl acetate should be so much higher than the normal value. In any ester $R{\cdot}CO_2R'$ electromeric interaction may occur as in (I) provided that the atoms of the ester group $\cdot CO_2R'$ are coplanar. It has been suggested that if R′ is a phenyl group, this can interact with the ether-oxygen atom as in (II) and thus strengthen the carbonyl bond by opposing the effect shown below (I). However, as noted by Edgerley and Sutton (*loc. cit.*), interference between the carbonyl-oxygen and the hydrogen atom in the *o*-position of the phenyl group prevents the coplanar configuration from being adopted, and the electromeric effect (II) should be very slight. The frequencies given in Table 3 for *p*-nitrophenyl acetate and *p*-dimethylaminophenyl acetate provide evidence that there is electromeric interaction between the ether-oxygen atom and its attached phenyl group. The differences produced by the *para*-substituents cannot be accounted for in terms of purely inductive effects but can be readily explained if a degree of interaction between the phenyl group and the ether-oxygen atom be assumed. The *p*-nitrophenyl group should then enhance the effect shown in (II) and so raise the carbonyl-bond frequency, while the *p*-dimethylaminophenyl group supports (I) and lowers the frequency. It seems likely, therefore, that the free pair of electrons of the ether-oxygen atom occupy an orbital which can have an appreciable component in a direction which allows interaction with the π-electrons of the benzene ring.

(I)





(II)

The carbonyl-bond stretching frequencies given by the dimers are found to be much higher than those of the trimers and tetramers. With the exception of tri-*o*-cresotide, the trimers and tetramers have their carbonyl-bond frequencies at about 1740 cm.$^{-1}$, while for the dimers it is at about 1770 cm.$^{-1}$ in carbon tetrachloride solution (see Table 1). Edgerley and Sutton (*loc. cit.*) have provided conclusive evidence that in the dimers the ester groups adopt the *cis*- rather than the more usual *trans*-form. It might be thought that the *cis*-configuration always leads to a high carbonyl frequency, but for the lactones which have been shown by Marsden and Sutton (*J.*, 1936, 1383) to adopt the *cis*-ester configuration, normal carbonyl frequencies are given if steric strain is absent (Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073).

Since there is no strain in the *cis*-form of the dimers, normal bond lengths and intervalency angles being possible, an alternative explanation of the high frequencies of the carbonyl-bond vibration must be sought. The ester groups in the dimers differ from the ester groups in, for example, phenyl benzoate, in one other feature. Instead of the carbonyl bond being coplanar with the benzene ring to which it is directly attached, it is directed at an angle of almost 90° to it. Conjugation between the benzene ring and its adjacent carbonyl group is therefore considerably reduced. The observed carbonyl frequencies of the dimers should approach that of phenyl acetate (1766 cm.$^{-1}$), and there is very good agreement with this expected value.

The trimers give a carbonyl-bond frequency a little above the normal value, with the exception of tri-*o*-cresotide, for which the frequency is still higher. Dipole-moment measurements (Edgerley and Sutton, *loc. cit.*) show that the ester groups in these compounds have the normal *trans*-configuration and these moments may be interpreted in terms of the pyramid-type structure discussed previously (see Baker, Ollis, and Zealley, and Edgerley and Sutton, *locc. cit.*). Such a structure serves to reduce the strain and steric interference which would be present if the molecule had the completely planar configuration. In the pyramidal structure for trisalicylide and tri-*m*- and -*p*-cresotides, the carbonyl groups can still be coplanar with the benzene rings to which they are directly attached, so that the carbonyl-bond frequencies of trisalicylide and tri-*m*- and -*p*-cresotide would be expected to be very close to that of phenyl benzoate, and this is found to be so.

In tri-*o*-cresotide, the replacement of three hydrogen atoms by larger methyl groups would tend to cause the molecule to depart even more from the planar structure (*i.e.*, increase the height of the pyramid) so that excessive steric interference could be avoided. The observed increase in the carbonyl-bond frequencies of tri-*o*-cresotide may be explained either by a resultant decrease in resonance interaction between the benzene rings and the carbonyl groups or by increased strain.

The carbonyl frequencies of the tetramers indicate that the steric conditions are very similar to those present in phenyl benzoate, and that the bonds of the 16-membered ring are free from strain. A pyramidal configuration similar to that of the trimers would necessitate considerable departure from the normal intervalency angles and so should lead to the higher carbonyl-bond frequencies characteristic of strained ring systems. The infra-red results support the structure proposed by Baker, Ollis, and Zealley (*loc. cit.*) in which the four, almost planar, $O{\cdot}C_6H_4{\cdot}CO$ units are alternately above and below the plane of the four bridge-oxygen atoms. This type of structure for tetrasalicylide is compatible with its dipole moment.

Since most of the compounds when measured in solution give a single intense carbonyl band, it is very unlikely that they exist in solution as equilibrium mixtures of different forms, in spite of the fact that examination of models of these large-membered ring compounds shows that a large number of strainless configurations are possible. The presence of weak bands in association with strong carbonyl bands for *cis*-di- and tri-*o*-cresotide and for tri-*m*-cresotide makes the position less certain for these, but it may be explained in terms of overtones or combination bands.

The carbonyl frequencies given by the substances in the solid state are shown in Table 2. No conclusion can be drawn from the difference in carbonyl frequency for a particular solid and its solution, but the same inter-relations were shown by the solids as by their solutions. Splitting of the bands in the case of solids is frequently encountered; it may be due to differences of the environment of particular carbonyl groups within the crystal lattice, as well as to the factors noted above.

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