

RAMAN EFFECT AND HYDROGEN BONDS

Part VI. Chelate Compounds: Esters of Salicylic Acid and their Mixtures

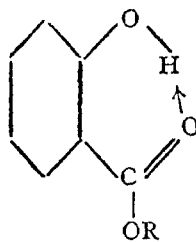
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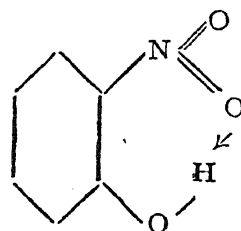
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In previous papers of this series¹ investigations on intermolecular hydrogen bonds formed between molecules of different kinds and of the same kind were described. It has been found that the formation as well as the stability of the hydrogen bonds depend mainly upon the chemical constitution of the molecular species involved. In this paper it is proposed to describe experiments relating to a few substances containing intramolecular hydrogen bonds and their mixtures with typical solvents. The procedure adopted has already been described; the changes brought about in the C=O frequency of carbonyl compounds are followed under different conditions.

As the most suitable substances the esters of salicylic acid have been selected. The C=O of the ester group serves as the donor centre and the phenolic hydroxyl situated in the ortho position acts as the acceptor group with the result that hydrogen bond is readily formed. This type of intramolecular hydrogen bond is known as chelate bond.



The study of chelation originated with the peculiar behaviour of nitrophenols observed by Auwers and Orton.² They noticed that while meta and para nitrophenols gave abnormally high values for their molecular weights ortho nitrophenol was normal. This has been explained as due to the existence of association in the first two compounds by means of intermolecular hydrogen bonds and to the impossibility of association in the ortho compound due to internal hydrogen bond formation as below:



The work of Sidgwick³ and his collaborators relating to physical properties such as solubility, volatility, etc., of a large number of benzene derivatives has been mainly responsible for our present definite knowledge of the subject of chelation. More recently Hilbert, Hendricks and Liddel⁴ have shown that the infra-red absorption method could be used for the study of chelation. They found that the absorption in the vicinity of 1.46 to 1.60 μ which is characteristic of NH or OH groups was absent in such well-known chelate compounds as salicylaldehyde, O-hydroxy acetophenone, methyl salicylate, O-nitrophenol, etc. It was shown by Freymann⁵ using the same method that rise of temperature has no effect on intramolecular hydrogen bonds. The Raman spectra of the above compounds have also been studied by other workers⁶ who have attributed the abnormally low C=O frequencies of these compounds (as compared with those having no hydroxyl group in the ortho position) to the existence of the chelate bond. It, therefore, comes under the category of true hydrogen bonds in which both anionoid and cationoid centres are affected by the linkage.

The Raman spectra of (1) methyl salicylate, (2) ethyl salicylate, (3) *n*-butyl salicylate, (4) isoamyl salicylate and (5) phenyl salicylate (molten condition) were studied after careful purification by distillation under reduced pressure. Of these (3) and (4) have been examined for the first time and the others reinvestigated. The frequencies recorded are given below:

Methyl salicylate.—142 (2) 187 (3) 266 (3) 360 (3) 443 (3) 514 (2) 565 (6) 669 (1) 812 (10) 849 (2) 877 (2) 1036 (8) 1139 (2) 1160 (2) 1192 (2) 1253 (6) 1335 (8) 1442 (3) 1465 (5) 1477 (1) 1582 (2) 1615 (3) 1679 (8b) 1722(1)*

Ethyl salicylate.—162 (2) 252 (2) 307 (2) 450 (4) 508 (1) 563 (8) 669 (2) 754 (1) 781 (1) 816 (8) 857 (7) 975 (2) 1033 (9) 1113 (1) 1136 (2) 1156 (2) 1190 (1) 1247 (10) 1326 (9) 1374 (2) 1400 (2b) 1464 (6b) 1585 (3) 1611 (4) 1676 (8b) 1724 (1)*

n-butyl salicylate.—438 (1) 453 (1) 527 (1) 565 (8) 665 (1) 764 (0) 818 (3) 845 (2) 1036 (5) 1137 (2) 1156 (2) 1199 (1) 1252 (10) 1329 (4) 1400 (3b) 1471 (4) 1586 (3) 1612 (4) 1674 (8b) 1721 (1)*

Isoamyl salicylate.—443 (1) 460 (1) 567 (8) 668 (3) 712 (2) 763 (3) 815 (5) 829 (2) 874 (1) 1033 (8) 1136 (3) 1157 (3) 1253 (10) 1326 (5) 1403 (5b) 1468 (6b) 1586 (3) 1616 (4) 1676 (8) 1721 (1)*

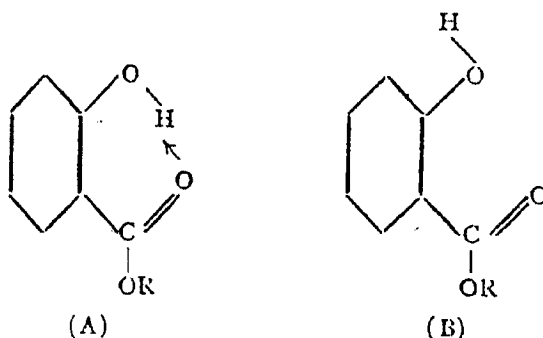
Phenyl salicylate (molten).—92 (3) 163 (3) 187 (3) 243 (4) 436 (0) 470 (2) 506 (2) 528 (2) 561 (8) 614 (2) 665 (1) 753 (2*b*) 798 (1) 812 (1) 841 (3) 861 (1) 914 (0) 938 (0) 998 (8) 1024 (4) 1034 (4) 1064 (1) 1096 (1) 1125 (1) 1156 (3) 1191 (3) 1247 (4) 1333 (5*b*) 1392 (1*b*) 1463 (6*b*) 1581 (3) 1594 (3) 1615 (3) 1687 (6*b*) 1739 (1)*

The frequencies marked * are recorded for the first time and their significance is discussed in this paper.

The C=O frequencies alone are collected in the following table:—

	Methyl salicylate	Ethyl salicylate	<i>n</i> -Butyl salicylate	Isoamyl salicylate	Phenyl salicylate
Bright line	1679	1676	1674	1676	1687
Faint line	1722	1724	1721	1721	1739
Difference in wave numbers	43	48	47	45	52

Thus there are two lines for each ester, the one with the lower frequency is stronger and the other with the higher frequency is very faint. The latter is a new line now noted for the first time and its existence seems to be highly significant. Further the first four esters derived from aliphatic alcohols have their frequencies almost the same, within the limits of experimental error, whereas those of phenyl salicylate are higher. This is in line with our observations with other phenyl esters.⁷ The lower frequencies of the bright C=O lines, also observed by earlier workers are attributed to chelation. It is now suggested that the new faint lines are due to the existence of small proportions of the ester molecules in which the chelate bonds do not exist and that there is an equilibrium between the two molecular types (A and B) in the liquids, type B being very small in amount.

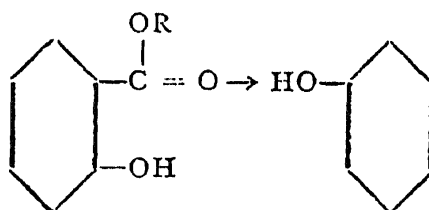


In support of this interpretation may be mentioned (1) the higher frequencies correspond to the C=O frequencies in the related compounds, methyl benzoate (1720), ethyl benzoate (1720) and phenyl benzoate (1740) in which the C=O groups are unco-ordinated owing to the non-existence of ortho hydroxyl groups and (2) the analogy between this

and the weak C=O lines of acetic acid which arise from a small proportion of open dimers existing in equilibrium with the ring types. In this connection it may be relevant to recall the explanation offered by Pauling⁸ for the existence of two hydroxyl absorption peaks in the infra-red spectra of ortho chlorophenols observed by Wulf and Liddel⁹. He postulated the presence of *cis* and *trans* forms existing in equilibrium, the *cis* being obviously in the chelate condition. It is quite possible that in the case of the chlorophenols more of the *trans* form exists than in the case of the carbonyl compounds. From the results recorded above it is clear that the phenomenon is more or less universal in chelate compounds.

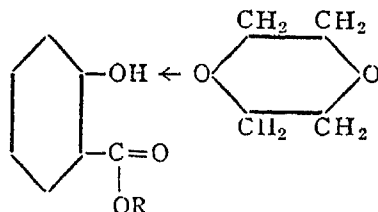
With regard to the chelate bond it may be stated that it is a fairly strong one since the lowering of the C=O frequency due to it is round about 46 wave numbers for the first four esters and somewhat higher for phenyl salicylate. The variation in strength is very little since the groups involved are practically the same all through. Still the existence of the influence of the groups is evident from the small difference noted in the case of phenyl salicylate. Other cases that have been studied, but not yet published, seem to confirm the general proposition¹⁰ that the strength of the hydrogen bond depends upon the donor and acceptor groups and that it holds good even in the case of chelate bonds.

Mixtures.—In order to get more information regarding the chelate bond the spectra of mixtures were obtained using methyl and ethyl salicylate as one component and various donor and acceptor liquids as the other. Admixture with chloroform was found to produce no changes. Since this solvent is not strong in its capacity as a cationoid reagent, phenol was next used. Even in this solvent the C=O lines of the salicylates were unaffected thereby indicating that no change had taken place. It may be argued that though there may be a change it may not be observable since the new intermolecular H bonds are also between an ester C=O and a phenolic hydroxyl and hence may closely resemble the chelate bond.



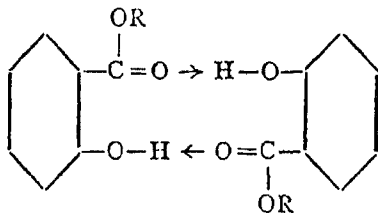
But this is not right for the reason that the intermolecular hydrogen bond between ethyl benzoate and phenol causes a lowering of only 20 wave numbers in the C=O frequency and a similar bond could, therefore, be distinguished from the chelate bond. As a typical donor solvent and also the most convenient one, dioxan was next employed. In analogy with its behaviour

with acetic acid¹¹ it could be expected to attack the hydroxyl centre as represented below and render the C=O groups free, thereby causing the higher C=O frequency to brighten up.



No such changes in the C=O frequencies were noticed in the mixture. It may, therefore, be concluded that the chelate bonds are strong and hence remain unaffected by these solvent molecules. Herein lies a marked difference between these chelate bonds and the intermolecular type of hydrogen bonds which are susceptible to be broken up. But this statement should be strictly taken for the present to apply only to the salicylates since other chelate bonds have yet to be studied in detail.

At this stage another point may also be dealt with. The fact that the salicylates have lower C=O frequencies is also capable of being explained by the possibility of their existing as bimolecular associates as shown below:



But this is unacceptable for many reasons, *viz.*, (1) the molecular weights correspond to single molecules, (2) such large rings involving twelve atoms may not be expected to be stable and (3) even if present they should be capable of easy break down (just as other ring dimers) by solvents like phenol and dioxan, thus leading to the brightening up of the higher C=O frequency.

The Raman Spectrum of a mixture of methyl salicylate and acetic acid (1:1) was also taken. It showed that the 1670 cm^{-1} line of the acid and the 1679 cm^{-1} line of the ester had merged into one and a bright broad line resulted. Otherwise there was no change and the faint lines of the acid (1710 and 1745 cm^{-1}) and of the ester (1722 cm^{-1}) were unchanged. In our work relating to the study of mixtures of acetic acid with esters it was shown that the esters produce marked change owing to their capacity to act as anionoid solvents. They brighten up the weak lines and reduce the intensity of the bright line at 1670 cm^{-1} . The salicylates are obviously exceptional owing to the fact that the ester C=O is already locked up in

a stable chelate bond. Further, from this experiment it could also be concluded that the acetic acid molecules are incapable of being affected by the phenolic hydroxyl of this ester which also cannot function. Thus salicylates are not only unaffected by other solvents (donor or acceptor) but are incapable of affecting other susceptible liquids containing hydrogen bonds.

Summary

The Raman spectra of methyl, ethyl, *n*-butyl, iso-amyl and phenyl esters of salicylic acid have been studied. Besides the bright frequency attributable to the C=O group of the chelate structure, a weaker line corresponding to the unchelate molecule has been observed in each case. Thus the liquids contain the two types existing in equilibrium, the chelate molecules being predominant. The extent of the lowering of the C=O frequency brought about by chelation indicates that this type of intramolecular hydrogen bond is strong. This is also supported by the study of the mixtures of methyl and ethyl salicylates, with chloroform, phenol, dioxan and acetic acid. The spectra are unaffected showing that the chelate bond cannot be broken by anionoid and cationoid solvents and that salicylates cannot function as other esters and phenols do in breaking down hydrogen bonds.

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