

RAMAN EFFECT AND HYDROGEN BONDS

Part IX. Solutions of Salicylic Acid and Aspirin

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IN previous publications of this series¹ the Raman spectra of some typical carboxylic acids and their solutions in various solvents were described and the phenomenon of association through hydrogen bonds discussed. Acetic and propionic acids represent normal aliphatic acids, formic acid is exceptional and exhibits greater complexity, and benzoic and cinnamic acids form a third type. Salicylic acid has now been taken up for study as a further interesting case since in it should exist two opposing influences, (1) formation of intermolecular hydrogen bonds leading to association and (2) formation of intramolecular hydrogen bonds (chelation) hindering association.

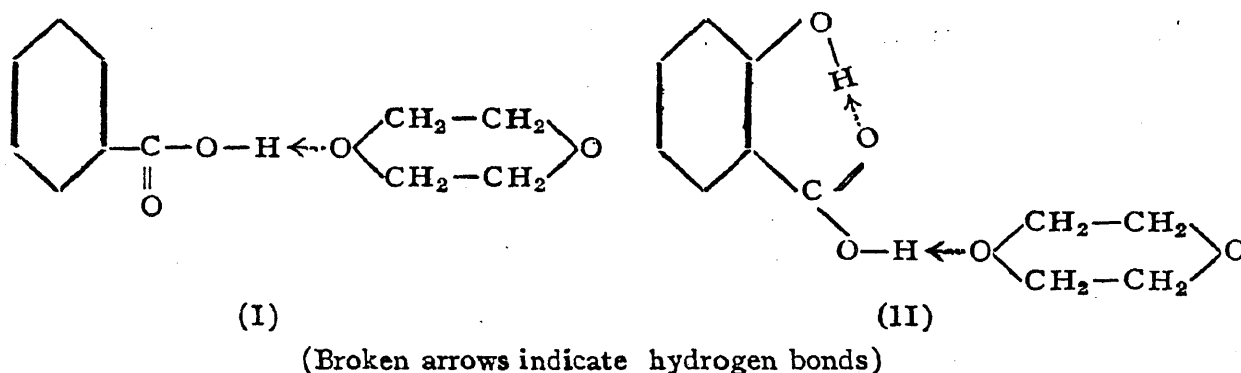
The Raman spectrum of salicylic acid does not seem to have been investigated completely before. The only reference to this substance relates to the low frequency Raman lines in the crystalline state by Venkateswaran.² The C=O frequencies have not so far been recorded. Since the present investigation deals mainly with these frequencies, Raman spectra of the solutions of the substance in dioxan and in benzene are now described. Due to the existence of fluorescence there was difficulty in recording the entire spectrum and hence the frequencies given below are not exhaustive. The picture obtained with the dioxan solution was bright and quite clear particularly in the C=O region.

Raman spectrum of salicylic acid in dioxan solution.—440 (1) 565 (5) 816 (3) 1036 (9) 1137 (1) 1156 (2) 1253 (10) 1328 (6) 1400 (1) 1465 (6) 1586 (2) 1670 (6).

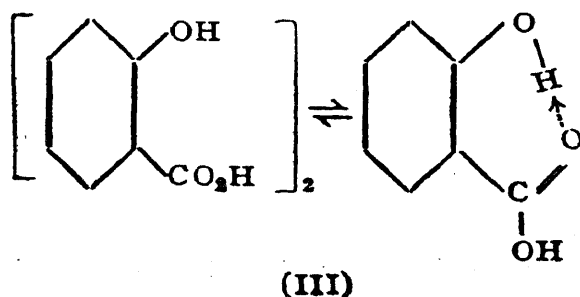
There is only one line in the C=O region and it is bright; the frequency corresponds to that of the bright C=O line of the esters of salicylic acid attributable to the chelate form. It could therefore be inferred that in dioxan solution salicylic acid has the chelate structure. Since it has already been shown in the case of benzoic acid that the dimers break down in

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dioxan solution into monomer solvent associates (formula I), a similar condition may be expected to prevail in regard to salicylic acid solution also, with the difference that chelation takes place in this acid due to the presence of the phenolic hydroxyl in the ortho position (formula II). It may be recalled here that dioxan does not disrupt the chelate ring form in the esters of salicylic acid.



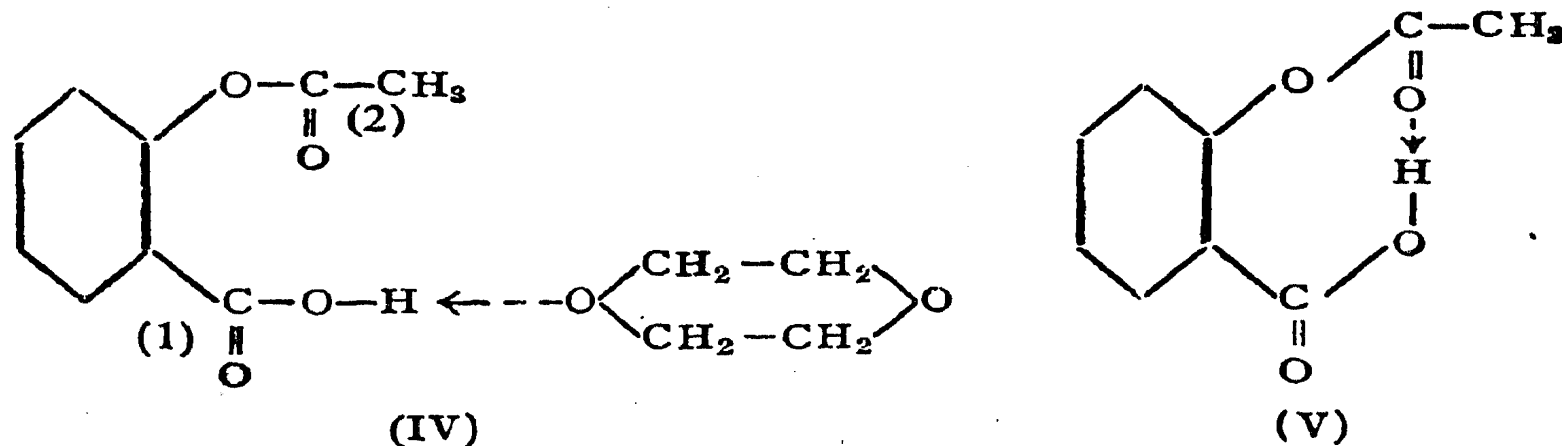
The spectrum of salicylic acid in benzene solution was not bright mainly due to low solubility at room temperature. But all the frequencies mentioned above could be found in it. There was however one marked difference; two $C=O$ frequencies were present, a feeble one at 1670 cm.^{-1} and a brighter one at 1700 cm.^{-1} . The state of the acid molecules in benzene solution therefore seems to be complex. The feeble line at 1670 cm.^{-1} could reasonably be attributed as before to chelate structures which are present to an appreciable extent. These most probably consist of the monomolecular form of the acid. Though molecular weight determinations in this solvent give values almost double that required for the ordinary formula, experiments carried out by Hendrixson³ on the partition of the acid between benzene and water indicate the existence of appreciable amounts of the monomeric form. In his partition experiments the effect of water present in the benzene solution may be expected to cause some discrepancy favouring the monomolecular form. However, the difference between benzoic acid and salicylic acid is quite marked even in these experiments. In the case of the latter the monomeric form is present in far greater amounts. This seems to be obviously due to the influence of the phenolic hydroxyl leading to increased stability of the monomers by chelation.



The brighter line at 1700 cm.^{-1} should then be attributed to the dimers of the acid. It is difficult to say at present what exact structure these have. The ring form similar to that of benzoic acid dimers seems to be precluded since such a structure may be expected to have a much lower $\text{C}=\text{O}$ frequency (about 1650 cm.^{-1} as in benzoic acid). Some type of open structure is therefore indicated.

More light could be expected to be thrown on this subject by a detailed study of salicylic acid in other solvents and also of some of its derivatives. This study could not at present be made due to dislocation caused by the global war now raging. However, the result obtained in a preliminary study of acetyl salicylic acid (aspirin) in dioxan solution may be here recorded since it is somewhat remarkable and interesting. The picture showed some continuous spectrum, but the $\text{C}=\text{O}$ region was clear. There was only one intense and broad line at 1726 cm.^{-1} . This corresponds to the $\text{C}=\text{O}$ frequency of ethyl benzoate (1720 cm.^{-1}) and the new faint line of salicylates attributable to the unchelated $\text{C}=\text{O}$ bonds. The dioxan solution of benzoic acid has also a $\text{C}=\text{O}$ line in this region.

In dioxan solution the monomeric form of aspirin could be expected to be produced just as in the case of benzoic acid and associated with the solvent by means of hydrogen bonds as represented by formula (IV). This contains two $\text{C}=\text{O}$ groups. The existence of $\text{C}=\text{O}$ (1) can account for the frequency at 1726 cm.^{-1} satisfactorily based on analogies quoted in the previous paragraph. But $\text{C}=\text{O}$ (2) corresponds to the carbonyl present in phenyl acetate and may be expected to give a strong line at about 1766 cm.^{-1} . This is definitely absent in the spectrum. Formula (IV) may not therefore represent the correct position, and it is possible that $\text{C}=\text{O}$ (2) is involved in hydrogen bond formation. A ring structure as in (V) appears to be more satisfactory; it involves the existence of a chelate hydrogen bond between the carbonyl of the acetate group and the hydrogen atom of the carboxyl group. This formulation not only locates the frequency of $\text{C}=\text{O}$ (1) at about 1726 cm.^{-1} but further suggests that the frequency of $\text{C}=\text{O}$ (2) should be lowered as the result of chelation by about 40 wave numbers to almost the same value as $\text{C}=\text{O}$ (1), namely 1726 cm.^{-1} . The observed line is rather broad and it may be due to the juxtaposition of the two $\text{C}=\text{O}$ lines merging into one. In support of this idea could be stated that $\text{C}=\text{O}$ (2) corresponds to the carbonyl group in phenyl esters and is a powerful donor and that the H atom of the carboxyl is a strong acceptor, and hence these could form intramolecular hydrogen bonds with facility. Further support could probably be obtained from a study of related compounds and derivatives which could not be undertaken now.



Summary

The Raman spectrum of salicylic acid has been studied for the first time in dioxan and benzene solutions. In the former monomolecular chelate structures associated with the solvent predominate; in the latter some chelate monomers exist, but the major portion consists of dimers whose structure is not quite clear. The spectrum of acetyl salicylic acid (aspirin) in dioxan seems to indicate that it has a chelate structure.

REFERENCES

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2. Venkateswaran .. *Ibid.*, **A**, 1939, **8**, 448.
3. Hendrixson .. *Zeit. Anorg. Chemie*, 1897, **13**, 73.