

635. The Crystal Structure of Potassium Hydrogen Bisphenylacetate.

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The infra-red absorption spectra of solid phenylacetic acid, potassium phenylacetate, and potassium hydrogen bisphenylacetate have been recorded between 650 and 3500 cm^{-1} . These spectra do not support the suggestion that a symmetrical hydrogen bridge occurs in the acid salt. The latter shows C—O frequencies which establish the presence in it of more or less normal carboxylic acid and carboxylate ion groups.

A RECENT X-ray investigation of the crystal structure of potassium hydrogen bisphenylacetate, $\text{KH}(\text{O}_2\text{C}\cdot\text{CH}_2\text{Ph})_2$ (Speakman, *J.*, 1949, 3357), has indicated that the structure consists of infinite layers of potassium ions and hydrogen atoms (or ions) situated between layers of phenylacetate residues, the carboxyl group of the residues being linked together from either side by the potassium ions and hydrogen atoms (or ions). Each hydrogen is situated between two oxygen atoms, thus forming a short hydrogen bridge.

Other X-ray studies of carboxylic acids in the crystalline form (Robertson and Woodward, *J.*, 1936, 1817; Brill, Hermann, and Peters, *Ann. Physik*, 1942, 42, 357; Dunitz and Robertson, *J.*, 1947, 142) indicated that the proton is nearer one of the oxygen atoms joined by a hydrogen bond than to the other; *i.e.*, the hydrogen is unsymmetrically placed. In potassium hydrogen bisphenylacetate it is reported that the hydrogen bridge is crystallographically symmetrical. This symmetry, it was indicated (*J.*, 1949, 3363), may be either statistical or the result of the hydrogen actually lying at the mid-point. The latter structure was thought to be possible as a resonance hybrid involving a number of valence-bond configurations. If this symmetrical H-location were correct a number of interesting points would emerge: in particular the covalent hydroxyl and carbonyl bonds which normally exist in the carboxylic acids would be considerably modified. It is to be expected then that, in the infra-red spectrum of the acid salt, the corresponding valence vibration frequencies would be displaced from their "normal" values. In order to verify these points the infra-red spectrum of potassium hydrogen bisphenylacetate has been studied. As an aid in the interpretation of the spectrum the spectra of phenylacetic acid and potassium phenylacetate were also recorded.

EXPERIMENTAL.

Materials.—Potassium hydrogen bisphenylacetate was prepared (Smith and Speakman, *Trans. Faraday Soc.*, 1948, 44, 1031) by dissolving an equivalent of the acid and half an equivalent of

(P = $\text{CH}_2\text{Ph}\cdot\text{CO}_2$).		Absorption frequencies in cm^{-1} .					
HP	3058 s	—	2710 m	2618 m	—	1710 s	—
KP	3049 s	2915 s	—	—	—	—	1600 s
KHP ₂	3042 s	2976 s	—	—	1946 w	1755 s	1570 s
Assignment	—	—	—	—	—	$\nu(\text{C}=\text{O})$	$\nu_*(\text{C}=\text{O})$
HP	1505 m	1458 m	1410 s	1295 s	1237 m	1195 m	1155 m
KP	1500 m	1460 m	1410 s	1290 s	—	1190 m	1158 s
KHP ₂	1500 m	1460 m	1375 s	1290 s	1245 s	1206 m	1155 s
Assignment	R	R	$\delta(\text{OH})$ or $\nu_*(\text{C}=\text{O})$	R	$\nu(\text{C}-\text{O})$	R	R
HP	1074 m	1030 m	985 w	965 m	—	927 s	906 s
KP	1073 s	1032 s	985 w	970 w	940 s	930 s	907 m
KHP ₂	1073 m	1036 m	985 w	965 w	945 m	925 m	—
Assignment	R	R	R	R	—	R	—
HP	893 s	—	840 m	755 s	—	701 s	680 m
KP	—	855 m	840 m	770 s	735 s	702 s	688 m
KHP ₂	890 s	860 s	841 s	763 m	728 m	695 w	—
Assignment	—	—	R	R	—	R	—



potassium hydroxide in hot alcohol. The acid salt crystallized out on cooling. It was recrystallized from alcohol and kept in a well-stoppered bottle.

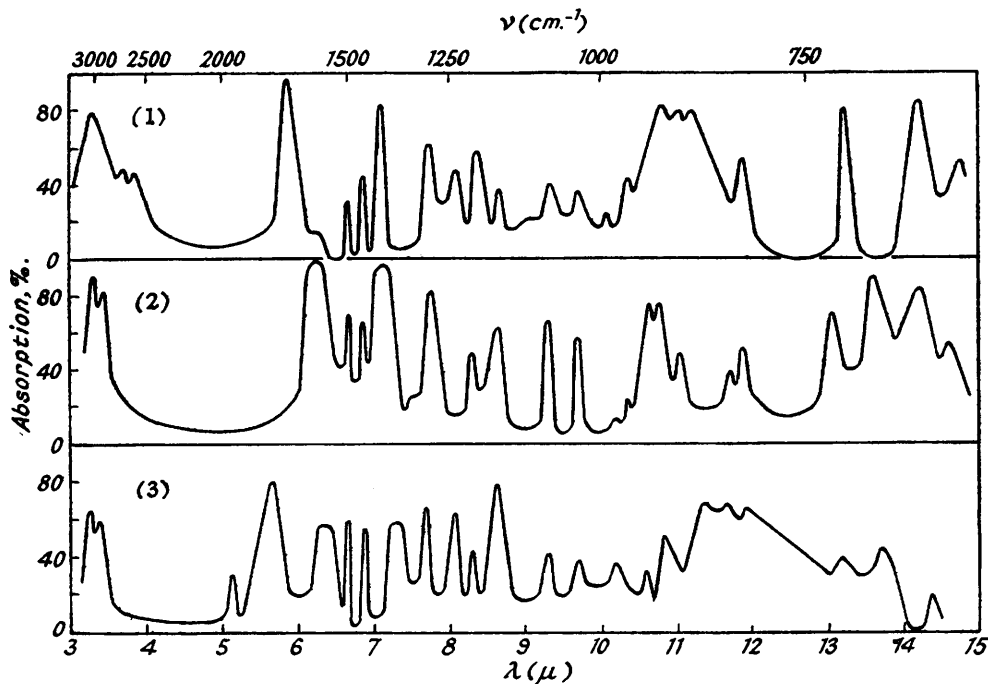
Potassium phenylacetate was prepared by the neutralization of a solution of phenylacetic acid with potassium carbonate. The salt was obtained by crystallization from 2 : 1 water-ethyl alcohol.

Apparatus and Technique.—A Grubb-Parsons S.3 spectrometer with rock-salt prism was used.

The crystalline specimens were melted as thin films between rock-salt plates. In order to check whether any breakdown of the double salt occurred on melting, samples were melted, allowed to resolidify, and remelted; no change in m. p. was detected. Intercomparison of the spectra confirmed that little, if any, decomposition of the acid salt resulted from this treatment.

The results obtained are given in the Table and Figure.

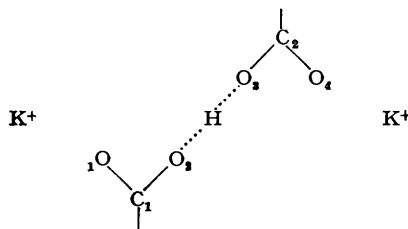
The infra-red absorption spectra of phenylacetic acid (1), potassium phenylacetate (2), and potassium hydrogen bisphenylacetate (3).



Examination of the Figure and Table shows that a large number of frequencies exists with the same or slightly altered values in the spectra of all the substances. These common frequencies are probably due to vibrations within the $C_6H_5-CH_2$ radical, since this is common to all the substances studied. These frequencies are labelled R in the Table. Similar values for these "hydrocarbon" frequencies are found in related structures (Bailey, Hales, Ingold, and Thompson, *J.*, 1936, 931; Angus, Ingold, and Leckie, *J.*, 1936, 925; Davies, *J. Chem. Physics*, 1948, **16**, 267).

DISCUSSION.

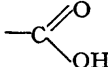
The carboxyl group structure in crystalline potassium bisphenylacetate may be represented as



where the bonds are shown diagrammatically. The hydrogen atom (or ion) is situated between two oxygen atoms that are some 2.55–2.65 Å apart (Speakman, *loc. cit.*). If the hydrogen

bridge is symmetrical then the O-H separation will be some 1.30 Å. This may be compared with the normal O-H bond length of 0.97 ± 0.01 Å. The increase in length of some 35% would be expected to modify the O-H bond vibrations considerably.

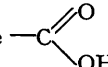
With a symmetrical hydrogen bridge groups $O_{(1)}C_{(1)}O_{(2)}$ and $O_{(3)}C_{(2)}O_{(4)}$ should have identical electronic structures. Effectively this would mean that only two different C-O bond distances would exist in the crystal structure. The values quoted for these lengths by Speakman, *viz.*, 1.18 and 1.24, each ± 0.05 Å, are lower than the values normally quoted for carboxylic acids (*loc. cit.*) and salts (Zachariassen, *J. Amer. Chem. Soc.*, 1940, **61**, 1011). In the spectrum of potassium bisphenylacetate we should expect to find, then, two frequencies only associated

with the symmetric and asymmetric stretching of the  group, and one associated with

the bending of the O-C-O angle.


The most striking feature in the Figure is that the spectrum of the bisphenylacetate is qualitatively almost an exact superposition of the spectra of potassium phenylacetate and phenylacetic acid. This may be taken as evidence that the bisphenylacetate is a complex of the other two. The strong absorption at 1710 cm^{-1} in the acid and at 1755 cm^{-1} in the bisphenylacetate is undoubtedly due to the carbonyl link which is, then, present in both structures. The frequency shift in the acid salt might indicate that the C=O bond length has been shortened. The shift and sharpness of the absorption in potassium bisphenylacetate suffice to show that the specimen of the latter contained negligible amounts of the free acid.

The value of this frequency is very close to that found for other carboxylic acids; the infrared evidence, therefore, indicates the presence of a normal acidic carbonyl group in the crystal of potassium bisphenylacetate. This view is strengthened by the appearance of a strong band at 1237 cm^{-1} in the acid and at 1245 cm^{-1} in the bisphenylacetate. This band is absent in potassium phenylacetate and is in all likelihood the band arising from the pseudo-symmetric

stretching of the  group, *i.e.*, $\nu(\text{C-O})$ (Thomas, *Discuss. Faraday Soc.*, 1951, **9**, 339).

In potassium phenylacetate there is a strong absorption band centred near 1600 cm^{-1} . This frequency is assigned to the asymmetric stretching of the ionized carboxyl group, *viz.*, $\nu_a(\text{C}^--\text{O})$, as its value is quite close to that found for similar strong absorptions in the salts of all carboxylic acids. Since this frequency is also present in potassium bisphenylacetate (1570 cm^{-1}), the inference is that the same type of group, *viz.*, an ionized carboxyl group is present in the acid salt. This interpretation is again supported by the presence of an equally strong broad band at 1410 cm^{-1} in potassium phenylacetate and at 1375 cm^{-1} in the bisphenylacetate. Sodium formate gives a strong band centred at 1370 cm^{-1} when the ionized carboxyl group stretches symmetrically (Thomas, *loc. cit.*) and similar bands are present in the absorption spectra of all carboxylate salts.

It may be pointed out here that the sharper absorption band which appears at 1410 cm^{-1} in phenylacetic acid arises from the bending of the O-H links in that crystal. This band decreases markedly in intensity on lowering the concentration of solutions of the acid in carbon tetrachloride. The absorption at 1363 cm^{-1} in carbon tetrachloride solutions of formic acid behaved similarly and was assigned the same deformation vibration in the associated carboxyl group (Thomas, *loc. cit.*). This band at 1410 cm^{-1} in phenylacetic acid should thus be absent in the spectra of potassium phenylacetate and bisphenylacetate; the broader bands found in this region for the salts have already been assigned to the symmetrical stretching of the

 group.

Thus, the important conclusion is established that potassium bisphenylacetate shows in the solid four frequencies arising from the stretching modes of the carboxyl group—*i.e.*, both those which are characteristic of the carboxyl group and those of the carboxylate ion.


In the region 680—950 cm^{-1} the position is less clear. Phenylacetic acid and the bisphenylacetate have strong absorptions at 893 and 890 cm^{-1} whilst potassium phenylacetate and bisphenylacetate have bands in common centred around 940, 850, and 730 cm^{-1} . No convincing explanation of these features is possible at present.

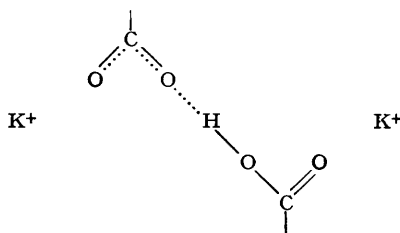
In the high-frequency region the spectrum of phenylacetic acid is appreciably different from that of the bisphenylacetate. The former shows a breadth of absorption typical of

associated carboxyl groups (Davies, *J. Chem. Physics*, 1940, **8**, 577); the latter shows sharp bands which arise from the C-H links (aromatic and aliphatic). It is not clear from the Figure where the O-H vibrational band is centred in potassium bisphenylacetate. A similar apparent disappearance of the O-H stretching frequency has been reported in a number of molecules showing intramolecular interaction (Buswell, Deitz, and Rodebush, *J. Chem. Physics*, 1937, **5**, 501, 726). In these cases where there is certainly no question of a symmetrical hydrogen bridge, it is caused by the overlapping with other (C-H) absorptions of the molecules. This is, of course, the most likely explanation in the present instance.

A band was found at 1946 cm^{-1} in potassium bisphenylacetate but not detected in phenylacetic acid or potassium phenylacetate. Randall *et al.* ("Infra-red Determination of Organic Structures," D. Van Nostrand Co. Inc., 1949) have, however, reported a band at 1969 cm^{-1} in phenylacetic acid and presumably this is to be identified with the bisphenylacetate band at 1946 cm^{-1} found during this work.

The infra-red absorption spectra of phenylacetic acid, potassium phenylacetate, and potassium bisphenylacetate indicate, then, the presence in the crystalline bisphenylacetate of

reasonably "normal" C=O, C-O, O-H, and  groupings. The crystal structure would then have the form :



Three different C-O bond lengths exist in this structure and the hydrogen bridge is not symmetrical. It may be emphasised that the X-ray analysis appears to be unable to distinguish between the C-O(H) and the C $\overline{\text{O}}$ (ion) bond lengths (cf. Davies and Thomas, *Discuss. Faraday Soc.*, 1951, **9**, 335; *Research*, in the press).

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