

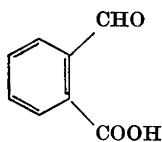
Structure of the *o*-Formylbenzoate Ion

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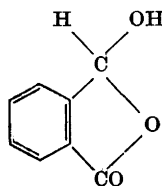
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Phthalaldehydic acid exists in aqueous solutions as 3-hydroxyphthalide. This formula has an asymmetric carbon atom, but the acid is not optically resolvable by means of alkaloid salts since its anion only exists in the open (*o*-formylbenzoate) form where no asymmetry occurs. Infra-red absorption shows that this is the case in solid salts as well as in aqueous solution.

Phthalaldehydic acid (*o*-formylbenzoic acid) has been represented as having both an aldehyde group and a carboxyl group (I), but also the ring-tautomeric hydroxyphthalide form (II) has been considered.



I



II

Grove and Willis² using infra-red absorption spectroscopy concluded that phthalaldehydic acid in the solid state existed exclusively in the cyclic lactol form (II). This was inferred from the single C=O absorption band at 1738 cm^{-1} , which is much closer to the five-ring lactone frequency of phthalide (1750 cm^{-1}) than to the aromatic carboxylic acid (1690 cm^{-1}) frequency of benzoic acid, and from the characteristic alcoholic OH absorption at 3250 cm^{-1} . Some years later Wheeler, Young and Erley³ reexamined phthalaldehydic acid and a long series of its functional derivatives. One of their main findings was that the cyclic lactol structure persisted also in aqueous solution. A water solution spectrum clearly indicated the presence of a lactol carbonyl absorption at 1748 cm^{-1} and the antisymmetric C—O—C stretch of the ring was observed at about 1090 cm^{-1} . Derivatives were prepared with alcohols, thiols, primary and secondary amines, acid amides, acid anhydrides, urea

and substituted ureas and carbamates. All of these substances existed in the solid state as phthalide derivatives. Esters of phthalaldehydic acid are of two types, normal and *pseudo*-esters (cyclic). These are readily distinguished by chemical methods, *e.g.*, the normal esters undergo a facile reaction with carbonyl reagents, a reaction which is absent in the *pseudo*-esters. Grove and Willis² investigated the infra-red absorption of the liquid normal methyl ester and the *pseudo*-ester (m.p. 46–47°) and could corroborate the chemical evidence.

From the cyclic formula (II) is seen that the carbon atom to which the hydroxyl group is linked is asymmetric. The question therefore arises whether a compound of this type is resolvable and in that case if the enantiomers have any degree of optical stability. Preliminary experiments were carried out where the strychnine and brucine salts of phthalaldehydic acid were subjected to fractional crystallisation. The salts were decomposed cautiously with mineral acid and the organic acid isolated, but in no case could any optical activity be observed. This negative result could have one or several causes. The active bases could have been ill-chosen if the diastereomers formed were of similar solubility, the acid itself or the *o*-formylbenzoate ion could have no optical stability, or the mentioned ion could exist entirely in the open non-cyclic form where the asymmetry of the carbon atom would disappear. To test the latter possibility solid state spectra of the strychnine and brucine salts were recorded. A main characteristic of these spectra was that no absorption band occurred between 1 700 and 1 800 cm^{-1} . This fact alone is decisive in ruling out a cyclic form of the *o*-formylbenzoate ion in the solid alkaloid salts. At 1 682 and 1 676 cm^{-1} strong carbonyl absorptions occurred, most likely due to the lactam grouping in strychnine and brucine, respectively. A shoulder on the latter absorption band at 1 690 cm^{-1} is probably due to the free aldehyde group in the *o*-formylbenzoate ion. Carboxylate ion absorption was observed at 1 575 and 1 555 cm^{-1} , but the other expected bands between 1 300 and 1 400 cm^{-1} could not be identified due to several skeletal vibrations in this region.

As a consequence of these observations it became desirable to investigate the infra-red absorption of aqueous solutions of phthalaldehydic acid at different pH (see Fig. 1).

In the spectrum of the free acid (A) is seen the ring carbonyl absorption at 1 756 cm^{-1} (Wheeler *et al.*³ reported, as mentioned before, the value 1 748 cm^{-1} . Evidently due to less accurate matching of their cell pair this band occurred only as a minor excrescence on a broad water-absorption band. From curve A it is evident that the matching in our case is very good. Further the spectrometer was calibrated in connection with this work and we therefore place more faith in the higher value). At 1 082 cm^{-1} is observed a band, which is due to the C—O—C antisymmetric stretch of the ring. In this region, however, the cell material (calcium fluoride) begins to absorb strongly and the sensitivity of the apparatus is therefore somewhat diminished. In the curve B where the acid is half-way neutralised with sodium hydroxide the ring carbonyl and C—O—C stretch frequencies are still observed, but in addition there has emerged two conspicuous bands at 1 565 and 1 392 cm^{-1} characteristic for the carboxylate ion. At about 1 695 cm^{-1} there is a smaller peak probably due to a free aldehyde group, but here the sensitivity of the spectrometer is

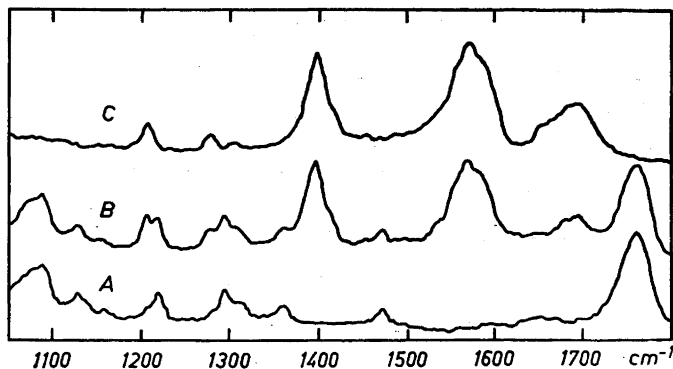


Fig. 1. Infra-red absorption in water of

- A: Phthalaldehydic acid
 B: Phthalaldehydic acid + half an equivalent of sodium hydroxide
 C: Fully neutralised phthalaldehydic acid.

diminished due to strong water absorption. The fully neutralised acid (C) shows no ring carbonyl or ring C—O—C stretch frequencies, while the carboxylate ion and aldehyde group bands are conspicuous. It must therefore be concluded that salts of phthalaldehydic acid in the solid state as well as in solution exist in the open form and hence no optical resolution of the acid can be effected through diastereomeric salts.

Phthalaldehydic acid undergoes the Cannizzaro reaction⁴, reduces ammoniacal silver solution and forms an oxime. This has been taken as an indication that phthalaldehydic acid has some of the properties which would be expected of the open form³. From the present experiments it is clear that the two former reactions deal with the non-cyclic *o*-formylbenzoate ion and throw therefore no light on the structure of the acid itself. Oxime formation can take place in alkaline solution as is by now to be expected (see exptl. part), but also under the slightly acid conditions obtained where phthalaldehydic acid and hydroxylamine hydrochloride are dissolved in water. This may mean that in aqueous solution the acid exists as an equilibrium between the open and the cyclic form, strongly displaced towards the cyclic form. Very small amounts of the open form cannot be detected in the spectra due to the slight solubility of phthalaldehydic acid in water. The solid-state spectrum of the oxime has been recorded and it clearly indicates an open form of the derivative *viz.* benzaldoxime-*o*-carboxylic acid. No ring carbonyl band is observed between 1700 and 1800 cm^{-1} and in the region 1000—1100 cm^{-1} only one minor band is found, the intensity being far too low for an antisymmetric C—O—C ring stretch band. Carboxyl C=O absorption is found at 1679 cm^{-1} , which is in the lower part of the region for aryl conjugated acids. There may exist a weak chelation between the carboxyl group and the oxime moiety, but at higher temperatures there must be stronger interaction as the oxime at 100° gradually loses water and is transformed into phthalimide probably through 2,3,1-benzoxaz-1-one and *o*-cyanobenzoic acid⁵.

EXPERIMENTAL

Phthalaldehydic acid was prepared by oxidation of naphthalene and recrystallised from water. M. p. 99°.

Strychnine and brucine salts. These salts were prepared in the usual way by heating an aqueous solution of phthalaldehydic acid with an equimolecular amount of the finely ground alkaloid until a clear solution remained. The salts which separated from the filtered solution on cooling were subjected to repeated fractional crystallisations from water.

Phthalaldehydic acid oxime. Phthalaldehydic acid (1.5 g) was dissolved in aqueous sodium carbonate and hydroxylamine hydrochloride (0.7 g) added. The solution was left for 2 h and acidified with hydrochloric acid whereupon the oxime separated immediately (1.4 g). Recrystallised from water. M. p. ca. 125° (rapid increase of temperature).

Infra-red spectra. The spectrometer was a Perkin-Elmer double beam apparatus (Model 21).

Solid compounds were first dried *in vacuo* over phosphorus pentoxide, and the spectra were obtained in Nujol mulls between rock-salt plates. Spectra of the aqueous solutions were obtained in a matched pair of calcium fluoride cells (0.025 mm) compensated with water.

The solutions whose infra-red absorption is recorded in Fig. 1 were made up as follows:

- A: 15 mg (0.1 mmole) phthalaldehydic acid per ml of water.
- B: 30 mg (0.2 mmole) acid and 4 mg sodium hydroxide (0.1 m equiv.) per ml of water.
- C: 15 mg (0.1 mmole) acid and 4 mg sodium hydroxide (0.1 m equiv.) per ml of water.

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