# *Infra-red Absorptions and Molecular Structures of Phenol, Phenolphthalein, Fluorescein, and Some Alkali Derivatives.*

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A study of the infra-red absorption spectra of phenol and the phenoxide ion has been combined with that of phenolphthalein, fluorescein, and alkali derivatives of these compounds with the aim of deciding between alternative structures suggested for these molecules and their derivatives. The results show that the "classical" representation for fluorescein is to be preferred and also provide definite indications as to the nature of the bivalent ions and alkali addition compounds of these phthaleins.

The present paper presents the infra-red absorption spectra of certain phthalein derivatives which have been examined with a view to deciding major uncertainties in their representations. Owing to the relative complexity of the molecules, the problem becomes one of identifying the infra-red absorption centres and, for this purpose, some of the absorptions of phenol and sodium phenoxide must be briefly considered. Between 650 cm.$^{-1}$ and 1500 cm.$^{-1}$ nearly 20 absorption peaks are found in dilute solutions of phenol—and thus all arise from monomeric molecules only (Davies, *J. Chem. Phys.*, 1948, **16**, 274). A number of sources [American Petroleum Institute Research Project 44, Catalog of Infra-red Spectral Data; Landolt–Börnstein, "Tabellen," 6th edn., Vol. 1, part 2 (1)] show that within this range absorptions characteristic of the phenyl ring in monosubstituted benzene derivatives in the solid or liquid state may appear (usually within 5 cm.$^{-1}$) at the following wave-numbers: 682, 740 (±10), 832, 901, 990, 1000, 1020, 1065, 1090 (±10), 1128, 1157, 1175, 1234, 1300, 1323, 1374, 1385, 1440, 1474, 1483 (±10), 1580. Corresponding to values in this sequence are absorptions in dilute phenol solutions at wave-numbers 689, 753, 827, (882), 993, 1020, 1064, 1101, 1163, (1314), 1382, 1471, (1497).

A total of 27 vibrational modes are associated with the phenyl group, and a further six will arise in phenol. The latter are the υ(O–H) and υ(C–O) stretching modes, the in-plane and out-of-plane angular oscillations of the hydrogen atom, *i.e.*, δ(O–H) and γ(O–H), and the similar angular oscillations of the hydroxyl group as a unit, *i.e.*, δ(C–O) and γ(C–O). The last two frequencies are expected to be close together if not, in practice, indistinguishable.

Of the marked absorptions in monomeric phenol not yet ascribed to the phenyl nucleus are those at 810, 1150, 1179, 1256, 1332, and 1342 cm.$^{-1}$. The identity of these absorptions is partly revealed by the spectrum of $C_6H_5{\cdot}OD$ in dilute solution (see Fig. 1). The 1332—1342 cm.$^{-1}$ doublet, though changed in relative intensity, is undisplaced on deuteration: the 1256 cm.$^{-1}$ centre moves to 1247 cm.$^{-1}$, and the 1150—1179 cm.$^{-1}$ absorptions virtually disappear, but are replaced by absorptions at 909 and 919 cm.$^{-1}$. This displacement identifies the absorptions as involving the hydroxyl group. That they correspond to both the in-plane and out-of-plane deformations is unlikely, as the out-of-plane mode is expected at a much lower frequency (*e.g.*, for methyl alcohol at 270 cm.$^{-1}$). Accordingly, they must be ascribed to δ(O–H) which appears, for some reason which is not understood, in two components. The 1256-cm.$^{-1}$ band can now, in conformity with previous suggestions (Kletz and Price, *J.*, 1947, 644), be confidently ascribed to the υ(C–O) mode. The displacement of 9 cm.$^{-1}$ on deuteration compares with that of 14 cm.$^{-1}$ calculated on the diatomic approximation in the model (C)–(OH).

The doublet at 1332—1342 cm.$^{-1}$ cannot be assigned with confidence. Although the 1340-cm.$^{-1}$ absorption in methyl alcohol has been described as δ(C–O), it has also been suggested that it at least involves some other mode, *i.e.*, as a combination tone, and Kuratani (*J. Chem. Soc. Japan*, 1952, **73**, 928) has described the 1280—1295 cm.$^{-1}$ doublet in pentachlorophenol as a vibration involving coupling between δ(O–H) and υ(C–O). This particular assignment is unlikely in the present instance owing to the constancy of the doublet on deuteration. That these frequencies are connected with the δ- and γ-(C–O) modes appears the least unsatisfactory suggestion when the behaviour on association is also considered (Davies, *loc. cit.*) : they might be the first overtones or combination tones of these angular deformation frequencies. The remaining phenol absorption, at 810 cm.$^{-1}$, is very probably one of the phenyl frequencies involving the out-of-plane deformation of the C–H aromatic bonds : its frequency varies with the substituents, and a strong band appears in fluorobenzene at 806 cm.$^{-1}$. It is of some importance that the phenyl absorption at 1163 cm.$^{-1}$ is present in both $C_6H_5{\cdot}OH$ and $C_6H_5{\cdot}OD$ : it appears in sodium phenoxide (solid), possibly accompanied by another vibration, as a strong doublet at 1156—1165 cm.$^{-1}$.

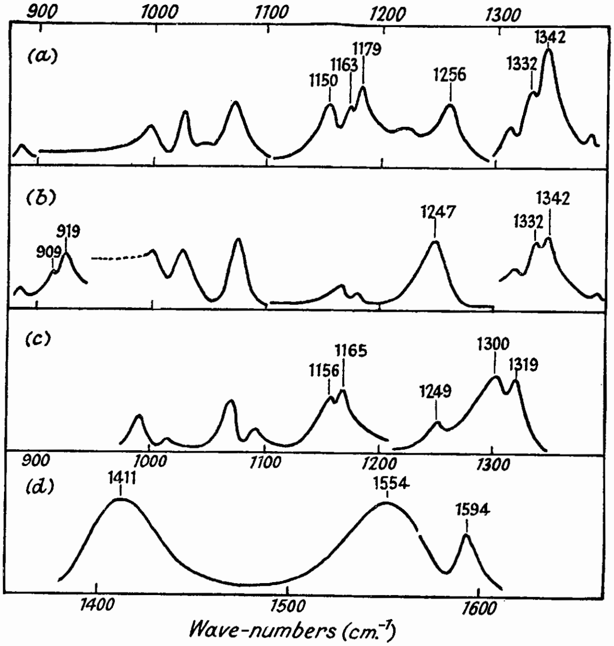


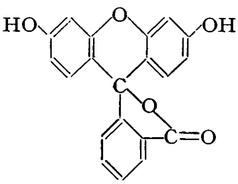
FIG. 1. *Infra-red absorption spectra of:* (a) *solutions of phenol in carbon tetrachloride;* (b) *solutions of deuterated phenol in carbon tetrachloride;* (c) *a solid film of sodium phenoxide;* (d) *a solid film of sodium benzoate.*

We have failed to find a record of the phenoxide ion absorptions. Comparison with phenol (Fig. 1) shows that the 1250-cm.$^{-1}$ absorption of the latter has become a very weak feature in the phenoxide : its presence is interpreted as due to traces of free phenol in most of the specimens. In its place an intense absorption having two incompletely resolved peaks at 1300 and 1319 cm.$^{-1}$ appears. At least one of the centres can be taken as the υ(C–$\bar{O}$) mode in the ion : the second, if really independent, may be the displaced 1337-cm.$^{-1}$ absorption of phenol. The only other marked difference from 650 cm.$^{-1}$ to 1800 cm.$^{-1}$ between phenol and phenoxide was the appearance of a broad absorption in the latter at 1435 cm.$^{-1}$, this being, it can safely be assumed (see above), a phenyl frequency.

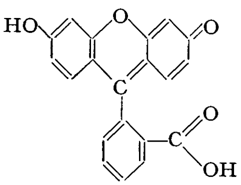
Sodium benzoate (Fig. 1) has been studied as a standard for aromatic carboxylate-ion features and because of the uncertainties in published partial records (Duval, Lecomte, and Douvillé, *Ann. Phys.*, 1942, **17**, 5; Lenormant, *Ann. Chim.*, 1950, **5**, 459). It may be noted that the two phenyl frequencies near 1160 cm.$^{-1}$ and 1480 cm.$^{-1}$ did not appear in our absorptions: the former is strong in benzoic acid and the latter is also missing for the dipotassium salt of phenolphthalein. However, the symmetric and antisymmetric carboxylate-ion frequencies are found in the benzoate at 1411 and 1554 cm.$^{-1}$: these values may be compared with 1418 and 1580 cm.$^{-1}$ in sodium acetate.

Coming now to the structures related to phenolphthalein, we can first consider the formulation of fluorescein itself. The classical formula for this is (I) but many modern organic texts (Karrer; Holleman; Richter; Finar; Fieser and Fieser) refer to this as unsatisfactory because, it is argued, such a formula does not account for the colour shown by fluorescein itself. Two of the frequently quoted alternatives described as more likely are shown as (II) and (III), containing quinonoid elements. In relation to (I), (II) is certainly a tautomer, but (III) can be regarded as a mesomeric structure; (II) is almost immediately eliminated from serious consideration by the absence from the solid of the characteristic intense associated carboxyl-group absorption extending from 3500 to 2500 cm.$^{-1}$: there is no reason why structure (II) should not show this strongly. For fluorescein the absorption gradually vanishes in this range at wave-numbers lower than 3100 cm.$^{-1}$, *i.e.*, there is little absorption beyond the aromatic CH centres. Again, both the associated carboxylic and the quinonoid carbonyl groups in (II) would absorb strongly near 1680 cm.$^{-1}$ (see, *e.g.*, Randall, Fowler, Fuson, and Dangl, "Infra-red Determination of Organic Structures," Van Nostrand Co. Inc., New York, 1949): the one centre recorded (Fig. 2) is, as expected for the lactone structure (I), near 1730 cm.$^{-1}$.

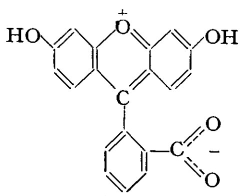
*Fluorescein.*



(I)

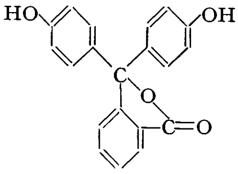


(II)



(III)

*Phenolphthalein.*



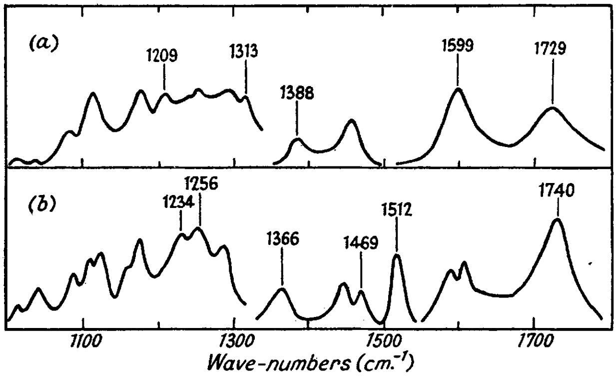
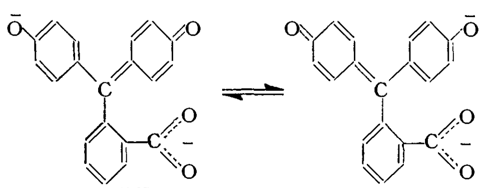


FIG. 2. *Infra-red absorption spectra of a solid film of:* (a) *fluorescein and* (b) *phenolphthalein.*

Likewise, the structure (III) is certainly not itself the correct representation of fluorescein, since the carboxylate-ion frequencies near 1560 and 1410 cm.$^{-1}$ are entirely lacking: in fact, it is difficult to account for the single 1729-cm.$^{-1}$ carbonyl absorption in fluorescein unless it be ascribed to a structure such as (I). Structure (III) is seen to involve the work of charge separation as between oxygen centres, and from our observations it is doubtful whether it contributes appreciably, even as a mesomer, to the actual state of the molecule. This very reduced, if not entirely eliminated, role of structure (III) is suggested by the close similarity throughout of the phenolphthalein and fluorescein absorptions —and particularly by the similarity in their carbonyl modes at 1740 and 1729 cm.$^{-1}$.

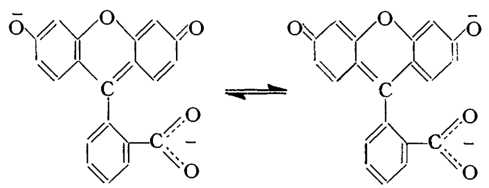
A comparison of these two spectra is instructive (Fig. 2). Apart from three or four absorptions which appear as doublets in phenolphthalein but are unresolved in fluorescein, there are perhaps only two significant differences between 950 cm.$^{-1}$ and 1800 cm.$^{-1}$ An absorption at 1209 cm.$^{-1}$ in fluorescein is probably related to the oxygen bridge : no such absorption is present in phenolphthalein, nor is it present in an appreciable number of related compounds, but it does appear with the oxygen bridge in the disodium salt of fluorescein. A frequency near 1200 cm.$^{-1}$ is, moreover, well established as characteristic of the ether linkage, C–O–C. A similar conclusion possibly applies to the 1313-cm.$^{-1}$ absorption of fluorescein, at least equally pronounced (1310—1319-cm.$^{-1}$ doublet?) in its disodium salt (Fig. 3) : the much greater uncertainty in this assignment arises from the appearance of absorptions at 1319 cm.$^{-1}$ in sodium phenoxide and (weakly) at 1314 and 1310 cm.$^{-1}$ in phenol and sodium benzoate. The apparent displacement from 1366 cm.$^{-1}$ in phenolphthalein to 1388 cm.$^{-1}$ in fluorescein probably corresponds to the appearance of different phenyl frequencies in these cases (see above). The only remaining difference is the non-appearance in our fluorescein records of the well-known 1510-cm.$^{-1}$ phenyl absorption.

*Dipotassium salt of phenolphthalein.*



(IV*a*) (IV*b*)

*Disodium salt of fluorescein (uranine).*



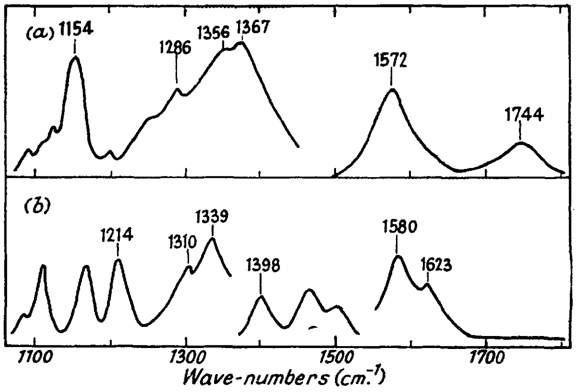


FIG. 3. *Infra-red absorption spectra of a solid film of:* (a) *the dipotassium salt of phenolphthalein,* (b) *the disodium salt of fluorescein (uranine).*

Of the derivatives of these structures which we have examined, the disodium and dipotassium salts of phenolphthalein have the ion which is the source of the pink indicator colour and has been ascribed an interesting resonating structure (IV*a* and IV*b*). Compared with phenolphthalein there are notable changes : many of the intense absorptions of the parent substance—*e.g.*, at wave-numbers 1234, 1256, 1470, and 1512—have disappeared. The 1256-cm.$^{-1}$ absorption of phenolphthalein is, of course, very probably the phenolic $\nu$(C–OH) mode in that structure. The 1470- and 1512-cm.$^{-1}$ absorptions are taken to be phenyl modes: they also disappeared in sodium benzoate. The new absorptions in the bivalent ion are the broad intense band at 1367 cm.$^{-1}$ with a shoulder at 1356 cm.$^{-1}$, and the carboxylate-ion absorption which has probably coalesced with the 1590-cm.$^{-1}$ phenyl absorption in giving a broad peak centred at 1572 cm.$^{-1}$. Certainly, no quinone frequency is observed near 1680 cm.$^{-1}$, nor is there any new absorption near 1300 cm.$^{-1}$ corresponding to the isolated $\nu$(C–$\bar{O}$) mode of a phenoxide ion. The mean of these individual frequencies is 1490 cm.$^{-1}$; for the carboxylate-ion frequencies (say 1554, 1411 cm.$^{-1}$) the mean is 1480 cm.$^{-1}$ As there is virtually no absorption between 1370 and 1570 cm.$^{-1}$ for the dialkali salt of phenolphthalein we can only assume that in-phase and out-of-phase modes of both pairs of oxygen-atom vibrations (phenoxide-quinonoid and carboxylate ion) have merged into the frequencies of 1367 and 1572 cm.$^{-1}$, whose mean is 1470 cm.$^{-1}$. This conclusion assumes that there is coupling between the distantly separated phenolic-quinonoid oxygen atoms of the bivalent anion. Although the carbonyl groups in an anhydride are coupled, yet in a study of related structures Flett (*J.*, 1948, 1441) has pointed out that they are not coupled in anthraquinones. That the electronic delocalisation in (IV) promotes this coupling is a possibility which requires further observations for practical confirmation.

The appearance in the dipotassium salt of phenolphthalein of an absorption of reduced intensity at 1740 cm.$^{-1}$ was taken to indicate the presence of a trace of phenolphthalein in our salts.

The disodium salt of fluorescein should likewise have two resonating oxygen systems and, for this derivative, the carbonyl frequency of the parent, at 1729 cm.$^{-1}$, disappeared entirely. The new absorptions are somewhat different in detail from those of the phenolphthalein salt (Fig. 3). It would seem that the carboxylate-ion frequencies may be placed as normally, near 1400 and 1580 cm.$^{-1}$, the other (phenoxode-quinonoid) pair at 1339 and 1623 cm.$^{-1}$. Unless one puts it at the unusually low value of 1623 cm.$^{-1}$, there is again no sign of a quinonoid absorption as such, but it is significant that in this case the second pair of frequencies above, *i.e.*, 1339—1623 cm.$^{-1}$, are more widely separated (and nearer the isolated group values) than in the phenolphthalein salt. In each case the frequencies are split about the expected value of approximately 1480 cm.$^{-1}$.

Two further derivatives of phenolphthalein have been examined, *viz.*, the white and the red monopotassium hydrated compounds described, amongst others, by Dehn (*J. Amer. Chem. Soc.*, 1932, **54**, 2949). Their compositions are given by him as: white salt, P,KOH,2$H_2O$; red salt, P,KOH,$H_2O$ (P = phenolphthalein molecule). These are described as additive compounds of phenolphthalein and the base, although Dehn also implies that in the red monohydrate the phenolphthalein is in a quinonoid form. Our preparations showed every appearance of being identical with Dehn's. The white potassium compound showed some few differences from the parent: absorptions at 1256 and 1366 cm.$^{-1}$ in the latter were replaced by peaks at 1215 and 1269 cm.$^{-1}$ and at 1355 and 1383 cm.$^{-1}$; and the 1512-cm.$^{-1}$ absorption in phenolphthalein disappeared—cf. sodium phenoxide and benzoate. The intensely red complex gave an absorption spectrum almost identical—even to relative intensities—with that of phenolphthalein. Thus it is concluded that both are essentially additive compounds and that the colour of the red complex, if characteristic of the material as a whole, requires some other explanation than a reference to possible quinonoid forms. In this case, as for fluorescein itself, it must be remembered that the colour of the solid might be due to traces of, *e.g.*, an ionic form, representing too small a proportion of the molecules to be detected in the infra-red. If this condition applied, the colours might well vary in intensity with treatment, such as the solvent from which the solid crystallised.

## EXPERIMENTAL

The spectrometer was the Grubb–Parsons single-beam S.3 instrument. At least duplicate specimens of the solid films were examined. These were prepared from solutions on thin NaCl and AgCl plates. In all cases when hydrolysis of the solid might occur some few units % excess of alkali were included in the preparation, and deposition and evaporation took place on a small controlled hot-plate in a vacuum desiccator. Some of the details of the spectra are summarised below: absorption centres, in cm.$^{-1}$; w. = weak; sh. = shoulder.

*Phenol.* Further details, for solutions see Davies (*loc. cit.*), for solid see Kletz and Price (*loc. cit.*).

*Sodium phenoxide.* 988, 1016(w), 1068, 1087(w), 1156, 1165, 1249, 1300, 1319, 1435, 1480, 1587.

*Sodium benzoate.* 1007(w), 1030, 1069, 1098(w), 1185(v.w), 1275(v.w), 1310, 1325, 1411, 1554, 1594.

*Phenolphthalein.* 1014(w), 1042, 1090, 1107, 1125, 1164(sh), 1173, 1234, 1256, 1291, 1366, 1444, 1469, 1512, 1595, 1606, 1740.

*Fluorescein.* 993, 1011(w), 1042(v.w), 1086, 1115, 1177, 1209, 1239(sh), 1251, 1285, 1313, 1388, 1459, 1599, 1729.

*Dipotassium salt of phenolphthalein.* 1089(w), 1115(sh), 1123, 1154, 1190, 1253, 1286, 1356(sh), 1367, 1572.

*Disodium salt of fluorescein* (*uranine*). 1092, 1112, 1172, 1214, 1310, 1339, 1398, 1469, 1505, 1580, 1623.

P,KOH,$H_2O$, *red.* 1016, 1050, 1092, 1108, 1124, 1170, 1253, 1290, 1378, 1450, 1468, 1513, 1594, 1604, 1746.

P,KOH,$2H_2O$, *white.* 998(w), 1054, 1105, 1127, 1163, 1215, 1235(sh. ?), 1269, 1292, 1355, 1383, 1449, 1466, 1581, 1594, 1730.

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