for comparison. The comparison is rendered easy since a complete normal vibrational analysis of cyclohexanone has recently been carried out by Fuhrer et al[5]. We have carried out a preliminary calculation of the normal vibrations of cyclohexanethione assuming the chair form and employing force constants similar to those of cyclohexanone[5]. A force constant 5.5 mdyn/Å for $\nu C = S$ seems to be satisfactory. The final assignments of the infrared bands in cyclohexanethione (I) are shown in Table 1, where, we have also denoted the normal vibrations in terms of group frequencies (GF) involving at least 66% of the potential energy associated with a single type of internal coordinate, zone frequency (ZF) and delocalized frequency (DF) following Fuhrer et al[5]. The assignments made in Table 1 establish clearly that the strong band at 1135 cm⁻¹ in the IR spectrum of cyclohexanethione is due to $\nu C = S$, the in-plane $C = S$ bending frequency being seen around 355 cm⁻¹.

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Infrared Spectra of Some Derivatives of Phenolphthalein & Sulphonphthalein

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The infrared absorption spectra of phenolphthalein, sulphonphthalein and some of their derivatives have been recorded in KBr matrix. The spectral patterns reveal that phenolphthalein and its derivatives exist mainly in the lactone form, while sulphonphthaleins display the quinone-like structure. This behaviour is attributed to the high tendency of sulphonphthalein to form the sulphonate ion and the phenolphthalein to attain the carboxylic structure.

A litrature survey reveals that no satisfactory treatment of the IR spectra of phenolphthalein, and sulphonphthalein has been published. apart from the work of Davis and Jones[1]. In the present study, the IR spectra of these compounds and some of their derivatives are recorded in KBr matrix, to throw some light on state of their molecules.

The compounds Ia-d and IIa-h were obtained from commercial sources (BDH and Schuchardt) and

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purified by repeated crystallisation from appropriate solvent.
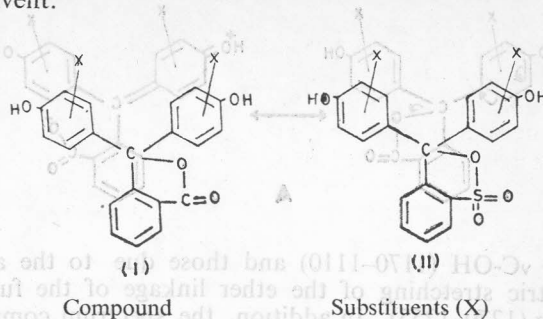
Compound	Substituents (X)
Phenolphthalein (Ia)	None
o-Cresolphthalein (Ib)	2,2'-dimethyl
Thymolphthalein (Ic)	3,3'-diisopropyl-6,6'-dimethyl
α-Naphtholphthalein (Id)	
Phenolsulphonphthalein (IIa)	None
Cresol red (IIb)	3,3'-dimethyl
Chlorophenol red (IIc)	3,3'-dichloro
Bromophenol red (IId)	3,3'-dibromo
Bromocresol green (IIe)	2,2'-dimethyl-3,3',5,5' tetrabromo
Bromocresol purple (IIf)	3,3'-dimethyl-5,5'-dibromo
Bromophenol blue (IIg)	3,3',5,5'-tetrabromo
Bromothymol blue (IIh)	2,2'-dimethyl-3,3'-dibromo-5,5'-diisopropyl

The band assignment (ν_{max} in cm⁻¹) is achieved by comparing the spectra of the compounds under investigation with those of other compounds having identical structure[2] and with those of substituted benzenes[3]; the treatment discussed by Looker[4] is considered.

The spectrum of Ia displays two bands for νOH at 3490–3410 and 3400–3240. The position of the bands is obviously influenced by the nature of the substituent. Since the substituents on both the aromatic rings containing phenolic OH are the same, the splitting of νOH band can only be ascribed to the difference in the energy states of the two rings. Thus, one ring would be involved in the mesomeric interaction with the phenolphthalein part of the molecule while the other would be isolated. The mesomeric interaction would lead to a lower charge density on the phenolic ring involved, hence a lower frequency for the OH-group would be observed. The variation of the energy of νOH is substantiated by the existence of two bands for the δOH and νC-OH.

The two bands in the region 1755–1720 can be ascribed to the $C = O$ group the high frequency value reveals that the $C = O$ group; is not of the carboxylic type but would be rather related to the ester type. This would be the case if the triphenylmethane carbon is bonded to the second oxygen atom forming the furan ring. The splitting of the carbonyl band reveals that the carbonyl group can have two energy states, one of the non-polarised form and the other of polarised one.

Since no band is observed in the region 1680–1620, which would correspond to the $C = O$ group of the quinone structure[2], the quinonoid form in the solid state is ruled out and the actual structures in the solid state would be the nonpolarised and polarised forms of the type (A).

In the 1500–1000 range the spectrum displays some intense bands corresponding to the in-plane deformation of the OH-group (1280–1240 or 1355),

A
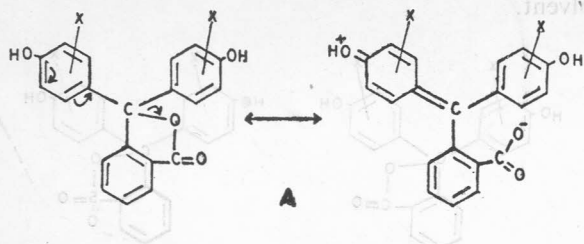
the νC-OH (1170–1110) and those due to the asymetric stretching of the ether linkage of the furan ring (1270–1255). In addition, the spectrum comprises the band due to the in-plane deformation of the aromatic >CH group. Compounds (Ib and Ic) display bands due to the asymmetric (1420–1415) and symmetric (1360–1340) deformation of the CH₃ groups.

The spectra of all compounds of series (I) display one intense band at 755–745 and a small band at 725–690, both of which are characteristic of the o-disubstituted phthalein ring. For Ia, the two bands at 845 and 805 characterise the p-disubstituted ring. For Ib the two bands at 835 and 805 correspond to the adjacent hydrogen atoms while the one isolated hydrogen in Ic and Id leads to the sharp medium bands at 905 and 900 respectively. Compound (Id) displays the bands characteristic of the naphthalene nucleus.

On the basis of the spectral pattern of sulphonphthalein and its derivatives, these can be subdivided into three categories : (A) compounds (IIa, IIc and IId), (B) compounds (IIb, IIe, IIf and IIg) and (C) compound (IIh) . The spectra of compounds of group (A) display a strong broad band in the region 3700–2500 due to νOH. The broad envelop and low frequency of the band reveals that the OH groups are either involved in a strong hydrogen bonding or a tautomeric shift. The vibration of the aromatic ring leads to the three bands near 1610, 1680 and 1560. The intensity of the band at 1630, 1640 or 1730 relative to the neighbouring ring vibrations increases in the order (IIa) < (IId) < (IIc), i.e. with increasing acceptor character of the substituent on the phenolic ring.

The spectra of compounds of group (B) are characterised by two bands for νOH, one of which is more or less sharp and appears at 3530, 3490, 3530 and 3540 in IIb, IIe, IIf and IIg respectively. In comparison to the intensity of the aromatic groups, the intensity of the band at 1650–1630 increases in the order (IIb) < (IIf) < (IIe) < (IIg), i.e. with increasing acceptor character of the substituents on the phenolic rings.

The spectrum of IIh displays two bands of strong intensity due to νOH ∼ 3510. The difference in the band position, being so small (∼40 cm⁻¹), it cannot be accounted for the hydrogen bonding. The aromatic C-H's appear as small peaks near 3090 and 3040 while the aliphatic groups lead to the bands at 2980, 2960 and 2990, This behaviour is analogus to the case of thymolphthalein (Ic).

In the 1500–1000 region, all the compounds (IIa-h) display more or less the same pattern. The main bands are those due to the $-SO_3H$ group (1330–

1290 and 1180–1130). These bands are of high intensity and broad, being more broadened with increased contribution of the quinonoid form to the total stretching. The OH group leads to two sets of bands at 1315–1290 and 1170–1125 due to the in-plane deformation and νC-OH. The bands tend to be more sharp as the donor character of the substituent on the phenolic ring increases. Below 1000 the important bands are those due to out-of-plane deformation of the aromatic rings which characterise the type of substitution. All the compounds display a medium to intense band at 765–745 and a weak band at 730–715 which can be assigned to the o-disubstituted sulphonphthalein ring. For the phenolic groups, compound (IIa) displays two bands near 840 and 760 due to the p-disubstituted rings. For IIb, IIc and IId, the two adjacent hydrogens lead to the bands in the rane 920–880. For compounds (IIe), (IIf), (IIg) and (IIh), the bands due to the isolated hydrogen atom appear in the range 900–880 having medium to low intensity. The bands due to the aromatic rings containing phenolic groups appear as two bands, similar to that observed in phenolphthalein.

The spectral behaviour in the 4000–1500 cm⁻¹ region can be explained on the basis that a tautomeric shift of the type (B) can exist in the molecule and

B
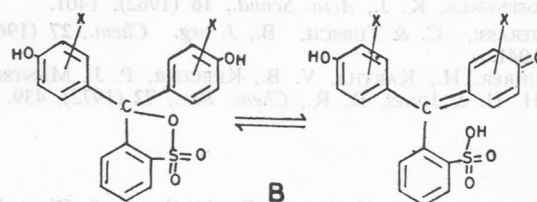
that this shift would be influenced by the charge density on the aromatic rings containing phenolic OH and the substituents. Donor substituents, which increase the charge density hinder the intramolecular charge migration from the OH group, hence lower the participation of the phenolic proton in the tautomeric shift. On the other hand, acceptor substituents decrease the charge density on the phenolic rings thereby favouring the charge migration from the OH group and in turn its contribution to the tautomeric shift increases.

On comparing the spectral behaviour of phenolphthaleins with that of sulphonphthaleins it becomes apparent that phenolphthaleins retain the lactone structure while the other compounds have a tendency to acquire a quinone-like structure with the destruction of the five-membered heterocyclic ring. This can be ascribed to the higher acceptor character of the sulphonphthalein due to its tendency to form the sulphonate ion as a result of higher electronegativity of the sulphur atom compared to the carbon atom.

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