

$\nu_{as}CS_2^-$ around 1210 and 1075 and $\nu_sCS_2^-$ bands around 980 and 920.

The diselenocarbamate ion (III) shows bands, around 1195, 1125, 950-1000 and 820-850. These bands can be readily ascribed to νCSe_2^- in the selenocarbamate ions. We have found similar bands in the morpholine derivative of III. Such constancy of the bands due to νCSe_2^- in the diselenocarbamates indicates less vibrational mixing as compared to dithiocarbamate ions. It is also interesting that νNCS_2^- are greater than these due to νOCS_2^- . The same appears to be true of the seleno analogues which show νNCS_2^- to be greater than those of νOCS_2^- .

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Normal Vibrations of Cyclohexanethione

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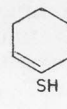
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Normal vibrations of cyclohexanethione, prepared by the method of Nomura and Takeuchi [*Bull. chem. Soc. Japan*, **33** (1960), 1743] are reported. The data show that it exists predominantly in the thione form (I).

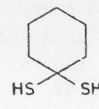
THE synthesis of cyclohexanethione (I) was first reported by Sen¹ who obtained it by passing hydrogen sulphide through a solution of cyclohexanone in concentrated hydrochloric acid. Nomura and Takeuchi² and Rosengren³ have more recently reported the preparation of (I) employing the enamine reaction and passing hydrogen sulphide through 1-morpholino-1-cyclohexene. It has been suggested that the tautomeric thiol form (II) becomes predominant as a function of time³. Djerassi and Tursch⁴



(I)



(II)



(III)

have, however, proposed that the compound obtained from the procedure of Nomura and Takeuchi² may predominantly be the dithiol (III).

As part of a programme of study of the vibrational spectra of thiocarbonyl compounds, we have synthesized cyclohexanethione by the procedure of Nomura and Takeuchi (palepink liquid, b.p. 77°/15mm) and recorded its infrared spectrum on a Perkin-Elmer model 580 spectrophotometer. The present study, besides providing the normal modes of the thione (I), shows that the compound prepared by the method of Nomura and Takeuchi, exists predominantly in the thione form.

In its IR spectrum, cyclohexanethione showed a very weak band due to $\nu S-H$ which could not account for more than 10% of the thiol form (II or/and III). The $\nu C=C$ which should be present in the monothiol (II) was seen in the spectrum only as a very weak inflexion around 1630 cm^{-1} . On the other hand, we could see an intense band around 1135 cm^{-1} ascribable to $\nu C=S$. We, therefore, feel that the thiol (II) or the dithiol (III) form would only be minor constituents. We have been able to analyze the IR spectrum on the basis of the thione form.

All the infrared bands of cyclohexanethione are listed in Table I along with those of the cyclohexanone

TABLE I — NORMAL VIBRATIONS (in cm^{-1}) OF CYCLOHEXANETHIONE

Symmetry	Cyclohexanone	THIONE ^(a)	
		Cyclohexanethione	Mode assigned
A''	2961 s		
	2940 s	2930 s	GF (C—H asym. stretch)
A''	2920 s		
	2894 s	2900 s	GF (C—H sym. stretch)
A''/A'	2867 s		
	2859 s	2850 s	GF (C—H sym. stretch)
A'	1718 s	—	GF (C=O stretch)
A'	1462 m	1460 m	GF (CH_2 scissor)
A'/A''	1449 s	1448 s	GF (CH_2 scissor)
A''	1429 s	1430 s	GF (CH_2 scissor)
A'	1346 s	1343 s	GF (CH_2 -bend)
A'	1338 s	1338 s	ZF
A'/A''	1311 s	1310 m	ZF
A''	1263 m	1270 m	ZF
A''/A'	1247 m	1250 m	ZF
A'	1220 s	1200 s	GF (CH_2 wag)
A'	—	1135 s	GF (C=S stretch)
A'	1117 s	1120 s	DF
A''	1072 w	1065 vw	ZF
A''	1049 m	1030 m	ZF
A'	1018 m	1015 s	DF
A'	990 w	930 vw	DF
A''	907	910 m	DF
A''	894 m	875 m	DF
A'	838 vw	810 m	DF
A'/A''	748 s	760 s	ZF
A'	652 m	565 m	DF
A''/A'	490 s	—	GF (C=O in-plane bend)
	—	355 m	GF (C=S in-plane bend)
A''	460 vw	455 w	DF

(a) Intensities; s : strong; m : medium; w : weak; vw : very weak.

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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 cyclohexanone⁵. A force constant 5.5 mdyne/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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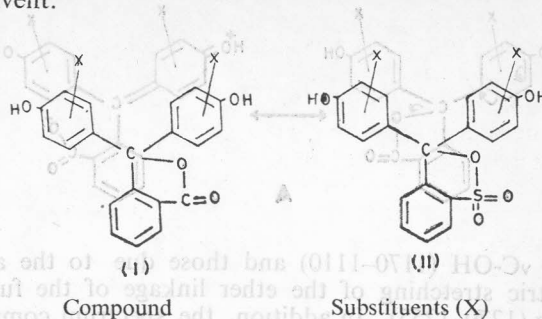
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The infrared absorption spectra of phenolphthalein, sulphonphthalein and some of their derivatives have been recorded in KBr matrix. The spectral patterns reveal that phenolphthalein and its derivatives exist mainly in the lactone form, while sulphonphthaleins 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 literature survey reveals that no satisfactory treatment of the IR spectra of phenolphthalein, and sulphonphthalein has been published, apart from the work of Davis and Jones¹. 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

purified by repeated crystallisation from appropriate solvent.



Compound	Substituents (X)
Phenolphthalein (Ia)	None
<i>o</i> -Cresolphthalein (Ib)	2,2'-dimethyl
Thymolphthalein (Ic)	3,3'-diisopropyl-6,6'-dimethyl
α -Naphtholphthalein (Id)	None
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 structure² and with those of substituted benzenes³; the treatment discussed by Looker⁴ is considered.

The spectrum of Ia displays two bands for ν_{OH} 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 ν_{OH} 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 ν_{OH} is substantiated by the existence of two bands for the δ_{OH} and $\nu_{\text{C-OH}}$.

The two bands in the region 1755–1720 cm^{-1} 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 structure², 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),

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