

### Infrared Spectra of Dithio- & Diseleno-carbamate Derivatives

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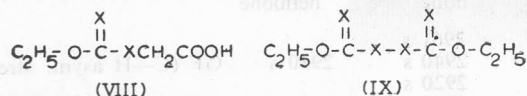
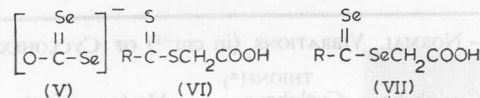
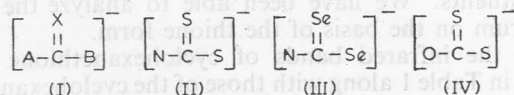
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Bands due to  $\nu$  NCS<sub>2</sub><sup>-</sup> and  $\nu$  NCSe<sub>2</sub><sup>-</sup> in dithio- and diseleno-carbamate ions respectively have been discussed in the light of the stretching modes in model thio- and seleno-carbonyl compounds.

A number of studies on the vibrational spectra of amide and thioamide derivatives including carbamates and thiocarbamates have been made<sup>1-3</sup>. As part of our studies on the normal vibrations of ions of the type (I).



where A is O, S or N and X and B are Group VIA elements, we have presently studied the IR spectra of dithiocarbamate (II) and diselenocarbamate (III) ions.

These ions would be expected to give characteristic stretching bands due to NCS<sub>2</sub><sup>-</sup> and NCSe<sub>2</sub><sup>-</sup> groups. In the case of II, the results of the normal vibrational analysis of N N-dimethyldithiocarbamate ion are available in literature<sup>4</sup>.

The IR spectra of the model compounds dithiocarbonate (IV) and diselenocarbonate (V) ions, have been investigated.

Here again, information on the normal vibrations of IV is available<sup>5</sup>. Furthermore, we have studied the IR spectra of covalent dithio-(VI)-and diseleno-(VII)-carbamates,

where R is a substituted amino group. The IR spectra of two other sets of covalent compounds, VIII and IX, containing C=S or C=Se groups have also been studied.

Potassium N, N-diethyldithiocarbamate was prepared by the standard procedure<sup>6</sup>. The corresponding seleno analogue was obtained using the same procedure, but using CSe<sub>2</sub> in the place of CS<sub>2</sub>. Diethylammonium N, N-diethyldithiocarbamate, piperidinium piperidine-1-carbodithionate; morpholinium morpholine-4-carbodithionate; pyrrolidinium pyrrolidine-1-carbodithionate, were all prepared by the reactions between the corresponding bases with ice cold solutions of CS<sub>2</sub> in petroleum ether. The seleno analogues were obtained by known procedures<sup>8,9</sup>. The carboxymethyldithiocarbamates were prepared by the literature procedures<sup>10</sup>. The carboxymethyl esters of ethylxanthogenic acid and corresponding bis compounds were also obtained by the literature procedures<sup>11</sup>. The corresponding seleno analogues were obtained by the standard methods<sup>9</sup>.

Infrared spectra were recorded in KBr on a Perkin Elmer 21 double beam spectrophotometer; IR  $\nu_{max}$  are expressed in cm<sup>-1</sup>. In the case of model compounds (VIII) and (IX) characteristic  $\nu$  C=S and  $\nu$  C=Se are seen respectively at 1045, 950 and 1030, 935. The dithiocarbamate derivatives (VI) show  $\nu$  C=S in the range 990-1008 [R=(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N, 992; (CH<sub>2</sub>)<sub>4</sub>N, 1008; (C<sub>5</sub>H<sub>10</sub>)N, 983; and O(CH<sub>2</sub>)<sub>4</sub>N, 995]. This stretching frequency is considerably lower than in VIII(X=S) and IX (X=S). The diselenocarbamate derivatives (VII) on the other hand, show  $\nu$  C=Se in the range 940-970 [R=(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N, 950; (CH<sub>2</sub>)<sub>4</sub>N, 970; (C<sub>5</sub>H<sub>10</sub>)N, 940; and O(CH<sub>2</sub>)<sub>4</sub>N, 955], which is close to the band positions shown by the model compounds (VIII) (X=Se) and (IX) (X=Se). This may be because  $\nu$  C=S modes in VI are involved in vibrational mixing with other modes like  $\nu$  C-N and so on. The  $\nu$  C=Se in diselenocarbamates is likely to be closer to a pure vibration in view of the constancy of the band position found by us. In all these model compounds,  $\nu$  C-S appears in the 700 region and the  $\nu$  C-Se, about 100 cm<sup>-1</sup> lower.

Infrared spectra of the model compound (IV) has been discussed elsewhere<sup>5</sup>. In this compound, there are bands at 1180 and 1110, with contribution from  $\nu_{as}$ CS<sub>2</sub><sup>-</sup>. Bands at 1045 and 944 have contribution from  $\nu_s$ CS<sub>2</sub><sup>-</sup>. We find bands due to corresponding  $\nu_{as}$ CSe<sub>2</sub><sup>-</sup> of V at 1150 and 1140, bands due to  $\nu_s$ CSe<sub>2</sub><sup>-</sup> are found around 1000 and 950. The lowering of the stretching frequencies in CSe<sub>2</sub><sup>-</sup> compared to CS<sub>2</sub><sup>-</sup> is as expected.

A comparison of the spectra of dithio- and diseleno-carbamate ions, (II) and (III) respectively where the substituent on the nitrogen is C<sub>2</sub>H<sub>5</sub> and the cation is K<sup>+</sup> or N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>H<sub>2</sub><sup>+</sup>, shows systematic shifts of some of the bands of thiocarbamate ions to lower frequencies. In the case of dithiocarbamate ion, the results of the normal vibrational analysis<sup>4</sup> show that  $\nu_{as}$ CS<sub>2</sub><sup>-</sup> contributes bands at 1257, 1049 and 966. The  $\nu_s$ CS<sub>2</sub><sup>-</sup> contributes to a band at 1134 and also to some of the bands below 600. The spectrum of the diethylammonium salt of II shows bands due to

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$\nu_{as}CS_2^-$  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  $\nu CSe_2^-$  in the selenocarbamate ions. We have found similar bands in the morpholine derivative of III. Such constancy of the bands due to  $\nu CSe_2^-$  in the diselenocarbamates indicates less vibrational mixing as compared to dithiocarbamate ions. It is also interesting that  $\nu NCS_2^-$  are greater than these due to  $\nu OCS_2^-$ . The same appears to be true of the seleno analogues which show  $\nu NCS_2^-$  to be greater than those of  $\nu OCS_2^-$ .

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Normal Vibrations of Cyclohexanethione

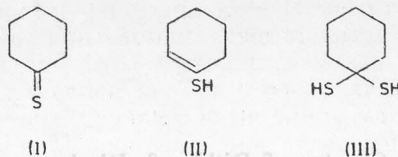
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Normal vibrations of cyclohexanethione, prepared by the method of Nomura and Takeuchi [*Bull. chem. Soc. Japan*, **33** (1960), 1743] are reported. The data show that it exists predominantly in the thione form (I).

THE synthesis of cyclohexanethione (I) was first reported by Sen<sup>1</sup> who obtained it by passing hydrogen sulphide through a solution of cyclohexanone in concentrated hydrochloric acid. Nomura and Takeuchi<sup>2</sup> and Rosengren<sup>3</sup> 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 time<sup>3</sup>. Djerassi and Tursch<sup>4</sup>



have, however, proposed that the compound obtained from the procedure of Nomura and Takeuchi<sup>2</sup> 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 <sup>(a)</sup>	
		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 <sub>2</sub> scissor)
A'/A''	1449 s	1448 s	GF (CH <sub>2</sub> scissor)
A''	1429 s	1430 s	GF (CH <sub>2</sub> scissor)
A'	1346 s	1343 s	GF (CH <sub>2</sub> —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 <sub>2</sub> 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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