

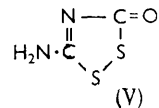
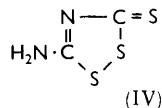
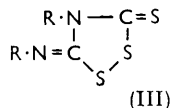
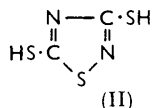
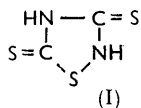
### 590. Infrared Spectra of Isoperthiocyanic Acid and Some Related Compounds.

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The infrared spectra of isoperthiocyanic acid,  $(\text{SCN})_2\text{H}_2\text{S}$ , and of the related compounds  $(\text{SCN})_2\cdot 2\text{HCl}$ ,  $(\text{SCN})_2\cdot 2\text{DCl}$ ,  $(\text{SCN})_2\cdot 2\text{HBr}$  and  $(\text{SCN})_2\cdot \text{H}_2\text{O}$  are reported. The results show that isoperthiocyanic acid in the crystalline state has structure (IV) and that in the other derivatives a  $\text{CCl}_2$ ,  $\text{CBr}_2$ , or  $\text{CO}$  group replaces the  $\text{CS}$  group of the parent compound.

THE structure of "isoperthiocyanic acid,"  $(\text{SCN})_2\text{H}_2\text{S}$ , has been discussed by several authors on the basis of chemical evidence<sup>1</sup> since its first isolation by Wöhler<sup>2</sup> as a product of the decomposition of a concentrated solution of thiocyanic acid.

Glutz<sup>3</sup> suggested structure (I) on chemical evidence. Klason<sup>4</sup> prepared the potassium salt of an isomer, called perthiocyanic acid, by treating the iso-acid with potassium hydroxide and also showed that the barium salt of perthiocyanic acid gave the iso-acid when treated with hydrochloric acid. Structure (II), suggested by him for perthiocyanic acid, will be discussed in the following paper. Freund,<sup>5</sup> studying the bromination of a series of alkyl isothiocyanates, isolated compounds of the type  $(\text{RNCS})_2\text{Br}_3$  which, on digestion with water or alcohol, gave compounds of the type  $(\text{RNCS})_2\text{S}$ , to which structure (III) was given. This type of ring was also postulated by Hantzsch and Wolfenkamp<sup>6</sup> for isoperthiocyanic acid. It is shown below, on the basis of infrared studies, that the same type of ring is present in the compounds  $(\text{SCN})_2\cdot 2\text{HCl}$ ,  $(\text{SCN})_2\cdot 2\text{HBr}$ , and  $(\text{SCN})_2\cdot \text{H}_2\text{O}$ , which were first prepared by Söderbäck,<sup>7</sup> but that this has the slightly different (tautomeric) formula (IV).



When we began to study the infrared spectra of these compounds Foss<sup>8</sup> had given a preliminary description of the crystallographic properties of isoperthiocyanic acid and of the compound  $(\text{SCN})_2\cdot \text{H}_2\text{O}$ , but no detailed structural study had been made. Hordvic<sup>9</sup> has recently published electron-density maps that show the presence of two adjacent sulphur atoms in each of these 5-membered rings, indicating a skeleton of the type (III) or (IV) for isoperthiocyanic acid, with  $\text{CO}$  replacing  $\text{CS}$  in the compound  $(\text{SCN})_2\cdot \text{H}_2\text{O}$  (V). Hordvic also considered that the  $X$ -ray work gave some indication that both hydrogen atoms in isoperthiocyanic acid might be present as an exocyclic  $\text{NH}_2$  group, as in (IV), which is a modification of the Freund-Hantzsch-Wolfenkamp formulation. The infrared evidence given below shows conclusively that the  $\text{NH}_2$  group is present, and the spectrum as a whole is consistent with all other features of this formula. The  $X$ -ray evidence on the above compounds being accepted, the infrared spectra also leave little doubt that

<sup>1</sup> Bambas, "The Chemistry of Heterocyclic Compounds," Interscience Publ., Inc., New York, 1952.

<sup>2</sup> Wöhler, *Ann. Phys.*, 1821, **69**, 273.

<sup>3</sup> Glutz, *Ber.*, 1870, **3**, 343.

<sup>4</sup> Klason, *J. prakt. Chem.*, 1888, **38**, 366.

<sup>5</sup> Freund, *Annalen*, 1895, **285**, 154.

<sup>6</sup> Hantzsch and Wolfenkamp, *Annalen*, 1904, **331**, 265.

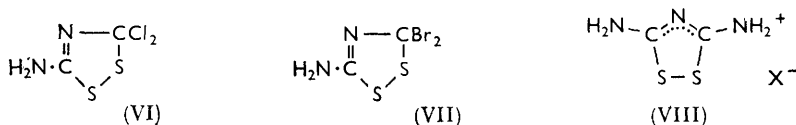
<sup>7</sup> Söderbäck, *Annalen*, 1919, **419**, 217.

<sup>8</sup> Foss, *Acta Chem. Scand.*, 1956, **10**, 871.

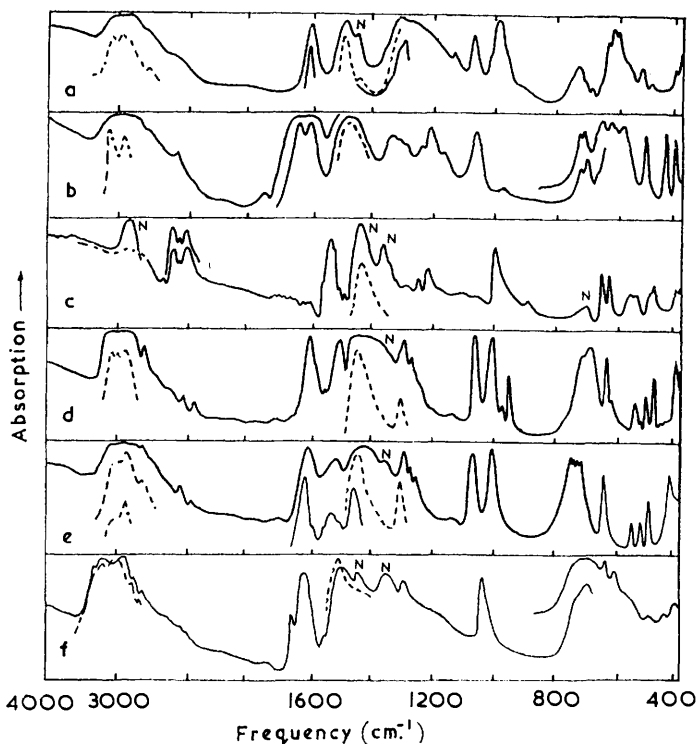
<sup>9</sup> Hordvic, *Acta Chem. Scand.*, 1960, **14**, 1218; 1961, **15**, 1186.

compounds  $(\text{SCN})_2 \cdot 2\text{HCl}$  and  $(\text{SCN})_2 \cdot 2\text{HBr}$  have formulæ (VI) and (VII), analogous to those proposed by Söderbäck, with  $\text{CCl}_2$  and  $\text{CBr}_2$  formally replacing the CS group.

The infrared spectra of isoperthiocyanic acid, and the compounds  $(\text{SCN})_2 \cdot \text{H}_2\text{O}$ ,  $(\text{SCN})_2 \cdot 2\text{HCl}$ , and  $(\text{SCN})_2 \cdot 2\text{HBr}$  are shown in the Figure. They have considerable resemblance as a family: in particular they all have: (1) broad absorption regions between



$3300$  and  $2900 \text{ cm}^{-1}$ , which must be attributed to N-H bonds, with two main absorption maxima and a long absorption tail with superimposed structure extending below  $2000 \text{ cm}^{-1}$ ; (2) a strong absorption band at  $1625$ — $1640 \text{ cm}^{-1}$ ; and (3) broad absorption bands between  $600$  and  $750 \text{ cm}^{-1}$ .



Infrared spectra of isoperthiocyanic acid and related compounds: (—) Nujol mulls; (---) hexachlorobutadiene mulls; (N) Nujol absorptions.

(a) iso- $(\text{SCN})_2 \cdot \text{H}_2\text{S}$ ; (b)  $(\text{SCN})_2 \cdot \text{H}_2\text{O}$ ; (c)  $(\text{SCN})_2 \cdot 2\text{DCl}$ ; (d)  $(\text{SCN})_2 \cdot 2\text{HBr}$ ; (e)  $(\text{SCN})_2 \cdot 2\text{HCl}$ ; (f) Thiuret,  $\text{HCl}$ .

Replacement of hydrogen atoms by deuterium in  $(\text{SCN})_2 \cdot 2\text{HCl}$  shows that all three of these absorption regions are shifted [to  $2300$ — $2150$  (a doublet), *ca.*  $1240$ , and *ca.*  $550 \text{ cm}^{-1}$ ] and that therefore they all originate in vibrations of NH bonds. Single NH bonds, as in disubstituted amine or imine ( $\text{C}=\text{NH}$ ) groups,<sup>10</sup> do not normally give other than weak

<sup>10</sup> Bellamy, "Infra red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958.

absorption in the 1500—1650  $\text{cm}^{-1}$  region but  $\text{NH}_2$  groups usually give strong absorption here. Amide and thioamide groups such as would occur in the Freund-Hantzsch-Wolfenkamp formulae for  $(\text{SCN})_2\text{H}_2\text{O}$  and  $(\text{SCN})_2\text{H}_2\text{S}$  (III) give strong absorption bands in the 1580—1510  $\text{cm}^{-1}$  region,<sup>11</sup> but these are not found above 1600  $\text{cm}^{-1}$  and, in any case, such groups cannot be present in compounds  $(\text{SCN})_2\text{2HCl}$  and  $(\text{SCN})_2\text{2HBr}$ . Thus the infrared spectra show that formula (IV) is correct rather than the earlier (III;  $\text{R} = \text{H}$ ) which has the same heavy atom skeleton. Although  $\text{NH}_2$  groups in organic amines usually have rather better defined and higher-frequency doublet absorption bands in the 3200  $\text{cm}^{-1}$  region caused by  $\nu(\text{NH})$  bond stretching vibrations,<sup>10</sup> hydrogen bonding in these crystalline materials, if stronger than usual, readily accounts for the spectra observed; somewhat analogous  $\text{NH}_2$  (and  $\text{ND}_2$ ) spectra have previously been found for crystalline aminopyrimidines.<sup>11</sup> The broad bands in the 600—750  $\text{cm}^{-1}$  region are assigned to  $\text{NH}_2$  wagging frequencies.

Thiuret hydrohalides, which are of related structure (VIII), have been characterised by X-ray diffraction.<sup>12</sup> The infrared spectrum of the chloride (VIII;  $\text{X} = \text{Cl}$ ) (cf. Figure) shows all the absorption features of the  $\text{NH}_2$  group described above [even to fine structure in the  $\nu(\text{NH})$  tail absorption between 2800 and 1800  $\text{cm}^{-1}$ ] and therefore strongly confirms the exocyclic  $\text{NH}_2$  group in the compounds discussed. The iodide has a similar spectrum, but the analogies with the spectra of isoperthiocyanic acid and the related compounds are less close owing to somewhat different frequencies of the  $\text{NH}_2$  absorption bands; apparently these groups are involved in weaker hydrogen bonding with the iodide ion.

Assignment of prominent absorption bands in the infrared spectra of isoperthiocyanic acid,  $(\text{SCN})_2\text{H}_2\text{S}$ , and related compounds.

Assignment *	$(\text{SCN})_2\text{2HCl}$	$(\text{SCN})_2\text{2DCI}$	$(\text{SCN})_2\text{2HBr}$	$(\text{SCN})_2\text{H}_2\text{O}$	iso- $(\text{SCN})_2\text{H}_2\text{S}$	Thiuret, $\text{HCl}^\dagger$
$\nu\text{NH}_2(\text{ND}_2)$ as.	3050	(2330)	3120	3265	3190	3210
$\nu\text{NH}_2(\text{ND}_2)$ s.	2900	(2150)	2950	3065	3030	3030
$\delta\text{NH}_2(\text{ND}_2)$	1636	(1238)	1625	1627	1630	1635
$\nu\text{C}=\text{O}$	—	—	—	1667	—	—
$\nu\text{C}=\text{N}$	1547	1557	1520	1515	1515	1515
$\nu\text{C}-\text{N}$ (coupled)	1465	1461	1470	(1515)	1310 ‡	—
$\nu\text{C}=\text{S}$	—	—	—	—	1006 ‡	—
$\text{NH}_2$ rocking	1080	?	1072	1077	1082	1043
$\text{NH}_2$ wagging	730	(555)	705	630	620	700

\*  $\nu$  denotes a bond-stretching vibration,  $\delta$  an angle-bending (scissors) vibration. † Formula (VIII). ‡ Coupled vibrations.

Detailed vibrational assignments for all the bands in these complex spectra will not be attempted but the annexed Table summarises the probable frequencies of the main group-characteristic vibrations, including the  $\text{C}=\text{N}$ ,  $\text{C}=\text{S}$ , and  $\text{C}=\text{O}$  bond stretching vibrations, the  $\text{NH}_2$  vibrations and another series of extremely strong absorption bands. This series is probably to be assigned to a mainly  $\text{C}-\text{N}$  vibration involving, to some extent, the  $\text{H}_2\text{N}\cdot\text{C}:\text{S}:\text{N}$  group as a whole. Complete lists of absorption bands are given in the Experimental section.

The multiple absorption peaks below 650  $\text{cm}^{-1}$  in most of the spectra are to be attributed to ring-skeleton vibrations involving the stretching of bonds containing the heavy sulphur atoms, or angle-bending vibrations. The only surprising, and therefore slightly unsatisfactory, point is that there appear to be no obvious bands for clear-cut assignment to  $\text{C}-\text{Cl}$  and  $\text{C}-\text{Br}$  bond-stretching vibrations, for most of the bands below 1000  $\text{cm}^{-1}$  seem little changed in frequency on passing from  $(\text{SCN})_2\text{2HCl}$  to  $(\text{SCN})_2\text{2HBr}$ . An exception is the band of medium strength at 961  $\text{cm}^{-1}$  in the spectrum of the bromide, whose chloro-counterpart may be masked in the 1015—1080  $\text{cm}^{-1}$  region, although 960

<sup>11</sup> Hadzi, J., 1957, 847; Mecke and Mecke, *Chem. Ber.*, 1956, **89**, 343; Angell, J., 1961, 504, and Ph.D. Thesis, Cambridge, 1956.

<sup>12</sup> Foss and Tjomsland, *Acta Chem. Scand.*, 1958, **12**, 1799.

cm.<sup>-1</sup> seems rather high for a C-Br frequency. The expected bands may alternatively occur below 400 cm.<sup>-1</sup> owing to strong coupling with other vibrations, as in the trifluoromethyl halides,<sup>13</sup> or they may be masked under the broad NH<sub>2</sub>-wagging absorption bands.

## EXPERIMENTAL

The compounds used were all prepared by recorded methods,<sup>2,14</sup> the deuterated compound (SCN)<sub>2</sub>,2DCI being made with deuterium chloride in place of hydrogen chloride. Spectra of the crystalline compounds, recorded for mulls in Nujol or hexachlorobutadiene by using a Perkin-Elmer model 21 spectrometer with sodium chloride and potassium bromide prisms, were as follows.

(SCN)<sub>2</sub>,2HCl. 3100—3000s, 2900s, 2700m, 2170w, 2030w, 1636s, 1552m, 1542m, 1465vs, 1315s, 1287m, 1265m, 1153vw, 1080s, 1015s, 988w, 752s, 740s, 725s, 710s, 646m, 552w, 520w, 496m, 422ms cm.<sup>-1</sup>.

(SCN)<sub>2</sub>,2DCI. 2330s, 2245m, 2150s, 1575w(sh), 1557s, 1545m, 1523w, 1510w, 1461vs(bd), 1315vw, 1267w, 1238m, 1013s, 920w, 655m, 630m, 566m(bd), 545m(bd), 495w(sh), 484m, 417m cm.<sup>-1</sup>.

(SCN)<sub>2</sub>,2HBr. 3120s, 3060m, 2950s, 2680mw, 2115w, 2040w, 1625s, 1520s, 1470vs, 1307m, 1282w, 1144vw, 1072s, 1015s, 982w, 961m, 717m(bd), 693s(bd), 644ms, 630w, 547w, 513w, 492m, 415ms cm.<sup>-1</sup>.

(SCN)<sub>2</sub>,H<sub>2</sub>O. 3265s, 3065s, 2680m, 2300w, 1667s, 1627s, 1515vs, 1362m, 1340m, 1314m, 1258w(sh), 1230ms, 1190w, 1077s, 748m, 731m, 660—675s(bd), 630—650s(bd), 603s(bd), 535ms, 445ms, 411ms cm.<sup>-1</sup>.

iso-(SCN)<sub>2</sub>,H<sub>2</sub>S. 3190s, 3030s, 2930ms(sh), 2680m, 2180vw, 2040vw, 1630s, 1515vs, 1430w, 1325s(sh), 1310vs, 1150w, 1082m, 1013s, 998s, 740m, 695w, 642m, 623s, 608s, 535m, 505w, 418w(sh), 406m cm.<sup>-1</sup>.

Thiuret,HCl. 3300ms, 3210s(bd), 3030vs(bd), 2825m, 2695m, 2130w, 1667m, 1635s, 1515s(bd), 1336s(bd), 1310s, 1043s, 750—662vs(bd), 635s, 603s, 573m, 500w(bd), 440w cm.<sup>-1</sup>.

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<sup>13</sup> Edgell and May, *J. Chem. Phys.*, 1954, **22**, 1808.

<sup>14</sup> Söderbäck, *Annalen*, 1928, **465**, 184.