483. *Organometallic and Organometalloidal Fluorine Compounds. Part IV.* Ultra-violet and Infra-red Spectra of Bistrifluoromethyl Sulphide, Bistrifluoromethyl Disulphide, and Related Compounds.*

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The ultra-violet and infra-red spectra of $(CF_3)_2S$ and $(CF_3)_2S_2$ are recorded, discussed, and compared with new data on the related compounds $(CH_3)_2S$, $(CH_3)_2S_2$, $(C_2H_5)_2S_2$, and $(n\text{-}C_4H_9)_2S_2$.

In Part III * the synthesis of bistrifluoromethyl disulphide and sulphide was described. The structures assigned are supported by the spectroscopic data now reported. The positions of the maxima in the ultra-violet spectra of bistrifluoromethyl disulphide and certain alkyl disulphides are compared in Table 1. These data show that the ultra-violet spectra of saturated aliphatic disulphides in solution are characterised by a broad maximum near 250 mμ (absent in saturated aliphatic sulphides) accompanied by high-intensity absorption at short wave-length. The position and intensity of the maximum at longer wave-length are not affected appreciably by change in dielectric constant of the solvent, whereas the short wave-length maximum decreases in intensity and moves to the red by *ca.* 4 mμ on change from ethanol to the less polar solvent light petroleum. The long wave-length maximum for dimethyl disulphide vapour is at the same position as in solution, but no short wave-length maximum is apparent down to 202 mμ; apparently a solvent is necessary to bring this maximum within the range of the instrument.

Table 1.

Compound	Solvent *	λ, max.	ε, max.	λ, min.	ε, min.
$(CF_3)_2S_2$	Vapour	235	290	212	110
$(CH_3)_2S_2$	Vapour	253	170	227	115
	Ethanol	254·5	340	229	205
		203	1850	—	—
	Petrol	255·5	350	228·5	195
		207	1200	—	—
$(C_2H_5)_2S_2$	Ethanol [1]	251·5	420	226	230
		202	2100	—	—
	Petrol	250	440	226	235
		206	1500	—	—
$(n\text{-}C_4H_9)_2S_2$	Ethanol	251·5	400	225	190
		204	2100	—	—
	Petrol	251·5	415	226	225
		207	1200	—	—
$(iso\text{-}C_5H_{11})_2S_2$	Ethanol [2]	251	390	230	280
*cyclo*Hexyl disulphide	Ethanol [2]	246	560	230	410
Polyethyleneformal disulphide	Dioxan [2]		Inflection 250, ε 710		
Cystine	Ethanol [3]	251			
Oxidised glutathione	Ethanol [4]	252			

[1] Ley and Arends, *Z. physikal. Chem.*, 1932, *B*, **15**, 311, report λ, max. 249 mμ, ε 430. [2] Koch, *J.*, 1949, 394. [3] Anslow and Foster, *J. Biol. Chem.*, 1932, **97**, 37. [4] Anslow and Lyman, *J. Opt. Soc. Amer.*, 1941, **31**, 114.

* Petrol = light petroleum, b. p. 68—70°, freed from olefinic impurities.

The peak near 250 mμ can be attributed to conjugation between unshared electrons on the sulphur atoms, and resonance forms may be postulated in which sulphur expands its valency shell to ten or more electrons. Bistrifluoromethyl disulphide vapour absorbs at appreciably lower wave-length than does dimethyl disulphide and a high-intensity absorption could not be detected down to 203 mμ. Clearly, the strongly electronegative CF_3 groups reduce considerably the conjugation between the non-bonding electrons on the sulphur atoms. It may be noted that the co-ordinating power of bistrifluoromethyl disulphide is much less than that of dimethyl disulphide, since the latter forms addition compounds with methyl iodide [$(CH_3)_3SI$; Hilditch and Smiles, *J.*, 1907, **91**, 1394] and with chlorine [$(CH_3)_2S_2Cl_2$; Rieche, *Annalen*, 1854, **92**, 353], whereas similar compounds from bistrifluoromethyl disulphide and methyl iodide, trifluoroiodomethane, or chlorine could not

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* Part III, *J.*, 1952, 2198.

be obtained. The perfluoroalkylamines and ethers (Haszeldine, *J.*, 1950, 1966; 1951, 102; *Research*, 1951, **4**, 338) similarly show greatly reduced basicity and absence of co-ordinating power.

The spectrum of bistrifluoromethyl sulphide vapour resembles the solution spectra of dimethyl sulphide. The low wave-length absorption of the fluoro-compound is much reduced in intensity relatively to that of the hydro-compound, however, The fine structure shown by dimethyl sulphide vapour (Table 2), and which is not shown by the fluoro-analogue, disappears when the alkyl sulphide is in solution, and a characteristic high-intensity absorption in the near ultra-violet accompanied by a low-intensity inflection at *ca.* 230 mμ becomes apparent (cf. Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84). As noted for the alkyl disulphides, a change in solvent from ethanol to light petroleum causes a marked shift to the red, accompanied by a decrease in intensity.

TABLE 2.

Solvent	λ, max.	ε, max.	λ, min.	ε, min.	Solvent	λ, max.	ε, max.	λ, min.	ε, min.
				Dimethyl sulphide.					
Vapour	228	630	227·5	285	Vapour	214·5	455	212·5	290
	226·5	300	226	230		203	2350	—	—
	224·5	395	223·5	335	Ethanol ...	207	960	—	—
	222·5	460	222	400		Inflection 230 mμ, ε 90			
	221·5	430	220·5	380	Petrol	214	620	—	—
	219·5	405	218·5	370		Inflection 231 mμ, ε 80			
	218	375	217	350					
				Bistrifluoromethyl sulphide.					
Vapour	210	6·85	—	—					

The infra-red spectrum of bistrifluoromethyl disulphide is shown in Fig. 1. The available spectroscopic data on compounds containing S–S and C–S bonds have been collected in Table 3.

TABLE 3.

Compound	S–S stretching vibration (μ)	C–S stretching vibration (μ)	Reference
Me_2S_2	19·3	14·5 [1]	Trotter and Thompson, *J.*, 1946, 481
Et_2S_2	19·6	—	,, ,, ,,
Pr_2S_2	—	15·9	Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429
n-Bu_2S_2	—	15·85	,, ,, ,,
tert.-Bu_2S_2	—	17·6	,, ,, ,,
$(C_6H_{11})_2S_2$	19·6	—	,, ,, ,,
Aromatic disulphides, thiosulphonates, sulphones, and sulphoxides	20·1—23·1	14·3—16·7	Cymerman and Willis, *J.*, 1951, 1332
Liquid sulphur	21·3 [2]	—	Venkateswaran (*Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 34)
S_2Cl_2	18·65 [2]	—	Feher and Baudler (*Z. Elektrochem.*, 1941, **47**, 844)
H_2S_2	19·6 [2]	—	,, ,, ,, ,,
Me_2S	—	14·4 [3]	Trotter and Thompson, *loc. cit.*
Et_2S	—	15·6	,, ,, ,,
Pr_2S	—	15·4	Trotter and Thompson, *loc. cit.*
Bu_2S	—	15·4	,, ,, ,,
MeSEt	—	15·3 [4]	Randall, Fowler, Fuson, and Dangl, " Infra-red Determination of Organic Structures," van Nostrand Co., New York, 1949, 203—207
Me·SBu^n	—	15·4 [4]	
Et·SBu^n	—	15·3 [4]	
Aliphatic thiols	—	14·3—16·65	Trotter and Thompson, *loc. cit.*

[1] Substantiated at 14·53 μ by our own work. [2] Raman data. [3] Confirmed at 14·6 μ by our own work. [4] Assignments made by the present authors from spectra recorded by Randall, Fowler, Fuson, and Dangl (*op. cit.*).

The data in Table 3 indicate that for *n*- and *sec.*-alkyl sulphides, disulphides, etc., the carbon–sulphur stretching frequency lies in the range 14·3—16·7 μ, and that in alkyl disulphides the sulphur–sulphur stretching vibration lies in the range 19·3—19·6 μ.

The bands at 7·69—9·56 μ in the infra-red spectrum of bistrifluoromethyl disulphide are due to carbon–fluorine stretching, with possible overtones and combination frequencies at 4·34 and 4·39 μ. These strong bands in the 8—9·5-μ region of the spectrum have been observed in a wide variety of fluorine compounds (Haszeldine, forthcoming communication), and in this instance are typical of compounds containing a CF_3 group.

The doublet at 13·12 and 13·18 μ is tentatively attributed to the carbon–sulphur stretching vibration (cf. CF_3Cl carbon–chlorine stretching vibration, below), and the band at 18·25 μ is believed to be caused by the sulphur–sulphur stretching vibration, although, like the 13·15-μ doublet, it might be caused by a CF_3 deformation frequency.

Thus, the introduction of fluorine into dimethyl disulphide causes a marked increase in the carbon–sulphur (690 to 759 cm.$^{-1}$) and the sulphur–sulphur (517 to 545 cm.$^{-1}$) stretching frequencies, which lie well outside the 600—700-cm.$^{-1}$ and 510—517-cm.$^{-1}$ ranges indicated above as " characteristic " for alkyl compounds. Again, if the 18·35 μ band has been assigned correctly, the fact that it is due to the S–S bond indicates that if there is restricted rotation about the S–S bond, then not all of the molecules of bistrifluoromethyl disulphide can be in the " *trans* " configuration (inset) which has a centre of symmetry. The low intensity of the S–S frequency has been attributed by Sheppard (*loc. cit.*) to the fact that the symmetrical vibration of this linkage involves little change in electric moment.

FIG. 1. *Bistrifluoromethyl disulphide. Vapour in* 50-*mm. cell.*

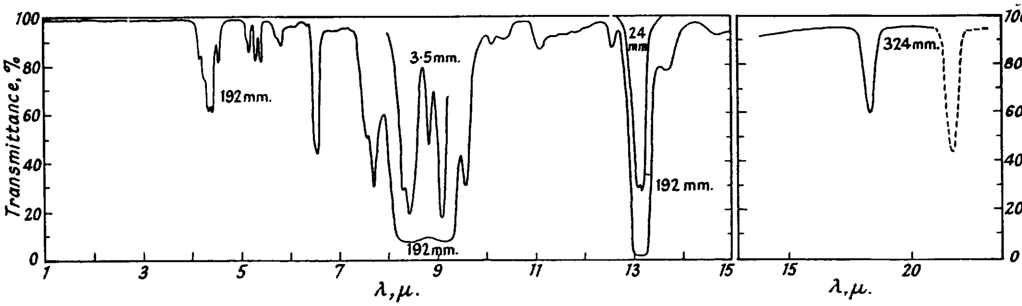
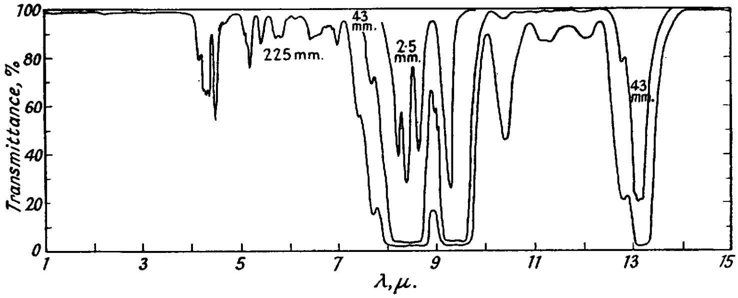
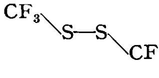


FIG. 2. *Bistrifluoromethyl sulphide. Vapour in* 50-*mm. cell.*





The infra-red spectrum of bistrifluoromethyl sulphide is shown in Fig. 2. The bands at 7·66—9·25 μ with weak overtone or combination bands at 4·27, 4·33, and 4·47 μ are again typical of the CF_3 groups. The doublet at 13·10 and 13·15 μ is assigned to the carbon–sulphur stretching frequency, and is in excellent agreement with the corresponding band in bistrifluoromethyl disulphide. The similarity of these C–S stretching frequencies indicates that the force constants have changed in a similar manner on introduction of fluorine. The absence of a band at 6·53 μ in the monosulphide indicates that this band in the disulphide is not an overtone of the carbon–sulphur stretching frequency.

The marked increase in the carbon–sulphur stretching frequency (690 to 760 cm.$^{-1}$) in bistrifluoromethyl disulphide and bistrifluoromethyl sulphide may be attributed to an increase in force constant. Trotter and Thompson (*loc. cit.*) and Sheppard (*loc. cit.*)

observed a decrease in the carbon–sulphur stretching frequency on passing from methyl to dialkyl to dibenzyl or diallyl type sulphides or disulphides, and Sheppard concludes that there is a qualitative decrease in force constant in compounds of the series methyl, primary alkyl, secondary alkyl, tertiary alkyl, allyl, benzyl. This decrease in carbon–sulphur bond strength is in agreement with the chemical properties of βγ-unsaturated sulphides, which, for example, undergo hydrogenolysis with nascent hydrogen (Farmer and Shipley, *J. Polymer Sci.*, 1946, **1**, 300) and are unstable to thermal or alkaline treatment (Hinsberg, *Ber.*, 1931, **64**, 2500). The increase in force constant suggested here for the increase in C–S stretching frequency of the trifluoromethyl sulphides would also be qualitatively in accord with their chemical properties. Both are extremely stable to heat and to attack by many reagents.

Sheppard (*loc. cit.*) pointed out that similar frequency and force-constant variations occur with C–S and C–Cl bonds, and showed the correspondence between the C–S and C–Cl stretching frequencies, *e.g.*, ν_{C-S} and ν_{C-Cl} for thiols and chlorides are : methyl, 702, 712; ethyl, 659, 655; *n*-propyl, 652, 651; *sec.*-propyl, 628, 612; *tert.*-butyl, 587, 570; allyl, 590, 594. A similar correspondence is found between the C–S stretching frequency of bistrifluoromethyl sulphide and disulphide (760 cm.$^{-1}$) and the carbon–chlorine stretching frequency in chlorotrifluoromethane (783 cm.$^{-1}$) and other perfluoroalkyl chlorides (Thompson and Temple, *J.*, 1948, 90, 1422; Haszeldine, unpublished).

Experimental.—Apparatus. The ultra-violet spectra were recorded by Beckman Model DU and Unicam Spectrophotometers. Sealed silica cells were used for vapours. Pressures were read to ±0·5 mm. and the molar extinction coefficient, ε, was calculated from the equation

$$\varepsilon = 760 \times 22{\cdot}4 \times DT/273\,lp$$

where D = optical density, T = temperature (°K), l = cell length (cm.), and p = pressure (mm.).

The infra-red spectra in the region 2—15 μ were taken by a Perkin-Elmer Model 21 Double Beam Instrument with sodium chloride optics, with cells of length *ca.* 50 mm. The spectrum of bistrifluoromethyl disulphide in the potassium bromide region of the spectrum was recorded on a Hilger double-beam instrument with potassium bromide optics; the authors thank Dr. N. Sheppard for recording the spectrum in this region, for valuable discussion, and for gifts of dimethyl and diethyl disulphides. Dimethyl sulphide was a redistilled commercial sample.

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