624. *The Raman Spectra of Bis(trifluoromethylthio)mercury and Derived Compounds.*

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The Raman spectra of bis(trifluoromethylthio)mercury, $Hg(S{\cdot}CF_3)_2$, in the molten state and in a variety of solvents have been recorded and analysed. The Raman effect has been used to compare the reactions in solution of this compound (*a*) with other mercuric salts, HgX_2 (where X = Cl, Br, I, or CN), and (*b*) with the corresponding tetramethylammonium or potassium salts, MX. Clear evidence has been obtained in (*a*) for the formation of derivatives of the type $CF_3{\cdot}S{\cdot}HgX$ in equilibrium with the reactants; the results from (*b*) are consistent with the formation of addition compounds of the type $M^+[Hg(S{\cdot}CF_3)_2X]^-$.

The properties of bis(trifluoromethylthio)mercury, $Hg(S{\cdot}CF_3)_2$, have recently been reported in some detail, but its Raman spectrum has not yet been published and the infrared spectrum has been incompletely described.[1,2] We have observed the Raman spectrum (over the range 100—1300 cm.$^{-1}$) of the mercury compound in the molten state, and also dissolved in benzene, carbon tetrachloride, ether, acetone, water, methanol and pyridine; in this paper the results are presented and interpreted. The complete infrared spectrum of the material is used, in conjunction with the Raman data, to make a partial frequency assignment. The molecule is presumably linear about the mercury atom and bent at each of the sulphur atoms, but since its symmetry is unknown, it is impossible to decide which of the 27 possible vibrational modes will be active in the infrared and Raman spectra. The observed spectra are incomplete and imperfectly resolved, so that any rigorous frequency assignment is out of the question; analysis has therefore been restricted to assignments to group frequencies rather than particular modes.

The Raman effect has been found particularly useful as a means of studying molecular species involved in labile chemical equilibria,[3] and we have applied this method to the study of the reaction of bis(trifluoromethylthio)mercury with mercuric chloride, bromide, iodide, and cyanide in solutions of methanol. The Raman spectrum of a particular mixture consists of a superposition of the spectra of the two pure compounds and, in addition, new lines not attributable to either of these; the new lines can be explained by the formation of the corresponding trifluoromethylthiomercuric halide in equilibrium with the reactants:

$$HgX_2 + Hg(S{\cdot}CF_3)_2 \rightleftharpoons 2CF_3{\cdot}S{\cdot}Hg{\cdot}X$$

Trifluoromethylthiomercuric chloride, which had been previously prepared and described,[2,4] was obtained by evaporating the solution and subliming the solid residue

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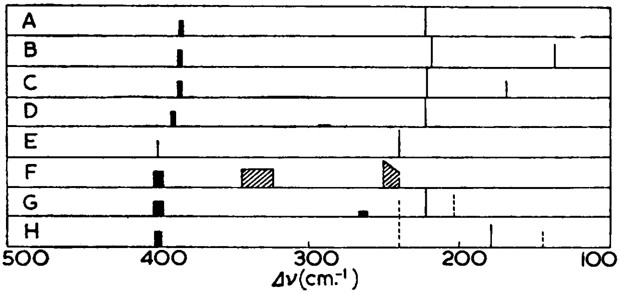
[1] Man, Coffman, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.
[2] Pugh, M.Sc. Thesis, Cambridge, 1959.
[3] Woodward, *Quart. Rev.*, 1956, **10**, 185; François and Delwaulle, *J. Chim. phys.*, 1949, **46**, 80.
[4] Haszeldine and Kidd, *J.*, 1953, 3219; 1955, 3871.

in a vacuum; attempts to isolate the corresponding bromide and iodide by similar methods led to recovery of the starting materials.

In direct contrast with such spectra are those of the products of reaction of bis(trifluoromethylthio)mercury with tetramethylammonium chloride, bromide, and iodide and with potassium cyanide. Earlier work has shown that bis(trifluoromethylthio)mercury reacts with tetramethylammonium chloride and iodide to give 1 : 1 adducts which have been formulated [5] as containing the complex anion $[Hg(S{\cdot}CF_3)_2X]^-$, where X is Cl or I. In the Raman spectra of acetone solutions of these compounds there is a marked lowering of the symmetrical Hg–S stretching frequency relative to the pure bis(trifluoromethylthio)-mercury, consistent with the formation of this anion. The formation of similar complexes between bis(trifluoromethylthio)mercury and tetramethylammonium bromide and potassium cyanide has been detected spectroscopically. An analogous frequency shift is found in the spectrum of a pyridine solution of the mercurial, in which complex-formation also takes place.[6] No unchanged bis(trifluoromethylthio)mercury was detected in such solutions, indicating that the complexes are not appreciably dissociated.

The experimental results may be summarised in the annexed line-diagram.

Raman spectra of bis(trifluoromethylthio)mercury and its derivatives.



Broken lines indicate scattering due to unchanged materials.

A, $Hg(S{\cdot}CF_3)_2$ *dissolved in pyridine.*
B, $NMe_4[Hg(S{\cdot}CF_3)_2I]$ *dissolved in acetone.*
C, $NMe_4[Hg(S{\cdot}CF_3)_2Br]$ *dissolved in acetone.*
D, $NMe_4[Hg(S{\cdot}CF_3)_2Cl]$ *dissolved in acetone.*
E, Pure $Hg(S{\cdot}CF_3)_2$ *dissolved in acetone or methanol.*
F, $Hg(S{\cdot}CF_3)_2 + HgCl_2$ (1 : 1) *dissolved in methanol.*
G, $Hg(S{\cdot}CF_3)_2 + HgBr_2$ (1 : 1) *dissolved in methanol.*
H, $Hg(S{\cdot}CF_3)_2 + HgI_2$ *dissolved in methanol.*

RESULTS

A. *Vibrational Spectra of Bis(trifluoromethylthio)mercury.*—The observed frequencies of the infrared and Raman spectra of the pure compound are set out in Table 1, with the probable vibrational assignments and corresponding values for other trifluoromethyl compounds (where available).

There are numerous coincidences between the frequencies, but most of the skeletal modes are to be expected at frequencies well below the infrared range studied, so that there is no definite evidence in favour of a particular molecular symmetry. In most cases, assignments have been made by analogy, or with the help of the polarisation data. The intense and complex band in the infrared spectrum at 1080—1220 cm.$^{-1}$ must include all the C–F bond-stretching vibrations, and there is a corresponding broad but weak band in the Raman spectrum in this region; the comparatively feeble scattering is in keeping with the observed results [7] for CF_3Cl and is to be attributed to the low derived polarisability of the C–F bond. The band of medium intensity close to 750 cm.$^{-1}$ found in both spectra is a characteristic feature of the infrared

[5] Jellinek and Lagowski, *J.*, 1960, 810.
[6] Downs, unpublished work.
[7] Plyler and Benedict, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 2245; Edgell and May, *J. Chem. Phys.*, 1954, **22**, 1808.

spectra of trifluoromethylthio-compounds[8] and is due to a coupled vibration involving both of the in-phase symmetrical CF_3 deformation and C–S stretching modes. On this basis the weak infrared band at 686 cm.$^{-1}$, with a very feeble Raman counterpart at 700 cm.$^{-1}$, has been assigned to the out-of-phase symmetrical CF_3 deformation. A similar pair of frequencies with almost the same separation is observed at 402 cm.$^{-1}$ (appearing as a relatively intense Raman line) and 467 cm.$^{-1}$ (a fairly weak band in both spectra). The stronger of these is complementary to the band near 750 cm.$^{-1}$, while the weaker is explained as arising from the out-of-phase C–S stretching vibration.

The line at 467 cm.$^{-1}$ is depolarised, and that at 402 cm.$^{-1}$ is polarised, in agreement with these assignments. There may be an infrared analogue to the strong Raman line at 400 cm.$^{-1}$, but it is so close to the limit of the range of the potassium bromide prism that no definite conclusion can be reached. The asymmetric CF_3 deformation, which has a frequency of 550—560 cm.$^{-1}$ in a wide range of trifluoromethyl compounds,[8] accounts for the weak infrared doublet

TABLE 1. *Infrared and Raman spectra of bis(trifluoromethylthio)mercury.*

Infrared (solid)		Raman (liquid)			
ν (cm.$^{-1}$)	Intensity, etc.	$\Delta\nu$ (cm.$^{-1}$)	Intensity, etc.	Assignment	Analogy
3650	w			3 × 1217	
2935	w			2 × 1123 + 686	
2860	w			2 × 1083 + 686	
2780	w sh			2 × (1103 or 1123) + 550	
2230	w br			2 × (1103 or 1123)	2210 in $(CF_3{\cdot}S)_2$
1453	w			1217 + 243	
1407	w			2 × ~700	
1369	w			1123 + 243	
1309	m			751 + 550	1300 in $(CF_3{\cdot}S)_2$
1217 1123 1103 1083	m sh vs vs vs	1140 to 1100	vw br	ν CF (sym. and asym.)	1208 1133 1109 1095 in $(CF_3{\cdot}S)_2$
923	w sh			2 × 467	
751	m	755	m pol	δ CF_3 (sym., in-phase) (ν CS in-phase)	755 in $(CF_3{\cdot}S)_2$
686	w	~700	w br	δ CF_3 (sym., out-of-phase) (ν CS, out-of-phase)	
550 542	w	~550	w br	δ CF_3 (asym.)	540 in $(CF_3{\cdot}S)_2$
467	w	465	w depol?	ν CS (out-of-phase) [δ CF_3 (sym., out-of-phase)]	468 in $CF_3{\cdot}SCl$
400?	?	402	s pol	ν CS (in-phase) [δ CF_3 (sym., in-phase)]	
		343	w	CF_3 rock	356 in CF_3Cl
		243	vs pol	ν HgS (in-phase)	

Intensities, etc.: w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad; pol = polarised, depol = depolarised.

The terms " in-phase " and " out-of-phase " have been used to describe vibrations which are symmetric or antisymmetric with respect to the molecule as a whole, in order to avoid confusion with the symmetry of the vibrations within the CF_3-groups.

TABLE 2. *Strong lines in the Raman spectrum of bis(trifluoromethylthio)mercury in various solvents.*

	Frequencies (±2 cm.$^{-1}$)						
Vibration	CCl_4	C_6H_6	Acetone	Ether	MeOH	H_2O	Pyridine
δ CF_3 (sym., in-phase) [ν C–S (in-phase)]	755	755	~750	755	756	~760	755
ν C–S (in-phase) [δ CF_3 (sym., in-phase)]	402	401	400	399	400	400	383
ν Hg–S (in-phase)	243	243	241	240	240	239	223

and broad Raman band at about 550 cm.$^{-1}$. Similarly, the CF_3 rocking frequency of 356 cm.$^{-1}$ in CF_3Cl[7] suggests that the weak Raman line at 343 cm.$^{-1}$ is to be ascribed to this type of vibration. The very intense and polarised Raman line at 243 cm.$^{-1}$ is clearly to be assigned to

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[8] Nabi and Sheppard, *J.*, 1959, 3439.

the in-phase Hg–S stretching mode; in subsequent work, the presence of unchanged bis(trifluoromethylthio)mercury was determined by the scattering at this particular frequency. No line corresponding to the out-of-phase Hg–S stretching vibration could be detected; the pseudo-linear nature of the molecule may lead to its being very weak, if not actually forbidden, in the Raman spectrum. Possible skeletal bending and torsional frequencies are expected to be low and no Raman lines likely to be associated with these modes could be observed. The weak bands remaining in the infrared spectrum are interpreted as combinations of the fundamentals.

The frequencies of the three strongest Raman bands for a series of solutions of bis(trifluoromethylthio)mercury are listed in Table 2. The position of the bands is unaffected by the concentration for solutions up to 3M. The frequency of the Hg–S stretching vibration decreases on passing from inert solvents, such as carbon tetrachloride, to oxygen-containing donor solvents, such as methanol. This change is small but may be significant in view of the tendency of the mercurial to form adducts with donor molecules; [1] the effect is very much smaller than that observed with mercuric chloride, for which the frequency shifts have been related to the influence of solvation.[9] There is a large frequency change when pyridine is used as a solvent, in which complex-formation undoubtedly takes place.[6]

B. *Equilibria with Mercuric Salts.*—In solutions containing the mercurial and a mercuric halide or cyanide, the in-phase skeletal frequencies of the mercurial and mercuric salt, ν_{Hg-S} and ν_{Hg-X}, are usually accompanied in the Raman spectrum of the mixture by two new lines, ν^1_{Hg-S} and ν^1_{Hg-X}, both at rather higher frequencies than ν_{Hg-S} and ν_{Hg-X} respectively; under some conditions, the pairs may merge to give two broad bands which cannot easily be resolved. The position of the new lines does not depend upon the relative proportions of reactants, and the ratio of intensities of ν^1_{Hg-S} to ν^1_{Hg-X} is also the same for all proportions, but the relative intensities of ν_{Hg-S} to ν^1_{Hg-S} and of ν_{Hg-X} to ν^1_{Hg-X} depend upon the molar proportions of the reactants. Excess of mercuric halide causes ν_{Hg-S} to disappear, whereas excess of mercurial causes ν_{Hg-X} to disappear. The observed principal frequencies are set out in Table 3. The other bands in the spectra can be accounted for by the presence of bis(trifluoromethylthio)-mercury, although there are minor changes in the contours.

TABLE 3. *Strong Raman lines* (cm.$^{-1}$) *in spectra of methanol solutions containing equimolar concentrations of bis(trifluoromethylthio)mercury and a mercuric halide or cyanide.*

	$HgCl_2$		$HgBr_2$		HgI_2 *		$Hg(CN)_2$	
Frequency	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
ν_{Hg-S}	240vs		240vs	—	240vs		240vs	
ν^1_{Hg-S}	251vs	253	264w	275	—	264	256w	259
ν_{HgX}	323s		204vs		145s		412w	
ν^1_{Hg-X}	243s	354	223vs	222	179s	176	—	425

* Solution contained excess of $Hg(S{\cdot}CF_3)_2$ because of the limited solubility of HgI_2.

For solutions containing mercuric cyanide, the expected weak fundamental ν^1_{Hg-X} could not be detected, but the line due to the pure cyanide at 274 cm.$^{-1}$ (w), arising from the Hg–C–N bending mode,[10] was accompanied by a new line at 298 cm.$^{-1}$ (w) to be ascribed to the corresponding mode of trifluoromethylthiomercuric cyanide: no new band associated with the C–N stretching vibration was observed.

For a molecule $CF_3{\cdot}S{\cdot}HgX$, there will be three skeletal modes of vibration involving, respectively, Hg–S·CF$_3$ stretching, Hg–X stretching, and deformation. All these modes are Raman-active, but the bending frequency is likely to be much the lowest and could not be detected in the present work. A rough calculation can be made of the two stretching frequencies corresponding to the two new Raman lines, ν^1_{Hg-S} and ν^1_{Hg-X}, by using the known values of the symmetrical stretching frequencies, ν_{Hg-S} and ν_{Hg-X}. For the pure mercury compounds (cf. ref. 11),

$$4\pi^2(\nu_{Hg-S})^2 = k_1/m_{SCF_3} \text{ and } 4\pi^2(\nu_{Hg-X})^2 = k_2/m_X \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_1 and k_2 are the force-constants, and m_{SCF_3} and m_X the appropriate masses of

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[9] Allen and Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786.

[10] Woodward and Owen, *J.*, 1959, 1055.

[11] Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 172, 173.

the trifluoromethylthio-group and halogen atom respectively. It is assumed that the force-constants are the same in the asymmetric molecule, the changes in frequency being purely a mass-effect. This is an over-simplification which can be justified only by the agreement between calculated and observed frequencies.[3] It can then be shown [11] that

$$(\nu^1_{\mathrm{Hg-S}})^2 + (\nu^1_{\mathrm{Hg-X}})^2 = (\nu_{\mathrm{HgS}})^2\{1 + m_{\mathrm{SCF_3}}/m_{\mathrm{Hg}}\} + (\nu_{\mathrm{Hg-X}})^2\{1 + m_{\mathrm{X}}/m_{\mathrm{Hg}}\} \quad . \quad . \quad (2)$$

and

$$(\nu^1_{\mathrm{Hg-S}})^2(\nu^1_{\mathrm{Hg-X}})^2 = [1 + (m_{\mathrm{X}} + m_{\mathrm{SCF_3}})/m_{\mathrm{Hg}}]\,(\nu_{\mathrm{Hg-S}})^2(\nu_{\mathrm{Hg-X}})^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from which $\nu^1_{\mathrm{Hg-S}}$ and $\nu^1_{\mathrm{Hg-X}}$ can be calculated. For $m_{\mathrm{SCF_3}}$ the mass of the sulphur atom is used. Fair agreement with the observed frequencies is obtained despite the assumptions involved in the calculation.

A value for the equilibrium constant can be calculated in favourable cases from the relative intensities of the principal Raman lines of solutions containing various proportions of bis(trifluoromethylthio)mercury and the corresponding mercuric halide, by using the method described by François and Delwaulle.[3] For the system $\mathrm{Hg(S{\cdot}CF_3)_2 + HgBr_2 \rightleftharpoons 2CF_3{\cdot}S{\cdot}HgBr}$, the equilibrium constant, K, given by

$$K = [\mathrm{CF_3{\cdot}S{\cdot}HgBr}]^2/[\mathrm{Hg(S{\cdot}CF_3)_2}][\mathrm{HgBr_2}],$$

is 2·3 ± 0·3 at room temperature. In the equilibrium with mercuric chloride, the spectra do not lend themselves so well to this sort of calculation, the various Raman lines being less clearly resolved; the value of K is of the order of 20 (±10). No such calculation could be made for the other mixtures.

C. *Adduct Formation.*—The Raman spectra of the pure tetramethylammonium compounds, $\mathrm{NMe_4[Hg(S{\cdot}CF_3)_2X]}$ (X is Cl, Br, or I), have been recorded for saturated acetone solutions. Potassium cyanide gives a much less stable adduct which could not be isolated in the pure state; in this case, the spectrum of an acetone solution containing a mixture of the cyanide with a small excess of mercurial was observed. The frequencies are listed in Table 4.

TABLE 4. *Raman spectra of adducts of bis(trifluoromethylthio)mercury over the range* 100—800 cm.$^{-1}$.

$\mathrm{NMe_4[Hg(S{\cdot}CF_3)_2Cl]}$ Δν (cm.$^{-1}$)	$\mathrm{NMe_4[Hg(S{\cdot}CF_3)_2Br]}$ Δν (cm.$^{-1}$)	$\mathrm{NMe_4[Hg(S{\cdot}CF_3)_2I]}$ Δν (cm.$^{-1}$)	$\mathrm{K[Hg(S{\cdot}CF_3)_2CN]}$ Δν (cm.$^{-1}$)
		137vs	
	169s		
223vs	222vs	219vs	221vs
290wbr			
390s	386s	386s	388s
470w	465w		
650?vw			
690?vw			
751m *	750m *	751m *	

* This may include scattering due to the $\mathrm{Me_4N^+}$ ion.

Most significant is the marked lowering in frequency of the in-phase Hg–S stretching vibration from 240 cm.$^{-1}$ (in solutions of the pure mercurial) to about 220 cm.$^{-1}$, a value close to that observed when the mercurial is dissolved in pyridine. This frequency varies little from compound to compound and seems to be characteristic of adducts of bis(trifluoromethylthio)-mercury. New bands at 290, 169, and 137 cm.$^{-1}$ in the spectra of the tetramethylammonium chloride, bromide, and iodide compounds, respectively, are ascribed to the Hg–X stretching vibration in the anion $\mathrm{[Hg(S{\cdot}CF_3)_2X]^-}$. A smaller frequency shift (about 12 cm.$^{-1}$) was observed in the prominent Raman line associated with bis(trifluoromethylthio)mercury close to 400 cm.$^{-1}$, which tends to be much broader than in the spectrum of the pure mercury compound; the change in the overall molecular symmetry probably accounts for this. The scattering near 750 cm.$^{-1}$ is probably due both to the 750 cm.$^{-1}$ vibration of $\mathrm{CF_3{\cdot}S}$ groups and also to the symmetrical " breathing " mode of the tetramethylammonium ion [12] at 752 cm.$^{-1}$. A number of missing bands are presumably too weak for detection in solutions of the concentrations used; no scattering could be assigned definitely to any of the frequencies characteristic of the tetramethylammonium ion [12] over the range 100—800 cm.$^{-1}$.

[12] Ebsworth and Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.

Analogous frequency shifts have been observed in the Raman spectra of mixed solutions of mercuric and alkali-metal halides, and correspond to the formation of the ions HgX_3^- and HgX_4^{2-};[13,14] the form of the spectrum depends on the molar ratio, R = $HgX_2 : MX$. When R exceeds 1, the spectrum contains a strong line associated with the symmetrical Hg–X stretching vibration of the HgX_3^- ion: when R is less than 0·5, this has shifted to a lower frequency corresponding to the formation of the HgX_4^{2-} ion. As R changes from 1 to 0·5, the band becomes broader and there is a continuous change in frequency of the centre between the two extreme values; in some cases, the band can be resolved into two components.[13] In the reaction of bis(trifluoromethylthio)mercury with tetramethylammonium halides, however, R cannot be made less than 1, since decomposition occurs under these conditions;[5] the ion $[Hg(S{\cdot}CF_3)_2X_2]^{2-}$ is evidently very unstable. For values of R greater than 1 the Raman spectrum of the solution contains, as expected, the bands characteristic of both the mercury compound and the complex.

The infrared spectra of the solid tetramethylammonium adducts have also been recorded over the range 400—4000 cm.$^{-1}$. Apart from the frequencies due to the tetramethylammonium ion and a change in the contour of the band associated with the C–F stretching mode, there is little essential difference between these spectra and that of pure bis(trifluoromethylthio)-mercury. In general, the spectra obtained give insufficient evidence for detailed analysis, and no definite conclusions can be reached concerning the molecular symmetry of the adducts.

EXPERIMENTAL

Bis(trifluoromethylthio)mercury was prepared by reaction between carbon disulphide and mercuric fluoride in an autoclave, and was purified by repeated vacuum-sublimation at room temperature and dried *in vacuo* over phosphorus pentoxide. The tetramethylammonium adducts were prepared by the method described by Jellinek and Lagowski.[5] For the solutions, dried " AnalaR " benzene, carbon tetrachloride, ether, acetone, methanol, and pyridine were used. Pure bis(trifluoromethylthio)mercury was examined in solutions of concentrations ranging from 0·3M to 3M. In all cases, the solutions were filtered through a fine glass sinter to obtain a suitably clear sample (4—5 ml.) for the Raman studies.

The Raman spectra were examined with a Hilger E612 spectrometer; the exciting line was the mercury line at 4358 Å. A filter consisting of a saturated aqueous solution of sodium nitrite was employed to suppress the primary lines of shorter wavelength; the level of background was such that no bands could be detected with any certainty within 120 cm.$^{-1}$ of the exciting line. The spectra were reproduced directly by means of a pen recorder operated by the amplified output from a photomultiplier unit. Qualitative determinations of the states of polarisation of the Raman lines were made by the method of polarised incident light,[15] successive records being taken with suitably oriented polaroid cylinders surrounding the sample-tube. Most of the solutions were colourless, but those containing mercuric iodide and the tetramethylammonium iodide adduct were tinted yellow; the slight colouring did not, however, appear to influence the spectra obtained. The observed frequencies were calibrated from the position of appropriate sharp bands in the spectra of pure carbon tetrachloride, benzene, and acetone, and are correct to within about ±2 cm.$^{-1}$ for all but the weak and diffuse bands. The temperature of the samples was kept roughly constant by a water-cooled jacket surrounding the sample-tube, except in the case of pure bis(trifluoromethylthio)mercury, when the heat of the lamps was used to keep the material molten (m. p. 39°).

The infrared spectra were recorded at frequencies between 400 and 4000 cm.$^{-1}$ with a Perkin–Elmer model 21 double-beam spectrometer, fitted with a sodium chloride or potassium bromide prism. The compounds were examined as mulls with Nujol or hexachlorobutadiene.

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[13] Delwaulle, François, and Wiemann, *Compt. rend.*, **206**, 1108.

[14] Delwaulle, *Bull. Soc. chim. France*, 1955, 1294; Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

[15] Rank and Kagarise, *J. Opt. Soc. Amer.*, 1950, **40**, 89.