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PREPARATION AND PROPERTIES OF SILYL- AND GERMYL-TRIFLUOROMETHYLACETYLENES (1,1,1-TRIFLUORO-4-SILABUT-2-YNE AND 1,1,1-TRIFLUORO-4-GERMABUT-2-YNE), AND MOLECULAR STRUCTURE OF SILYLTRIFLUOROMETHYLACETYLENE DETERMINED BY ELECTRON DIFFRACTION *

DUNCAN W.W. ANDERSON, STEPHEN CRADOCK, E.A.V. EBSWORTH, ANTHONY R. GREEN, DAVID W.H. RANKIN,

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ (Great Britain)

and ALAN G. ROBIETTE

Department of Chemistry, University of Reading, Whiteknights Park, Reading RG2 7NG (Great Britain)

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Summary

The compounds $MH_3C{\equiv}CCF_3$ (M = Si, Ge) and their fully deuterium-substituted analogues have been prepared by reaction of silyl or germyl halides with the Grignard reagent derived from $CF_3C{\equiv}CH$. They have been characterised by a variety of physical and spectroscopic measurements, including a full vibrational analysis and electron diffraction and microwave studies of $SiH_3C{\equiv}CCF_3$.

Introduction

As part of a systematic study of acetylene derivatives of silane and germane we have prepared silyl- and germyl-trifluoromethylacetylenes and their fully deuterium-substituted derivatives, and characterised them by a wide range of physical and spectroscopic techniques, including a molecular structure determination by gas-phase electron diffraction of SiH_3CCCF_3. We have already reported [1] the analysis of the sub-band structures of some of the vibrational bands of these molecules, showing that the barrier to internal rotation must be negligibly small, as fine-structure appeared on bands due to motions of the MH_3 groups of *e* symmetry that was very similar to that found for molecules lacking the CF_3 group, such as silyl halides and SiH_3CCH. We have also reported [2] the reactions of the silyl compound with some Pt^{II} complexes. The present paper reports the details of preparations, the characterisation of the new compounds, the vibrational spectra, with an analysis in terms

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* Dedicated to Professor M. Kumada.

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of the expected fundamentals, the electron diffraction study of the silyl compound, and a microwave study of the same compound.

Experimental

Preparations. The title compounds were prepared by reaction of bromosilane or chlorogermane with the Grignard reagent $CF_3C{\equiv}CMgI$ prepared from $CF_3C{\equiv}CH$ and CH_3MgI. In a typical preparation, CH_3MgI was prepared by reaction of CH_3I (0.425 g; 2.97 mmol) with magnesium turnings (0.075 g; 3.09 mmol) under nitrogen in refluxing diethyl ether (2 h). The solution was cooled to 77 K and the nitrogen atmosphere removed; excess $CF_3C{\equiv}CH$ (3.5 mmol) was condensed into the flask and the contents allowed to warm to room temperature and react for 2 h. The solution was again cooled to 77 K and the methane formed removed. At this stage the diethyl ether solvent was replaced by the much less volatile diglyme (bis(2-methoxyethyl)ether); the diglyme was condensed into the flask before the diethyl ether was pumped off, finally at room temperature for 15 min. The solution was again cooled to 77 K and SiH_3Br (2.8 mmol) condensed in; the contents of the flask were allowed to warm to room temperature and react for 30 min. Effervescence was observed, and a precipitate of Mg halide formed. Volatile products were removed at room temperature and separated by trap-to-trap distillation; the major impurity was monosilane, which passed a trap held at 153 K. The product, silyltrifluoromethylacetylene, was retained at this temperature; the yield was 1.4 mmol (50%). Careful adherence to the above method was necessary to avoid the presence in the product of CH_3SiH_3, $CF_3C{\equiv}CH$, SiH_3Br or $(C_2H_5)_2O$, all of which were difficult to remove by trap-to-trap distillation. A similar reaction with SiD_3Br gave the deuterium-substituted analogue.

In the preparation of germyltrifluoromethylacetylene, the above method was followed, using GeH_3Cl in place of SiH_3Br. The major impurity was GeH_4, which was removed by trap-to-trap distillation, the product being retained at 177 K; a minor impurity of Ge_2H_6 was removed by repeated fractionation at 177 K. The yield of the germyl product was somewhat lower (40%) than that of the silyl compound.

All compounds were characterised by NMR, IR, Raman and mass spectroscopy, including exact mass determination on the parent ions. They were handled in conventional glass vacuum apparatus.

Instruments. Mass spectra were obtained using an AEI MS 902 instrument; ^1H NMR spectra with a Varian HA 100 spectrometer; Raman spectra using a Cary 83 instrument with Ar^+ (488 nm) excitation, and infrared spectra using either a

TABLE 1

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS

Camera height (mm)	s (nm^{-1})	s_{min} (nm^{-1})	s_{w1} (nm^{-1})	s_{w2} (nm^{-1})	s_{max} (nm^{-1})	Correlation parameter	Scale factor
250	4	68	84	280	292	0.1937	0.708(25)
500	2	24	35	140	150	0.3896	0.981(25)

Perkin–Elmer 225 spectrophotometer (5000–200 cm^{-1}) or a Beckman-RIIC IR 720 interferometer below 200 cm^{-1}. Microwave spectra were obtained using a Hewlett Packard 8460A instrument, in the range 26.5–40 GHz, with sample pressures around 25 mTorr at room temperature. Electron diffraction patterns for gaseous SiH_3-$CCCF_3$ were obtained using a Balzers KD.G2 apparatus; the sample was held at 228 K with a nozzle temperature of 333 K. Nozzle-to-plate distances, data point intervals, s ranges and weighting points, correlation and scale parameters are collected in Table 1; the electron wavelength used was 5.663 pm. Diffraction patterns were analysed using our usual programmes [3,4], and are illustrated in Fig. 1.

Results

^1H NMR spectra of $MH_3C{\equiv}CCF_3$ ($M = Si, Ge$) showed a quartet (due to $^5J(HF)$); ^{19}F NMR spectra of the silyl compound confirmed this assignment. The chemical shifts and coupling constants are collected in Table 2. Samples were dilute solutions in a mixture of CCl_3F and tetramethylsilane (TMS).

Mass spectra

Facile loss of hydrogen atoms from the parent and fragment ions was apparent from the spectra, as usual for MH_3 compounds, and other fragmentations involving rupture of single bonds led to the presence of peaks assigned to ions of the types: $SiH_nCCCF_3^+$; $SiH_nCCCF_2^+$; SiH_nCCCF^+ and SiH_nCC^+ ($n = 0,1,2,3$) and $CCCF_m^+$ and CF_m^+ ($m = 1,2,3$) with similar fragmentations for the germyl analogue. Exact mass measurements were carried out on selected peaks in the parent ion group ($MH_nCCCF_3^+$) in each case to confirm the identity of the molecule responsible; the results are collected in Table 3.

Physical properties

Both silyl and germyl compounds are volatile liquids, boiling around room

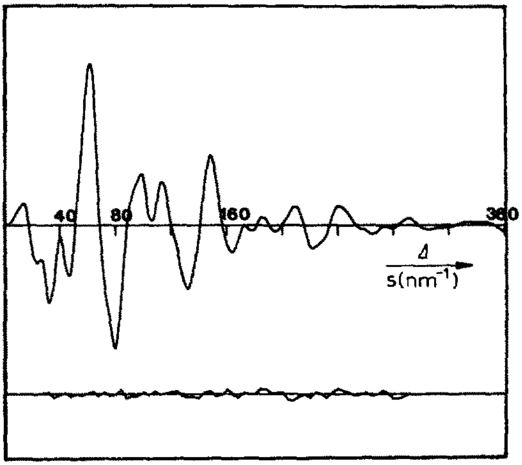

Fig. 1. Observed and final weighted difference molecular scattering intensities—combined curves for both nozzle-to-plate distances.

TABLE 2

NUCLEAR MAGNETIC RESONANCE SPECTRA OF $MH_3C{\equiv}CCF_3$

M	$\delta(^1H)$ (ppm)	$\delta(^{19}F)$ (ppm) [a]	$^5J(HF)$ (Hz)	$^1J(^{29}SiH)$ (Hz)
Si	3.91	−53.0	1.7	226
Ge	4.11	not observed	1.8	–

[a] From internal CCl_3F; positive shift is high frequency.

TABLE 3

EXACT MASS MEASUREMENTS FOR $MH_3C{\equiv}CCF_3$

Ion	Mass found	Mass expected	Error (ppm)
$^{28}SiH_2CCCF_3{}^+$	122.987524	122.987785	2
$^{28}SiHCCCF_3{}^+$	121.979780	121.979960	1.5
$^{28}SiCCF_3{}^+$	120.972156	120.972136	<1
$^{72}GeH_2CCCF_3{}^+$	166.932745	166.932556	1
$^{74}GeCCCF_3{}^+$	166.916407	166.916345	<1

temperature, and have low melting points; the melting point of SiH_3CCCF_3 was measured as 146 ± 1 K ($-127\,^\circ C$). Vapour pressure data between about 200 and 250 K were collected and fitted using a $\log_{10}p/(1/T)$ plot to relationships

$$\log_{10}p\ (\text{cmHg}) = \frac{-1320}{T} + 6.695 \text{ for } SiH_3C{\equiv}CCF_3$$

and

$$\log_{10}p\ (\text{cmHg}) = \frac{-1710}{T} + 7.705 \text{ for } GeH_3C{\equiv}CCF_3$$

The boiling points and vapourisation parameters derived are listed in Table 4.

Vibrational spectra

The spectra observed for SiH_3CCCF_3, SiD_3CCCF_3, GeH_3CCCF_3 and GeD_3CCCF_3 are collected in Table 5, and the suggested assignment of fundamentals in Table 6. The fundamentals are assigned assuming C_{3v} symmetry, ignoring the internal rotation; we have shown [1] the latter motion to be essentially free, giving rise to splittings of the perpendicular bands such as we have reported [5] for SiH_3CCCH_3, but to no other effects in the infrared or Raman spectra. The internal rotation is of A_2 symmetry, and thus formally forbidden in both effects, though its overtone could in principle be observable. The suggested assignments are based on systematic correlations within the set of spectra reported here and on comparison with other silyl and germyl compounds on the one hand and other CF_3 compounds on the other, and especially with the spectra of other CF_3-substituted acetylenes. The vibrations assigned to the CF_3CC-moiety are in general fairly insensitive to the nature of the other group involved, though systematic mass-related effects are observable in respect of most of them. One large shift, of the bands assigned to $\delta_s(CF_3)$ in the MH_3 and MD_3 species, may reflect mixing with the $M(H/D)_3$ symmetric deformation. The symmetric CF_3 deformation is quite sensitive to the

TABLE 4

BOILING POINTS AND VAPOURISATION PARAMETERS FOR $SiH_3C{\equiv}CCF_3$ AND $GeH_3C{\equiv}CCF_3$

Compound	B.p. (K)	ΔH_{vap} (kJ mol^{-1})	ΔS_{vap} (J mol^{-1} K^{-1})
$SiH_3C{\equiv}CCF_3$	274±4	25.2±0.4	91.9
$GeH_3C{\equiv}CCF_3$	294±6	32.7±0.6	111.2

nature of the attached group in CF_3 compounds in general; the fairly constant value found in our compounds is rather different from that found in CF_3CCH (535 cm^{-1}) [6], but closer to the values reported in the simple halides CF_3X (X = Cl, Br, I) [7] where bands in the range 780–740 cm^{-1} may be assigned to motions involving both this vibration and the CX stretch. The two lowest-frequency bands must be attributed to combinations of the two skeletal bends δ(CCC) and δ(CCM), as both show significant shifts depending on the mass of the $M(H/D)_3$ group. We have carried out normal coordinate calculations based on these assignments; the resulting amplitudes of vibration are useful in connection with the electron diffraction study, but otherwise the calculations merely confirm the plausibility of the assignments, and we do not report the resulting force fields here. The assignments are consistent with the observed band contours in the gas-phase infrared spectra, and the polarisations of

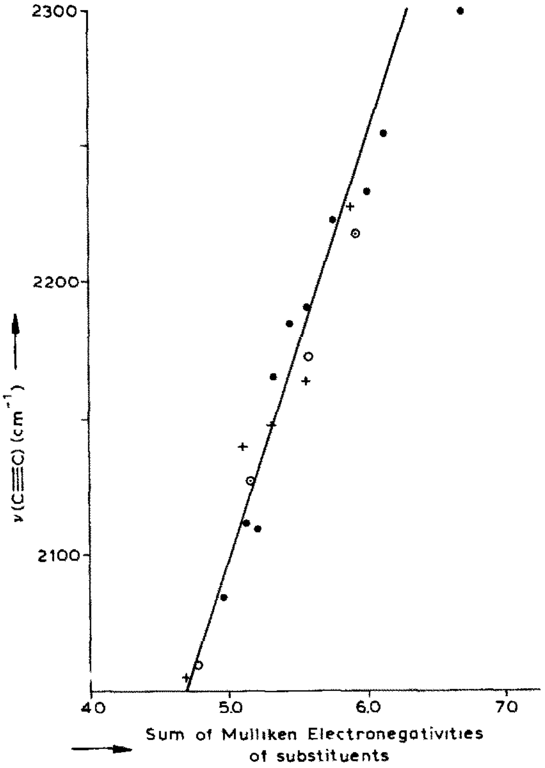

Fig. 2. Relationship between C≡C stretching frequency and electronegativities of substituents in some haloacetylenes (●), some silylacetylenes (+) and some germylacetylenes (○).

the Raman lines; we have reported the results of an analysis of the sub-band structures of some of the perpendicular bands associated with $M(H/D)_3$ group motions [1].

It has been shown [8] that the C≡C stretching frequency of substituted acetylenes correlates well with the Mulliken electronegativities of the substituents; using the frequencies for disilyl- and digermyl-acetylenes one can deduce effective electronegativities for silyl and germyl groups of 2.55 and 2.58 respectively. The frequencies for other silyl and germyl acetylenes, including the present CF_3 derivatives, are then quite consistent with the correlation found for other substituted acetylenes (Fig. 2).

Structural studies

(i) Microwave spectrum

Each $J+1 \leftarrow J$ transition in the characteristic symmetric rotor spectrum is accompanied by a long sequence of vibrational satellites to high frequency, assigned to molecules in excited states of the lowest doubly-degenerate chain-bending frequency (denoted ν_b). The intensity distribution is consistent with a frequency for this motion of less than 100 cm^{-1}, confirming the assignment of this mode to the band at 87 cm^{-1} in the gas phase infrared spectrum. The appearance of a given $J+1 \leftarrow J$ absorption arising from molecules in the ground vibrational state is consistent with a positive value of D_{JK}, i.e. an absorption with a sharp high-frequency edge, degrading to lower frequencies. The width at half-peak intensity is typically some 7 to 8 MHz. These absorptions were studied over a wide range of Stark voltages in an attempt to resolve the K structure: experiments were also carried out with a non-zero-based Stark waveform as described by Kirchhoff and Lide [9] in an attempt to identify the $K=0$ transitions of different internal rotation states. In neither case could any individual K transitions be distinguished, but this is almost certainly an indication that the barrier to internal rotation is essentially zero, and that the observed spectrum is the superposition of spectra of many different internal rotation states. Given the relatively small value of D_{JK} expected for such a heavy molecule, and the high J values for which the spectrum was observed, the large number of K transitions then leads to a broad unresolved band.

Since it proved impossible to assign the K structure, the frequency measurements reported here refer simply to the peak of the unresolved envelope. The peak is close to the high-frequency edge for each transition, and the measurements should thus provide reasonable estimates of the B rotational constant. The measurements quoted in Table 7 were recorded for the abundant isotopic species and for the species $H_3{}^{29}SiCCCF_3$, observed in natural abundance (4.7%). Searches were carried out for the spectra of the various ^{13}C-substituted species in natural abundance, but no convincing assignments could be made. Measurements were also made for the peak absorptions of the first main vibrational satellite, $v_b = 1$. In each case the measurements were fitted to the equation

$$\nu = 2B(J+1) - 4D_J(J+1)^3,$$

and the resulting constants B and D_J are also given in Table 6.

The B_o value for the ground vibrational state, 841.6 MHz, is in fairly good agreement with that calculated from the r_α^0 parameter set derived from electron diffraction data alone, 835.0 ± 1.7 MHz. The calculated B_o to B_z correction from the

(Continued on p. 244)

TABLE 5a

OBSERVED BANDS ASSIGNED TO FUNDAMENTAL VIBRATIONS OF $M(H,D)_3C{\equiv}CCF_3$ (s = strong; m = medium; w = weak; v = very; p = polarised; dp = depolarised; Assignments are in terms of the numbering appropriate to SiH_3CCCF_3, see Table 6)

$SiH_3C{\equiv}CCF_3$				$SiD_3C{\equiv}CCF_3$			$GeH_3C{\equiv}CCF_3$			$GeD_3C{\equiv}CCF_3$		Assignment
IR			Raman liq.	IR		Raman liq.	IR		Raman liq.	IR gas	Raman liq.	
gas	Ar matrix	solid		gas	Ar matrix		gas	Ar matrix				
–	2215s	2221m	2228vs dp	2219m	2224w	2225m p	2219m	2220w	2225m p	2218s	2220m p	ν_1
2209.2vs [a]	2162vs			1606s	1626w 1606w	1618m	2133.6s [a]		–	1547vs	1540s dp	ν_8
2202.0vs PQR [b]	2158ms	2202m	2206vs p	1583s	1583vw	1587vs p	2128.1s PQR [b]	2140m	2135vs p	1524vs	1525vs p	ν_2
1265.0vs PQR [b]	1247vs	1276s 1250s	1265w p	1264vs	1262s 1257vs	1265w p	1262.5vs PQR [b]	1255vs	1255w p	1260.6vs PQR [b]	1260w	ν_3
1175vs	1168vs	1142vs	1170w dp	1176vs	1165vs 1160s	1160w dp	1173vs	1157vs	1160w dp	1172.5vs	1160w dp	ν_9
949.9vs [a]	951vs	938m	946s dp	685s	675m	688m dp	886.0vs [a]	878s	885s	623.7m [a]	635s dp	ν_{10}
926.2vs PQR [b]	912.5s 906.5vs	917s	924s p	712vs	707s	712m p?	821.8vs PQR [b]	818vs	825s p	597.5vs PQR [b]	605m p?	ν_4
858.3m	851w	897s	878vs p	874vs	881w 874w	877m p	862s PQR [b]	859s	865m	852m PQR [b]	855m p	ν_5
690s PQR [b]	686s	673s	695s p	660vs	657s	663m p	685m	–	660w p	658m PQR [b]	660m p	ν_6
681.2s [a]	684s		–	536vs	533m	538w	626.8vs [a]	630s 627s	–	489s	–	ν_{11}
617m	611.5m	608m	620w dp	598m	595w	620w dp	–	609s	615w dp	618m	620m	ν_{12}
464vw	–	–	465m dp	458w	–	462w dp	474w 440w	–	460m dp	449m	455m dp	ν_{13}
349m	–	344w	358s p	340vs	339w	348m p	264m	268s	270s p	261s	275m p	ν_7
240w	–	–	250vs dp	230w	–	238vs dp	235w	230m	245vs p?	221m	235vs dp	ν_{14}
87vw	–	–	98vs dp	–	–	93s dp	76vw	–	90m dp	76vw	90m dp	ν_{15}

TABLE 5b

OBSERVED BANDS ASSIGNED TO OVERTONES AND COMBINATIONS

$SiH_3C{\equiv}CCF_3$		$SiD_3C{\equiv}CCF_3$		$GeH_3C{\equiv}CCF_3$		$GeD_3C{\equiv}CCF_3$	
4405vw	$2\nu_2$	3108vw	$\nu_2+\nu_8$, $2\nu_2$, $2\nu_8$	4195vw [a]	$\nu_2+\nu_2$, $2\nu_2$, $2\nu_8$	3460w	$\nu_1+\nu_3$?
4360vw	$2\nu_2$, $\nu_2+\nu_8$, $2\nu_8$	3088vw		4190vw PQR [b]		2516w	$2\nu_3$
4345vw [a]		3058vw		3478w	$\nu_1+\nu_3$	2486vw	$\nu_1+\nu_7$
4340vw		2870vw	$\nu_1+\nu_6$	3390vw	$\nu_1+\nu_9$	2429w	$\nu_3+\nu_9$
3482vw	$\nu_1+\nu_3$	2436w	$\nu_3+\nu_9$	2980w		2360vw	
3143vw [a]		2359w	$2\nu_9$	2951w	$(\nu_2,\nu_8)+(\nu_4,\nu_{10})$	2348vw	
3122vw PQR [b]	$(\nu_2,\nu_8)+(\nu_{4,10})$	2329w	$\nu_4+\nu_8$	2870w		2321m	$2\nu_9$
2962vw		2045w	$\nu_5+\nu_9$	2517w	$2\nu_3$	2160w	$(\nu_2,\nu_8)+(\nu_4,\nu_{10})$
2880vw	$\nu_1+\nu_6$?	1984vw	$\nu_3+\nu_4$??	2486w	$\nu_1+\nu_7$	2125w	
2571vw	$\nu_1+\nu_7$?	1885vw	$\nu_3+\nu_{12}$	2430m	$\nu_3+\nu_9$	2033w	$\nu_5+\nu_9$
2523vw	$2\nu_3$	1820vw	$\nu_6+\nu_9$?	2382vw	$\nu_2+\nu_7$	1827vw	
2481vw		1805vw		2355w	$2\nu_9$	1778vw	$\nu_9+\nu_{12}$
2439w	$\nu_3+\nu_9$	1495vw	$\nu_3+\nu_{14}$	2323m	$\nu_1+\nu_{15}$	1707vw	$2\nu_5$
2316m	$\nu_1+\nu_{15}$	1482w		1994w		1612vw	

1879vw PQR[b]	$2\nu_4, \nu_4 + \nu_{10},$	1395w	$\nu_4 + \nu_{10}$	1778vw	$2\nu_{10}, \nu_9 + \nu_{12}$	1221a	$2\nu_{12}$
1871vw[a]		1358w	$2\nu_{10}$	1817vw	$2\nu_5, \nu_4 + \nu_{10}?$	1138s	
1861vw		1348w	$2\nu_6?$	1624w	$2\nu_4$	1112m	$\nu_5 + \nu_7$
1785vw	$\nu_9 + \nu_{12}?$	1245s	$\nu_4 + \nu_{11}$	1580w		995w	$2\nu_{11}?$
1745vw	$2\nu_5$	1231s	$2\nu_{12}$	1524w PQR[b]	$\nu_5 + \nu_6?$	890w	$\nu_7 + \nu_{10}$
1716w	$\nu_3 + \nu_{13}?$	1223s	$\nu_{10} + \nu_{11}$	1478w PQR[b]	$\nu_5 + \nu_{12}, \nu_3 + \nu_{14}$	760m	$\nu_7 + \nu_{11}$
1618w PQR[b]	$\nu_{10} + \nu_{11}?$	1206s	$\nu_5 + \nu_7$	1435vw	$\nu_{10} + \nu_{11}?$	712w	$\nu_6 + \nu_{15}$
1478w PQR[b]	$\nu_5 + \nu_{12}?$	1140m	$\nu_{10} + \nu_{13}$	1406vw	$\nu_9 + \nu_{14}?$	688m	$\nu_{13} + \nu_{14}?$
1411vw	$\nu_9 + \nu_{14}$	1092m	$2\nu_{11}?$	1357vw PQR[b]	$2\nu_6?$	408vw	$\nu_7 + 2\nu_{15}$
1373w PQR[b]	$2\nu_6$	910w	$2\nu_{13}$	1350vw PQR[b]		377vw	$\nu_{14} + 2\nu_{15}$
1355w	$2\nu_{11}$	846w	$\nu_{12} + \nu_{14}$	1340m		339vw	$\nu_7 + \nu_{15}$
1217s PQR[b]	$2\nu_{12}$	375w	$\nu_{14} + 2\nu_{15}$	1311w PQR[b]		303w	$\nu_{14} + \nu_{15}$
374w	$\nu_{14} + 2\nu_{15}?$	305w (312vw p)	$\nu_{14} + \nu_{15})$	1294vw		150vw (185vw p)	$2\nu_{15}$
319w (340w p?)	$\nu_{14} + \nu_{15}$	(170s)	$2\nu_{15}$	1220s	$2\nu_{12}$		
				1137m	$\nu_7 + \nu_{10}?$		
				1059w	$\nu_{12} + \nu_{13}?$		
				536vw (535vw p)	$2\nu_7$		
				474w	$2\nu_{14}$		
				382w	$\nu_{14} + 2\nu_{15}$		
				339vw	$\nu_7 + \nu_{15}$		
				314w	$\nu_{14} + \nu_{15}$		
				150w (185vw)	$2\nu_{15}$		

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[a] Perpendicular contour. [b] PQR = parallel contour.

TABLE 6

FUNDAMENTAL VIBRATION FREQUENCIES OF $CF_3C{\equiv}CR$ (cm^{-1})[a]

Symmetry	R = SiH_3	R = SiD_3	R = GeH_3	R = GeD_3	Assignment
A_1	~ 2220	2219	2219	2218	ν_1 $\nu(C{\equiv}C)$
	2202.0	1583	2128.1	1524	ν_2 $\nu_s M(H/D)_3$
	1265.0	1264	1262.5	1260.6	ν_3 $\nu_s CF_3$
	926.2	712	821.8	597.5	ν_4 $\delta_s M(H/D)_3$
	878[b]	874	862	852	ν_4 $\nu(C-CF_3)$
	690	660	685	658	ν_6 $\delta_s CF_3$
	349	340	264	261	ν_7 $\nu(C-M)$
E	2206.8	1606	2131.6	1547	ν_8 $\nu_{as} M(H/D)_3$
	1175	1176	1173	1172.5	ν_9 $\nu_{as} CF_3$
	945.1	685	882.0	622.7	ν_{10} $\delta_{as} M(H/D)_3$
	680.5	536	626.6	489	ν_{11} $\rho M(H/D)_3$
	617 (620[b])	620[b]	615[b]	618	ν_{12} $\delta_{as} CF_3$
	464	458	440	449	ν_{13} ρCF_3
	240	230	235	221	ν_{14} skeletal bend
	87 (98[b])	n.o. (93[b])	76 (90[b])	76 (90[b])	ν_{15} skeletal bend

[a] Gas phase infrared frequencies unless otherwise noted. [b] Liquid phase Raman.

normal coordinate analysis is only −0.1 MHz, and may be ignored.

Normally the three D_J constants reported here would be expected to have very similar values. This is so for the abundant isotopic species and the ^{29}Si species: D_J for the latter is barely determined at the 3σ level, but constraining D_J instead to the value obtained for the abundant species causes B to change by only 0.003 MHz, which is insignificant from the point of view of the structure calculations. D_J for the $v_b = 1$ state should be regarded simply as a fitting parameter, which has absorbed

TABLE 7

OBSERVED MICROWAVE SPECTRUM, FREQUENCY FIT AND MOLECULAR CONSTANTS OF $H_3SiCCCF_3$

$J+1$	J	$H_3{}^{28}SiCCCF_3$ Ground state		$H_3{}^{28}SiCCCF_3$ $v_b = 1$ state		$H_3{}^{29}SiCCCF_3$ Ground state	
		ν_{obs}(MHz)	Δ(MHz)[a]	ν_{obs} (MHz)	Δ (MHz)[a]	ν_{obs}(MHz)	Δ(MHz)[a]
16	15	26931.69	0.07	26984.78	0.00	–	
17	16	28614.83	0.00	28671.25	−0.02	28141.87	−0.04
18	17	30298.00	−0.02	30357.74	−0.01	29797.37	0.09
19	18	31981.20	−0.01	32044.19	−0.03	31452.69	0.05
20	19	33664.32	−0.08	33730.81	0.13	33107.85	−0.15
21	20	35347.63	0.05	35417.07	−0.06	34763.47	0.12
22	21	37030.69	−0.07	37103.58	0.02	36418.63	−0.06
23	22	38713.99	0.07	38789.96	−0.02	38073.90	−0.12
24	23	–		–		39729.45	0.10
B(MHz)		841.619		843.287		827.712	
3σ (MHz)		0.007		0.007		0.012	
D_J (kHz)		0.011		0.025		0.015	
3σ (kHz)		0.008		0.008		0.014	

[a] $\Delta = \nu_{obs} - \nu_{calc}$.

some of the effects of l-doubling which we are unable to include in the absence of resolved K structure. The normal coordinate analysis resulted in a calculated value of $D_J = 0.01(1)$ kHz. Finally, the rotation constant for the $v_b = 1$ state allows us to estimate $\alpha_b^B = -1.66_8$ MHz.

(ii) Electron diffraction

Analysis of the results assumed local C_{3v} symmetry for both end-groups, and a linear SiCCC skeleton. Refinement was begun using spectroscopically-calculated amplitudes of vibration, and a fixed silyl group geometry. Heavy-atom parameters refined smoothly despite the severe overlapping of all bonded distances except r(SiC) in the radial distribution curve (Fig. 3), because of the clearly-separated peaks due to the various non-bonded distances, and it was finally possible to refine all bond lengths including r(SiH), bond angles HSiC and CCF and amplitudes for all bonded and non-bonded distances not involving hydrogen, plus $u(\mathrm{H} \cdot\cdot \mathrm{F})$. The final R-factors for the r_a refinement were $R_G = 7.8\%$, $R_d = 5.3\%$, with no shrinkage corrections or skeletal angle bends. The refinement was concluded by applying the usual K corrections and refining the electron diffraction data together with the observed B value, corrected to a frozen linear geometry by addition of α_b^B, giving what we may term an $r_{av}^{\star}$ structure, details of which appear in Table 8. The correlation matrix corresponding to this refinement is given in Table 9.

The structure is well-defined, and the CF_3 group geometry is unremarkable. The SiH_3 group geometry is also apparently normal, the expected r(SiH) of 148 pm being very close to the refined value. The C≡C bond length is close to that found in $CF_3C{\equiv}CH$ (121.1(5) pm) [10] and in $SiH_3C{\equiv}CSiH_3$ (120.6(5) pm) [11]. An interesting trend is suggested by the C–C bond length, which is intermediate between those reported for $CF_3C{\equiv}CCl$ [12] and $CF_3C{\equiv}CH$ [10] (145.3(2) and 150.0(5) pm respectively). The SiC bond appears somewhat long (r_a distance of 184.4 pm) in comparison with those found in other silyl acetylenes $SiH_3C{\equiv}CR$ (R = CH_3, 181.3(5) [4]; R = H, 182.6 (r_s) [13]; R = SiH_3, 182.5(3) [11] pm), and is closer to the value found

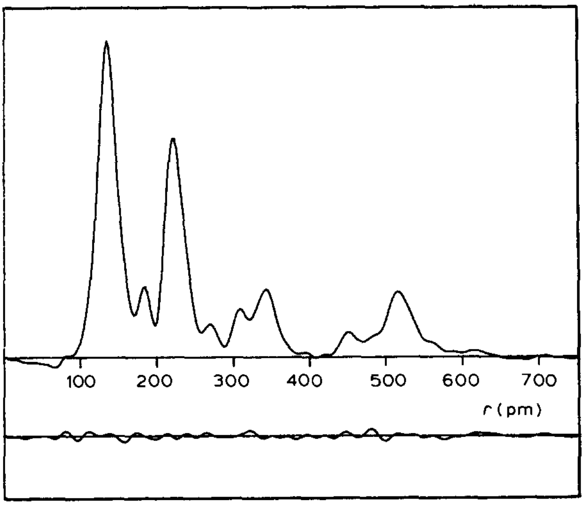

Fig. 3. Observed and final difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s.\exp[-0.00002s^2/(Z_{Si} - f_{Si})(Z_F - f_F)]$.

TABLE 8

REFINED PARAMETERS[a] AND INTERATOMIC DISTANCES AND AMPLITUDES (pm)

Parameters ($r^{\star}_{av}$)		Interatomic distances (r_a) from $r^{\star}_{av}$		Amplitudes (u)	
				Electron diffraction	Spectroscopic
r(Si–H)	147.3(21)	r(Si–H)	149.1(23)	8.9 fixed	8.9
r(Si–C)	182.7(6)	r(Si–C)	184.7(6)	4.7 (9)	4.4
r(C≡C)	121.8(8)	r(C≡C)	122.4(8)	4.4(25)	3.6
r(C–C)	148.2(8)	r(C–C)	149.1(8)	6.3(10)	5.3
r(C–F)	134.1(3)	r(C–F)	134.9(3)	4.9(8)	4.5
∠HSiC	107 fixed	r(H··H)	245.7(44)	15.3 fixed	15.3
∠FCC	110.3(4)	r(H··C)	268.7(31)	12.8 fixed	12.8
twist	0.0 fixed	r(H··C)	376.9(33)	15.2 fixed	15.2
		r(H··C)	515.5(36)	18.5 fixed	18.5
		r(H··F)	604.3(33)	18.3(30)	16.0
		r(H··F)	558.5(36)		26.6
		r(Si··C)	306.0(8)	5.8(12)	4.6
		r(Si··C)	452.7(11)	10.6(19)	5.0
		r(Si··F)	514.5(9)	15.9(7)	14.5
		r(C··C)	270.5(9)	4.7(22)	4.8
		r(C··F)	341.1(7)	10.1(7)	10.6
		r(C··F)	233.0(6)		7.8
		r(F··F)	218.8(5)	7.1(6)	5.5

[a] Distance parameters in pm, angles in degrees.

in silyl cyanide (185.0 pm) [14]. The refined amplitudes are in good agreement with the spectroscopically-calculated values in most cases, the major exception being the value for $u(\mathrm{Si}\cdot\cdot\mathrm{C_F})$, which is clearly larger than the spectroscopically-calculated value. This probably indicates that the lower-frequency skeletal bending motion involves *cis*- rather than *trans*-bending. Only the long-distance H· · F peak in the radial distribution curve is expected to be affected by the essentially-free internal rotation; as this peak is weak it is not possible to distinquish between a free-rotation model and the various fixed-conformation models, and we have simply shown using an *R*-factor plot that the staggered conformation (twist angle 0 °) corresponds more reasonably with the electron diffraction data than any other fixed conformation with twist angles in the range 0–60 °.

TABLE 9

CORRELATION MATRIX (×100)[a]

r(C≡C)	r(C–C)	r(C–F)	u(C≡C)	u(C··F)	u(F··F)	Scale 1	
−64							r(SiC)
−58	100	−54					r(C–C)
	−54	100	−64				r(C–F)
	−71	71					∠FCC
53			83				u(C–F)
					100	63	u(F··F)
				52	60	68	Scale 2

[a] Only those entries whose absolute magnitude exceeds 51 are included.

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