

Structure of Molecules of Type $(\text{CH}_3)_3\text{X}-\text{C}\equiv\text{C}-\text{Y}$ ($\text{X}=\text{Si}, \text{Ge}, \text{Y}=\text{H}, \text{Cl}$) determined by Electron Diffraction

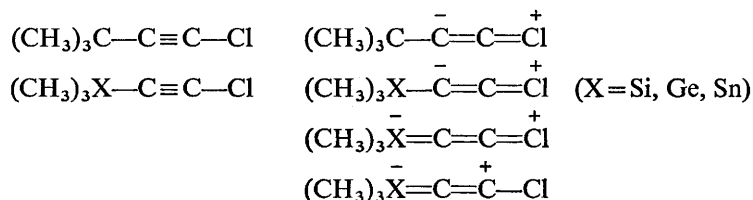
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The structure of the molecules $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$ and $(\text{CH}_3)_3\text{Ge}-\text{C}\equiv\text{C}-\text{Cl}$ as gases have been determined using electron diffraction. The lengths of the $\text{C}\equiv\text{C}$ bond show no significant differences from the corresponding bond length in carbon compounds. We conclude therefore that the length of the $\text{C}\equiv\text{C}$ bond is insensitive to π -electron delocalization.

We have reported the structure of the molecule $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Cl}$ as determined by the gas electron-diffraction method and by microwave spectroscopy,¹ and the values of nuclear quadrupole coupling constants of the following molecules: $(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}-\text{Cl}$, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$, $(\text{CH}_3)_3\text{Ge}-\text{C}\equiv\text{C}-\text{Cl}$, $(\text{CH}_3)_3\text{Sn}-\text{C}\equiv\text{C}-\text{Cl}$, measured by nuclear quadrupole resonance spectroscopy have been published.² From these results there is strong evidence of a bond type in the halogenated acetylenes which will be described by the following mesomeric formulas:



With silicon and germanium compounds of the type described above we would therefore expect an increase of the length of the $\text{C}\equiv\text{C}$ bond and a decrease of the force constant of the $\text{C}\equiv\text{C}$ bond with increasing number of the mesomeric structures. The prediction concerning the dependence of the force constant have been fulfilled.³

TABLE 1

	distance (mm)	range of s -values (\AA^{-1})	number of plates
$(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$	250	4.0-26.0	8
	500	2.0-14.3	6
$(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$	250	4.0-26.0	4
	500	1.8-12.0	6
	1000	0.75-7.5	6
$(\text{CH}_3)_3\text{Ge}-\text{C}\equiv\text{C}-\text{Cl}$	250	4.0-25.0	8
	1000	1.0-7.0	6

In this work we report the determination of the structures of the following molecules: $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$, $(\text{CH}_3)_3\text{Ge}-\text{C}\equiv\text{C}-\text{Cl}$. The method used was the electron diffraction by the gases. The compounds were prepared by methods described elsewhere.⁴ The electron diffraction patterns of the

molecules under investigation have been recorded on our KD-G2 apparatus,⁵ developed by us in collaboration with Balzers AG (former Trüb-Täuber & Co.) under the sponsorship of the Deutsche Forschungsgemeinschaft. Exposures were made with 2-3 nozzle-to-photographic-plate distances in each case. Table 1 give the distances and the range of s -values. The s -value is given by

$$s = (4\pi/\lambda) \sin (\vartheta/2)$$

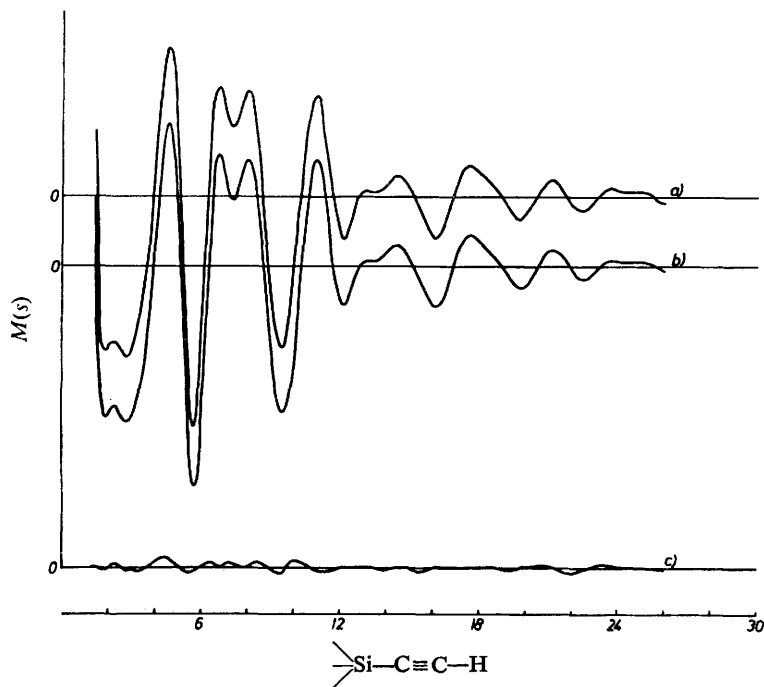


FIG. 1.—Intensity curve of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$; expt., (a); theor., (b); (a)–(b), (c).

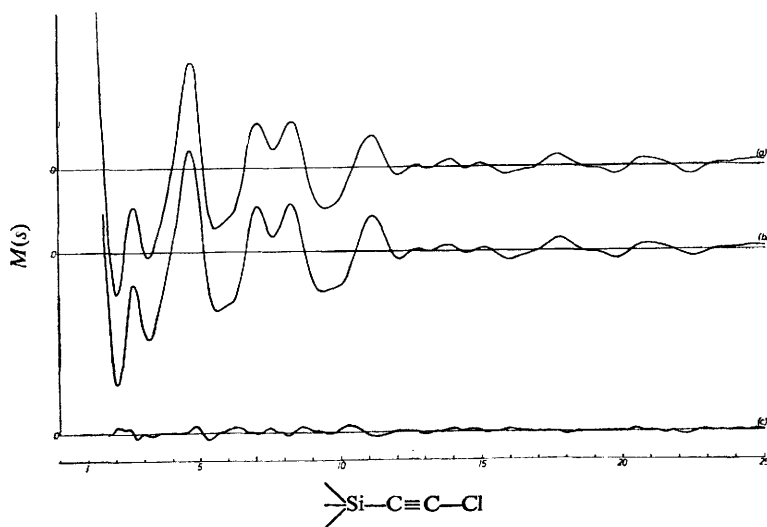


FIG. 2.—Intensity curve of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$; expt., (a); theor., (b); (a)–(b), (c).

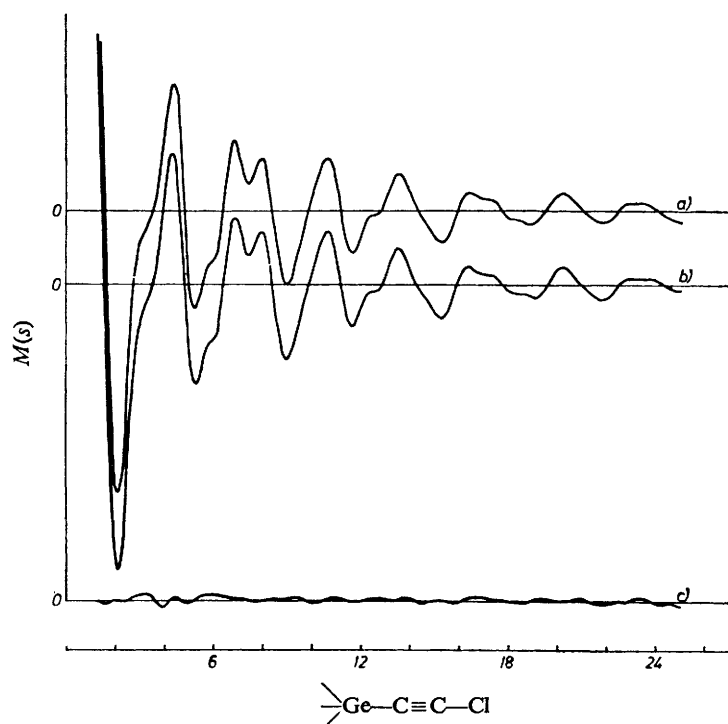


FIG. 3.—Intensity curve of $(\text{CH}_3)_3\text{Ge-C}\equiv\text{C-Cl}$; expt., (a); theor., (b); (a) - (b), (c).

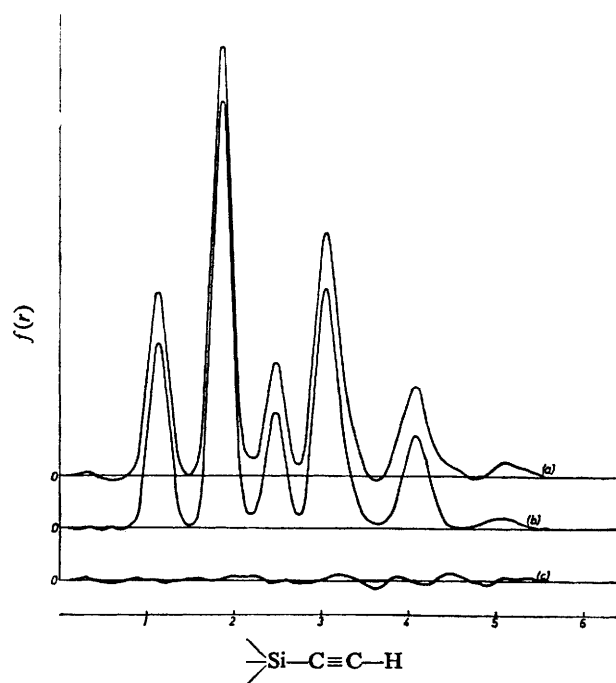


FIG. 4.—Radical distribution function of $(\text{CH}_3)_3\text{Si-C}\equiv\text{C-H}$; expt., (a); theor., (b); (a) - (b), (c).

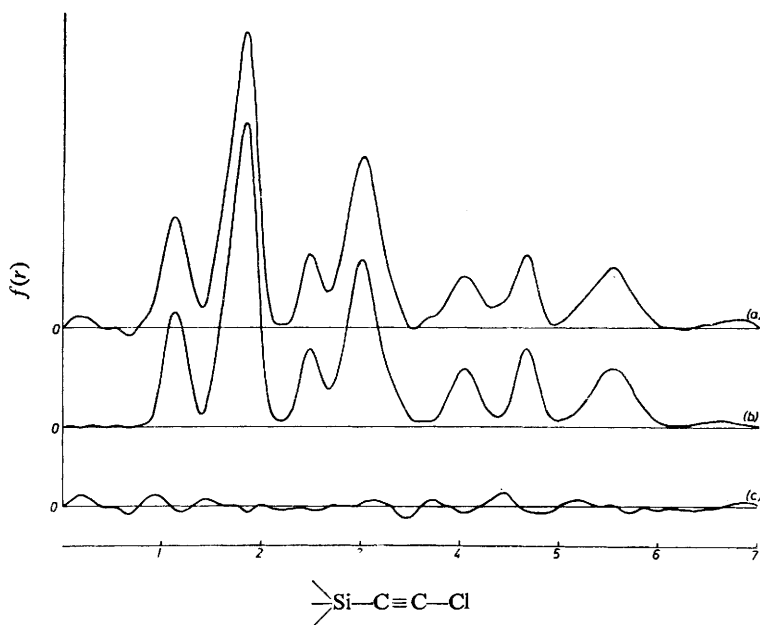


FIG. 5.—Radial distribution function of $(\text{CH}_3)_3\text{Si-C}\equiv\text{C-Cl}$; expt., (a); theor., (b); $(a)-(b)$, (c).

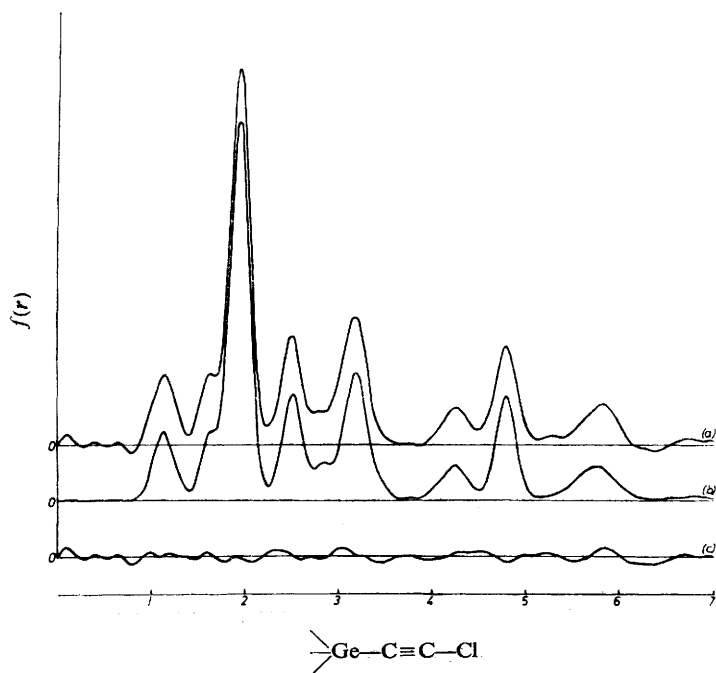


FIG. 6.—Radial distribution function of $(\text{CH}_3)_3\text{Ge-C}\equiv\text{C-Cl}$; expt., (a); theor., (b); $(a)-(b)$, (c).

The accelerating voltage was 45 to 46 kV. This voltage corresponds to a wave length of 0.0615 to 0.0604 Å. The wave length was calculated from the diffraction pattern of ZnO and the distances between the nozzle and the plate in the different positions. The experimental data were corrected and processed in the usual way.⁶ The resulting molecular intensity curves are shown in fig. 1*a*, 2*a* and 3*a*. The radial distribution curves obtained by Fourier inversion from the observed intensity curves are shown in fig. 4*a*, 5*a*, 6*a*.

Fig. 1-6 give also the theoretical curves (*b*) of the intensity functions and of the radial distribution functions together with the curves of the difference (*c*) between observed and theoretical curves. The theoretical curves have been calculated from the molecular data given in tables 2, 3 and 4. In fig. 7, 8 and 9 the results concerning

TABLE 2.—INTERATOMIC DISTANCES r_{ij} , BOND ANGLES AND MEAN AMPLITUDES l_{ij} OF $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$

	r_{ij} (Å)	l_{ij} (Å)
H—C≡	1.05 ± 0.008	0.055 ± 0.008
—C≡C—	1.20 ± 0.008	0.055 ± 0.008
≡C—Si	1.825 ± 0.006	0.065 ± 0.01
Si—C _m	1.865 ± 0.004	0.073 ± 0.01
C _m —H	1.100 ± 0.008	0.063 ± 0.01
Si...H	2.475 ± 0.002	0.077 ± 0.008
C _m ...C _m	3.018 ± 0.008	0.080 ± 0.02
Si...≡C	3.02 ± 0.01	0.079 ± 0.02
C _m ...C≡	3.04 ± 0.01	0.085 ± 0.02
H...C≡	2.27 ± 0.01	0.100 ± 0.02
C _m ...≡C	4.075 ± 0.006	0.100 ± 0.02
Si...H _{acet}	4.08 ± 0.01	0.073 ± 0.02
C _m ...H _{acet}	5.06 ± 0.01	0.183 ± 0.02

∠ C _m SiC _m	107°59'	
∠ HC _m H	108°25'	

TABLE 3.—INTERATOMIC DISTANCES r_{ij} , BOND ANGLES AND MEAN AMPLITUDES l_{ij} OF $(\text{CH}_3)_3\text{SiC}\equiv\text{C}-\text{Cl}$

	r_{ij} (Å)	l_{ij} (Å)
Cl—C	1.630 ± 0.005	0.060 ± 0.01
—C≡C—	1.210 ± 0.008	0.055 ± 0.008
≡C—Si	1.825 ± 0.008	0.065 ± 0.008
Si—C _m	1.855 ± 0.006	0.070 ± 0.008
C _m —H	1.095 ± 0.008	0.060 ± 0.01
Si...H	2.488 ± 0.005	0.077 ± 0.008
C _m ...C _m	3.040 ± 0.008	0.080 ± 0.02
Si...≡C	3.035 ± 0.01	0.077 ± 0.02
C _m ...C≡	2.993 ± 0.01	0.080 ± 0.02
Cl...≡C	2.850 ± 0.01	0.070 ± 0.015
C _m ...≡C	4.040 ± 0.01	0.100 ± 0.02
Si...Cl	4.672 ± 0.006	0.078 ± 0.01
C _m ...Cl	5.549 ± 0.006	0.190 ± 0.01

∠ C _m SiC _m	110°05'	
∠ HC _m H	106°21'	

TABLE 4.—INTERATOMIC DISTANCES r_{ij} , BOND ANGLES AND MEAN AMPLITUDES l_{ij} OF $(\text{CH}_3)_3\text{GeC}\equiv\text{C}-\text{Cl}$

	r_{ij} (Å)	l_{ij} (Å)
Cl—C≡	1.630 ± 0.005	0.060 ± 0.01
—C≡C—	1.215 ± 0.005	0.055 ± 0.01
≡C—Ge	1.930 ± 0.007	0.065 ± 0.01
Ge—C _m	1.960 ± 0.005	0.070 ± 0.01
C _m —H	1.095 ± 0.005	0.060 ± 0.008
Ge ... H	2.520 ± 0.005	0.077 ± 0.008
C _m ... C _m	3.180 ± 0.01	0.080 ± 0.02
Ge ... ≡C	3.150 ± 0.01	0.077 ± 0.02
C _m ... C≡	3.200 ± 0.01	0.080 ± 0.02
Cl ... ≡C	2.840 ± 0.01	0.070 ± 0.01
C _m ... ≡C	4.250 ± 0.007	0.100 ± 0.01
Ge ... Cl	4.775 ± 0.005	0.078 ± 0.01
C _m ... Cl	5.780 ± 0.02	0.190 ± 0.02

∠ C _m GeC _m	$108^{\circ}18'$	
∠ HC _m H	$111^{\circ}07'$	

the geometry of the molecules are shown. The diagrams show all the measured values. In table 2, 3, 4 the interatomic distances, the calculated bond angles and the mean amplitudes are given. The most interesting distances concern the question

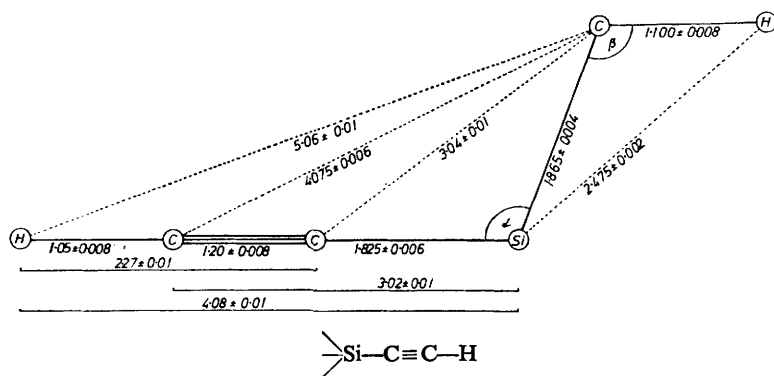


FIG. 7.—The interatomic distances of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{H}$.

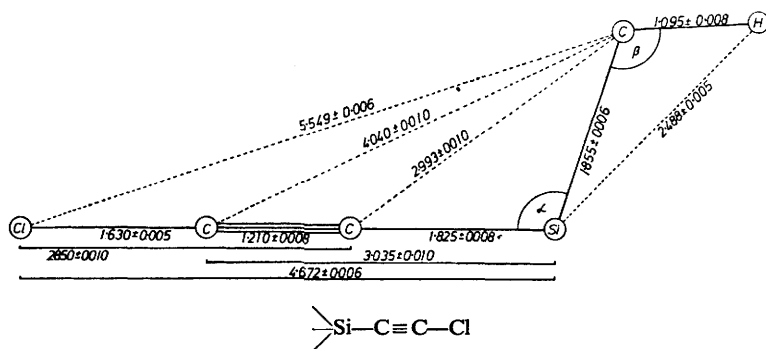


FIG. 8.—The interatomic distances of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{Cl}$.

TABLE 5.—BOND DISTANCES, FORCE CONSTANTS AND NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF MOLECULES OF TYPE $Z_3X-C\equiv C-Y$

	<i>d</i> (Å)			angle ZXZ	<i>f</i> (dyn cm ⁻¹)			<i>eQq</i> (MHz) ³⁵ Cl		
	Z—X	X—C≡	C≡C		C—Y	Z—X	X—C≡		C≡C	C—Y
H ₃ C—C≡C—H ⁷	1·105	1·459	1·206	1·056	108°39'	5·06	5·13	15·76	6·06	
H ₃ C—C≡C—Cl ⁸	1·117	1·458	1·207	1·637	108°8'	4·84	5·13	15·8	5·30	—79·6
(CH ₃) ₃ C—C≡C—H	1·529	1·498	1·210	1·056	110°40'	4·50	4·20	15·6	5·84	
(CH ₃) ₃ C—C≡C—Cl	1·525	1·468	1·210	1·637	110°9'	4·23	4·79	14·8	5·50	—78·29
H ₃ Si—C≡C—H ⁹	1·488	1·826	1·208	1·058	110°12'					
(CH ₃) ₃ Si—C≡C—H	1·865	1·825	1·200	1·050	107°59'	2·80	2·55	15·0	5·84	
(CH ₃) ₃ Si—C≡C—Cl	1·855	1·825	1·210	1·630	110°05'	2·75	2·24	13·9	5·94	—76·39
H ₃ Ge—C≡C—H ¹⁰	1·521	1·896	1·208	1·056	109°54'					
(CH ₃) ₃ Ge—C≡C—Cl	1·960	1·930	1·215	1·630	108°18'					—76·40

whether there are any correspondence between the physical behaviour and the mesomeric structures proposed by the chemists; these are the $\text{C}\equiv\text{C}$ bonds and the $\text{Si}-\text{C}\equiv$, $\text{Ge}-\text{C}\equiv$ and the $\equiv\text{C}-\text{Cl}$ bond distances. Table 5 gives our results relating to the force constants and nuclear quadrupole coupling constants. The table also

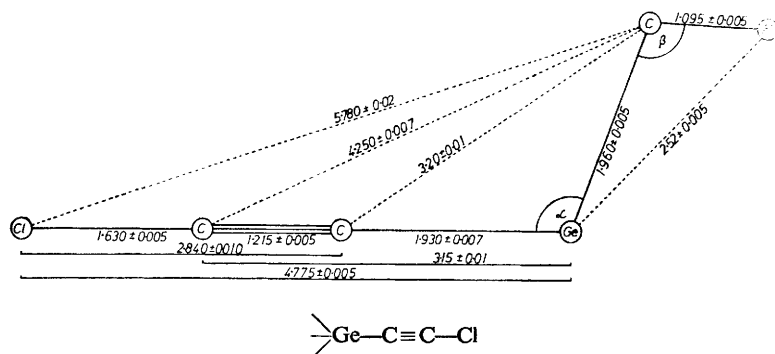


FIG. 9.—The interatomic distances of $(\text{CH}_3)_3\text{Ge}-\text{C}\equiv\text{C}-\text{Cl}$.

contains values, reported by other authors for molecules of a similar type.⁷⁻¹⁰ There are no significant differences, within the limit of error in the length of the $\text{C}\equiv\text{C}$ bond, between the molecules with two and four mesomeric structures. This is contrary to the behaviour of the force constants and the nuclear quadrupole coupling constants which show considerable differences. The $\text{Si}-\text{C}\equiv$ and $\equiv\text{C}-\text{Cl}$ bond lengths are in good agreement with the earlier measurements on similar molecules. The long distance of the $\text{Ge}-\text{C}\equiv$ bond is remarkable.

If the force constants and nuclear quadrupole coupling constants indicate the existence of the $pd-\pi$ -bond, then we must conclude that the geometry of molecules of the type $(\text{CH}_3)_3\text{X}-\text{C}\equiv\text{C}-\text{Y}$ will not be affected within the error limits of electron diffraction data, by this bond type.

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