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A STUDY OF SOME SPECTROSCOPIC PROPERTIES OF GROUP IVA ACETYLIDES

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Summary

Ionization and appearance potentials, proton NMR chemical shifts and characteristic vibrational stretching frequencies have been measured for $(CH_3)_3CC{\equiv}CH$, $(CH_3)_3SnC{\equiv}CH$, $(CH_3)_nSi(C{\equiv}CH)_{4-n}$, and $(CH_3)_nGe(C{\equiv}CH)_{4-n}$ where $n = 0$—3.

Analysis of these spectral results reveals strong influences from both the type of central atom and the number of acetylene groups, which may be explained by electronegativity changes and by the interaction of the π-orbitals of the unsaturated moiety with the unfilled higher orbitals of the central atom.

Introduction

Extensive research by Bock and co-workers [1—24] over the past five years has produced evidence for π-electron back-donation†, Si ← C_π, in many trimethyl substituted quinones, benzenes, xylenes, ethylenes, aryl ethers, butadienes, polyenes, naphthalenes, acetylenes, polyacetylenes, aryl ketones, pyridenes, aniline and *p*-phenylenediamine. Vertical ionization energies, characteristic vibrational frequencies, proton NMR signals, ESR spectra, half-wave reduction potentials and electronic transitions were measured for alkyl and silyl substituted compounds, and the data interpreted in terms of inductive polarization $+I(SiR_3) > +I(CR_3)$ and additional electron back-donation. In Part XII of their series, Bock and Seidl [12] were concerned with a single acetylene bond. Ionization potentials were measured for $(CH_3)_3CC{\equiv}CH$ and $(CH_3)_3SiC{\equiv}CH$ and related to back-donation in comparison to other acetylides.

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† By π-electron back-donation, sometimes called p_π—d_π bonding, is meant the interaction of the π-orbitals of the unsaturated moiety with unfilled *d*-orbitals of the central metal atom. A detailed discussion of this effect may be found in ref. 42.

In addition to the mass spectral work, some ^1H NMR data on monosilylacetylenes have been reported by Kraihanzel and Losee [25]. Chemical shift data for $(CH_3)_3SiC{\equiv}CH$ and $(CH_3)_2Si(C{\equiv}CH)_2$ were given and the existence of p_π—d_π bonding was discussed in relation to these data. Also Simmonin [26] reported the NMR data of the compounds $R_3MC{\equiv}CR'$ (R' = H, Me; M = Si, Ge, Sn).

Zeil and co-workers [27—30] determined the bond distances in $(CH_3)_3XC{\equiv}CH$ (X = C, Si, Ge, Sn, Pb) by microwave spectroscopy and electron diffraction techniques. In his more recent work [30] Zeil found the lengths of the C≡C bond to exhibit no significant differences from the corresponding bond lengths in the carbon compounds for $(CH_3)_3SiC{\equiv}CH$, $(CH_3)_3SiC{\equiv}CCl$ and $(CH_3)_3GeC{\equiv}CCl$. It was concluded that the length of the C≡C bond is insensitive to π-electron delocalization. A decrease in force constant was found for the C≡C bond.

West and Kraihanzel [31] discussed differences in the experimental and calculated vibrational frequencies of monosubstituted acetylenes $(CH_3)_3MC{\equiv}CH$ (M = C, Si, Sn) as being due to p_π—d_π bonding. Measured relative acid and base strengths by means of hydrogen bond studies in solutions containing dimethylacetamide and phenol also supported the hypothesis of back-bonding.

The purpose of the investigation reported here was twofold: To systematically study the spectroscopic properties of the series $(CH_3)_nM(C{\equiv}CH)_{4-n}$ where n = 0—3 and M = C, Si, Ge, Sn, and also to test further the extent of applicability of the well-substantiated theory of π-electron back-donation. Although several studies of the monoacetylides of Group IVA compounds have been published over the last decade [25—34], the only data available on compounds containing more than one acetylide group are from Kraihanzel and Losee's proton NMR chemical shift study of dimethyldiethynylsilane [25]. The following compounds have been used in our study: $(CH_3)_3CC{\equiv}CH$; $(CH_3)_nSi(C{\equiv}CH)_{4-n}$, n = 0—3; $(CH_3)_nGe(C{\equiv}CH)_{4-n}$, n = 0—3; $(CH_3)_3SnC{\equiv}CH$.

Experimental

Ionization potentials (*IP*) corresponding to a "vertical" excitation in the Franck—Condon scheme were measured on a Bendix Model 3012 time-of-flight mass spectrometer by a modified retarding potential difference technique [35]. A five-grid electron gun system [36] was utilized under the conditions stated in Table 1. The control grid pulse height was +15 and the DC bias zero volts. The electron voltage were measured on a Hewlett—Packard (Model 3440A) digital voltmeter and step curves recorded on a Honeywell Electronic-19 recorder. Values of repeated measurements deviated no more than 0.1 eV from the mean. Krypton (*IP* 14.00 eV) was the standard.

Proton magnetic resonance spectra of 0.1 molar 5% benzene/95% carbon tetrachloride solutions were measured with a Varian HA-60-IL NMR spectrometer. Proton shifts were measured as differences from either the tetramethylsilane (TMS) central peak or one of the sidebands generated by a Hewlett—Packard 200 AB audio oscillator. The calibration peak and the desired proton resonance were written five times on the 50 Hz scale (the calibration of which was checked before use). The chemical shift reported is either the number of

TABLE 1

EXPERIMENTAL CONDITIONS FOR THE 5-GRID ELECTRON GUN SYSTEM USED IN THE MODIFIED RETARDING POTENTIAL DIFFERENCE TECHNIQUE FOR MEASURING IONIZATION POTENTIALS.

Element	Bias
Filament	Variable (this determines electron energy)
Grid 1	Pulsed
Grid 2	—0.2 eV with respect to filament
Grid 3	—0.2 eV with respect to filament
Grid 4	Same as Grid 2
Grid 5	Ground
Chop voltage on Grid 3	—0.1 eV with respect to Grid 3 (this is the retarding voltage)

Hz added to the zero Hz reading from TMS or the peak to peak separation added or subtracted from the known audio sideband frequency reading.

Most of the infrared results were taken from the literature: $(CH_3)_3CC{\equiv}CH$ and $(CH_3)_3SiC{\equiv}CH$ were measured in the gaseous and liquid state from 4000—400 cm^{-1} with a Beckman IR-12 infrared spectrophotometer. The important absorptions were expanded by a factor of 10 to give frequency data accurate to ± 0.5 cm^{-1}.

Preparation and purification of compounds

The compounds were either purchased, donated or synthesized:

$(CH_3)_3CC{\equiv}CH$. Purchased from Farchan Research Laboratories.

$(CH_3)_3SiC{\equiv}CH$, $(CH_3)_2Si(C{\equiv}CH)_2$, $CH_3Si(C{\equiv}CH)_3$, $(CH_3)_2Ge(C{\equiv}CH)_2$, $CH_3Ge(C{\equiv}CH)_3$, $Ge(C{\equiv}CH)_4$. Donated by Dr. W. Davidsohn, U.S. Army Materials and Mechanics Research Center, Watertown, Massachusetts.

$Si(C{\equiv}CH)_4$. A 500 ml three necked flask equipped with stirrer, condenser and gas inlet tube was installed and flame dried under argon. SiF_4 was bubbled into a mixture of 5 g of $NaC{\equiv}CH$ and 250 ml of tetrahydrofuran. An exothermic reaction took place immediately, after which the flask temperature gradually cooled to room temperature. It was then assumed that the reaction had terminated. The reaction mixture was filtered, the tetrahydrofuran removed, and the remaining solid sublimed at room temperature to yield about 50 mg of $Si(C{\equiv}CH)_4$. The structure was established by mass spectrometric measurements.

$(CH_3)_3GeC{\equiv}CH$. A 1000 ml three necked flask equipped with a stirrer, condenser and gas inlet tube was installed and flame dried under argon. To a mixture of 12.0 g of $NaC{\equiv}CH$ and 500 ml of nitrobenzene, 38.2 g of distilled $(CH_3)_3GeCl$ was added and the mixture was stirred for 4h. The reaction mixture was then filtered and distilled. A 60.3% yield (21.5 g) was realized.

$(CH_3)_3SnC{\equiv}CH$. A 500 ml three necked flask equipped with magnetic stirrer, vented addition funnel, condenser and gas inlet tube was installed and flame dried under argon. To a mixture of 9.80 g of $NaC{\equiv}CH$ and 200 ml of dry pentane was slowly added a small portion of the 40.9 grams of $(CH_3)_3SnCl$ dissolved in 120 ml of pentane. Since no reaction took place the mixture was heated slightly but to no avail. When 5 ml of hexamethylphosphoramide $[(CH_3)_2N]_3P{=}O$ was added the reaction started as indicated by the commencement of refluxing with no external source of heat. The mixture was stirred for 16 h without refluxing and then it was refluxed over low heat for 6 more hours. Volatiles were pumped into a liquid nitrogen trap; the pentane was distilled off to leave about 3.06 g of pure $(CH_3)_3SnC{\equiv}CH$. Some unidentified white solid remained in the trap (m.p. 89—91°).

All compounds with the exception of the solid tetraacetylides were purified on an Aerograph Autoprep Model A-700 gas chromatograph using a QF-1 fluorosilicone column.

Results and discussion

Ionization and appearance potentials, ^1H NMR chemical shifts and vibrational frequencies have been measured for the compounds $(CH_3)_3CC{\equiv}CH$, $(CH_3)_3SnC{\equiv}CH$ and $(CH_3)_nM(C{\equiv}CH)_{4-n}$ where $n = 0$—3 and M = Si, Ge. The spectrometric results are presented and analyzed for trends as *(1)* the number of acetylene groups attached to a given central atom is increased and as *(2)* the central atom is changed for a given number of acetylene groups.

Number of acetylene groups

Spectral data for the silicon Group IVA acetylide series are presented in Table 2. Both the ionization potential and the chemical shift for the $(CH_3)_3$-$SiC{\equiv}CH$ compound agree well with previously reported values of Bock [12] [*IP* 10.14 ± 0.04 eV, and $\tau(C{\equiv}CH)$ 7.76 ppm]. From an analysis of the fragmentation processes taking place in the mass spectrometer ion source for these compounds [38] and from preliminary MO calculations we have carried out, it appears that the electron escaping in the ionization process comes primarily from the metal atom.

The steady increase in ionization energy as the number of acetylene groups is increased from 0 to 4 may be understood from the following consideration. The more electronegative *sp* acetylene carbon is replacing the sp^3 methyl carbon, thus increasing the molecule's hold on the outer electrons. Also, electrons from the π-orbitals of the acetylene group may be entering the outer orbitals (probably *d*-orbitals) of the silicon atom, i.e. the π-electron back-donation effect may also be contributing to the stabilization of the molecule. However,

TABLE 2

IONIZATION POTENTIALS, APPEARANCE POTENTIALS, CHEMICAL SHIFTS AND STRETCHING FREQUENCIES FOR THE SERIES $(CH_3)_nSi(C{\equiv}CH)_{4-n}$, WHERE $n = 0$—4

(Appearance potentials are reported for the parent compounds minus one methyl group.)

Compound	$(CH_3)_4Si$	$(CH_3)_3SiC{\equiv}CH$	$(CH_3)_2Si(C{\equiv}CH)_2$	$CH_3Si(C{\equiv}CH)_3$	$Si(C{\equiv}CH)_4$
Ionization Potential (eV)	9.99 ± 0.03	10.40 ± 0.02	10.85 ± 0.10	11.06 ± 0.03	11.34
Appearance Potential (eV)	10.63 ± 0.05	10.79 ± 0.04	12.05 ± 0.05	12.81 ± 0.07	
$\tau(C{\equiv}CH)$, (ppm)		7.77	7.61	7.51	
$\tau(CH_3)$, (ppm)	10.00	9.81	9.64	9.49	
$\nu(Si{-}C{\equiv})$, (cm^{-1})		555	595	632	534

one would expect this π-bonding effect to be less pronounced as the competition between the acetylene groups for the d-orbitals of the silicon increased. Therefore, the 0.4 and 0.5 eV increases in ionization potential as the first and second acetylene groups replace methyl, followed by 0.2 eV increases for the addition of the third and fourth acetylenes, are in reasonable accord with this theory.

Appearance potentials for the parent compound minus one methyl group reveal significant increases in the stability of the compound as the second and third acetylenes replace methyl groups, whereas the first acetylene group is less effective.

Proton NMR spectra of both acetylene and methyl protons shift steadily to lower fields as C≡CH groups are added. This observed deshielding of electrons further supports the explanation given above. Analysis of the infrared data in Table 2 is deferred.

Ionization and appearance potentials, chemical shifts and stretching frequencies were measured for members of the germanium series $(CH_3)_nGe(C{\equiv}CH)_{4-n}$, where n = 0—4. Results are summarized in Table 3. Trends observed are similar to those found in the silicon series, with the single exception of the appearance potential for $CH_3Ge(C{\equiv}CH)_3$.

The parent peak of the triacetylide member of the germanium series was too small to allow determination of its ionization potential. However, it seems reasonable to take the value of the appearance potential for the parent compound minus one methyl group as a good approximation to the ionization potential of $CH_3Ge(C{\equiv}CH)_3$. If one considers the ionization of this compound brought to a repulsive state, as in the neo-structure of paraffins [37], the ion should decompose immediately upon the removal of an electron and the lowest appearance potential of a fragment ion should be equal to or greater than the ionization potential of the parent molecule. In this case the $Ge(C{\equiv}CH)_3^+$ ion is the most stable ion observed [38] and thus has the lowest appearance potential of the fragment ions. Further support for this argument is the fact that the observed value of the appearance potential for the $Ge(C{\equiv}CH)_3^+$ ion fits neatly into the ionization potential series (see Table 3).

TABLE 3

IONIZATION POTENTIALS, APPEARANCE POTENTIALS, CHEMICAL SHIFT AND STRETCHING FREQUENCIES FOR THE SERIES $(CH_3)_nGe(C{\equiv}CH)_{4-n}$, WHERE n = 0—4.

(Appearance potentials are reported for the parent compound minus one methyl group)

Compound	$(CH_3)_4Ge$	$(CH_3)_3GeC{\equiv}CH$	$(CH_3)_2Ge(C{\equiv}CH)_2$	$CH_3Ge(C{\equiv}CH)_3$	$Ge(C{\equiv}CH)_4$
Ionization Potential (eV)	9.56 ± 0.06	9.77 ± 0.04	10.57 ± 0.07	[10.74 ± 0.05][a]	11.04 ± 0.05
Appearance Potential (eV)	10.07 ± 0.07	10.56 ± 0.07	10.94 ± 0.04	10.74 ± 0.05	
$\tau(C{\equiv}CH)$ (ppm)		7.94	7.79	7.71	7.60
$\tau(CH_3)$ (ppm)	9.86	9.65	9.42	9.22	
$\nu(Ge{-}C{\equiv})$ (cm^{-1})		497	530	542	516

[a] C.f. text for derivation of this value.

TABLE 4

VIBRATIONAL FREQUENCIES (CM^{-1}) FOR STRETCHING MODES

(g = gas, l = liquid, s = CCl_4 solution)

Compound		$H{-}C{\equiv}$	$C{\equiv}C$	$M{-}C{\equiv}$	$M{-}CH_3$	Ref.
$(CH_3)_3CC{\equiv}CH$	g	3330	2117, 2147			
	s	3312	2105, 2135			
$(CH_3)_3SiC{\equiv}CH$	g	3313	2047	557, a_1	654, a_1	
	l	3287	2035	555, a_1	697, e ; 650, a_1	
$(CH_3)_2Si(C{\equiv}CH)_2$	g	3314	2052		700, a_1 ; 792, b_2	40
	l	3284	2041	595, a_1; ? b_1	701, a_1 ; 794, b_2	
$CH_3Si(C{\equiv}CH)_3$	g	3314.5	2057.5	663, e	761 and 775, a_1	40
	l	3282	2046	605, a_1; 658, e	756, a_1	
$Si(C{\equiv}CH)_4$	g	3315	2062	708 or 687, f_2		41
	s	3298	2053	534, a_1		
$(CH_3)_3GeC{\equiv}CH$	g	3310	2040	498, a_1	620, e	33
	l	3290	2030	497, a_1	518, a_1 ; 616, e	
$(CH_3)_2Ge(C{\equiv}CH)_2$	g	3313	2049	522, b_1	599, a_1 ; 621, b_2	40
	l	3283	2041	538, a_1; 521, b_1	598, a_1 ; 622, b_2	
$CH_3Ge(C{\equiv}CH)_3$	g	3314	2055.5	523, a	619.5, a_1	40
	l	3282	2046	562, a_1; 522, e	624, a_1	
$Ge(C{\equiv}CH)_4$	g	3315.5	2062	523, f_2		41
	s	3298	2057	507, a_1		
$(CH_3)_3SnC{\equiv}CH$	g	3304	2013		517, a_1	33
	l	3280	2005	432, a_1	538	
$(CH_3)_2Sn(C{\equiv}CH)_2$	g	3308	2029	448, b_1	532, a_1; 568, b_2	40
	l	3276	2016	454, a_1; 445, b_1	532, a_1; 552, b_2	
$CH_3Sn(C{\equiv}CH)_3$	g	3305	2018		540, a_1	40
$Sn(C{\equiv}CH)_4$	g	3311	2043	504 or 447, f_2		41
	s	3293	2037			

Infrared spectroscopic data for the stretching frequencies of the $H{-}C{\equiv}$, $C{\equiv}C$, $M{-}C{\equiv}$ and $M{-}CH_3$ bonds are summarized in Table 4. Vibrational frequencies for $(CH_3)_3CC{\equiv}CH$ and $(CH_3)_3SiC{\equiv}CH$ have been measured; all other values have been gathered from the literature. Only the a_1 band at 595 cm^{-1} could be found for $(CH_3)_2Si(C{\equiv}CH)_2$. The value for the b_1 band would have a lower frequency than the a_1 fundamental and would be expected to have the same value as the analogous germanium compound. This would yield an average of 586 cm^{-1} which is still well above the value of 555 cm^{-1} for $(CH_3)_3SiC{\equiv}CH$. Averages were computed for molecules with more than one stretching frequency. Liquid absorption values are normally used in the following discusion but solution values are used for $Si(C{\equiv}CH)_4$ and $Ge(C{\equiv}CH)_4$.

As the number of acetylene groups attached to the metal atom is increased from 1 to 4 the frequency of the $M{-}C{\equiv}$ stretch increases significantly, which suggests that the double-bond character of the $M{-}C{\equiv}$ bond is enhanced (c.f. also Tables 2 and 3). However, this trend is broken by the $M{-}C{\equiv}$ (a_1) stretching frequency for $M(C{\equiv}CH)_4$, which drops to the lowest value in the silicon series and to a value between the mono- and di- acetylide for the germanium analog.

TABLE 5

IONIZATION POTENTIALS, APPEARANCE POTENTIALS AND CHEMICAL SHIFTS FOR THE SERIES SERIES $(CH_3)_3MC{\equiv}CH$, M = C, Si, Ge, Sn

(Appearance potentials are for the species $(CH_3)_2MC{\equiv}CH^+$. Values in parentheses are those of Bock [12].)

$(CH_3)_3MC{\equiv}CH$	Ionization pot. (eV)	Appearance pot. (eV)	$\tau(C{\equiv}CH)$, (ppm)
C	10.67 ± 0.02 (10.31 ± 0.04)	10.76 ± 0.06	8.09 (8.08)
Si	10.40 ± 0.03 (10.14 ± 0.04)	10.79 ± 0.04	7.77 (7.76)
Ge	9.77 ± 0.07	10.56 ± 0.07	7.94
Sn		9.84 ± 0.08	8.00

This anomaly may be a result of differences in bond-stretching force constants, since the symmetry is changing rather drastically.

The frequency of the $M{-}CH_3$ stretch decreases as the number of methyl groups attached to the central atom increases, a fact which lends support to the electronegativity effect.

An analysis of trends for the C≡C stretch frequencies does not appear to favor the π-bond back donation theory. According to this theory one would expect the $M \leftarrow C_\pi$ effect to increase, although at a decreasing rate, as the number of acetylene groups is increased. This was seen above in connection with ionization potentials. Thus the M—C≡ bond would be enhanced at the expense of a weakened C≡C bond with consequently lower C≡C stretch frequencies. However, the contrary is observed: in the silicon, germanium and tin series the frequency of the C≡C stretch increases as acetylenes are added (Table 4). Similarly the H—C≡ stretch in the gaseous state increases with added acetylenes. An explanation of these trends fails us.

Change of central atom

Trends in ionization and appearance potentials and in chemical shifts [$\tau(C{\equiv}C)$] for the series $(CH_3)_3MC{\equiv}CH$, where M = C, Si, Ge and Sn, may be seen in Table 5. A study of the NMR data leads one to expect an increase in the vertical ionization potential as the central atom changes from carbon to silicon and then a decrease as M changes to Ge and then Sn. (It was not possible to measure the ionization potential of the tin analog.) However, the ionization potential of $(CH_3)_3SiC{\equiv}CH$ is 0.3 eV *lower* than the carbon analog, as was also observed by Bock [12].

From another viewpoint the observed trend in ionization potentials is quite reasonable when both the decreasing electronegativity (on the Pauling scale 2.6 for C, 1.9 for Si and 2.0 for Ge and Sn) and the greatly increasing atomic radii down the series are considered (0.77 for C, 1.17 for Si, 1.22 for Ge and 1.4 Å for Sn). In this case the anomalous chemical shift for the carbon analog remains unexplained.

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