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Structures and Ionization Energies of Some Bis- and Tris(3,4-dimetala-1-butyne-1,4-diyl)s Containing Group 14 Elements as Key Metal Atoms: Tetragermacycloocta-1,5-diyne, Hexasilacyclododeca-1,5,9-triyne, Hexagermacyclododeca-1,5,9-triyne, and Related Compounds

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By X-ray crystallographic analysis, the molecular structure of 3,4,7,8-tetragermacycloocta-1,5-diyne **1b** has been established to be planar and quite similar to that of silicon analog 3,4,7,8-tetrasilacycloocta-1,5-diyne **1a**. The detailed comparison of structures of cyclic acetylene analogs including a group 14 element shows that ring strain induced by the ethynylene units may be released in a different manner by the carbocycle and by its group 14 metalloid analogs. In contrast to cycloocta-1,5-diynes, structures of the higher homologs, 3,4,7,8,11,12-hexasilacyclododeca-1,5,9-triyne **2a** and 3,4,7,8,11,12-hexagermacyclododeca-1,5,9-triyne **2b** were determined by X-ray crystallographic analyses to adopt a chair-like conformation. Ionization energies of these 3,4-dimetala-1-butyne-1,4-diyls in condensed phase were obtained by photoelectron spectroscopic methods.

The chemistry of macrocyclic oligoalkynes has been an area of active research in recent years, and their characteristic electronic properties are discussed actively.[1—12] Earlier we developed a unique cyclic acetylene system, a 3,4-disila-1-butyne-1,4-diyl[13—19] having alternating C–C π and Si–Si σ bonds in the ring. In the ring system, especially 3,4,7,8-tetrasilacycloocta-1,5-diyne **1a**, the geometrical arrangement of these two kinds of bonds as well as the orbital energy requirement is ideally suited to a strong through-bond interaction and this causes the σ orbital level of the Si–Si bond to be destabilized substantially. Moreover, recently we have newly prepared and characterized germanium analogs of 3,4-disila-1-butyne-1,4-diyl **1a**, namely, 3,4,7,8-tetragermacycloocta-1,5-diyne **1b** and 3,4-disila-7,8-digermacycloocta-1,5-diyne **1c**.[20,21] Their photoelectron and UV spectral properties clearly indicate that germanium analogs **1b** and **1c** have basically similar electronic characteristics to that of the silicon analog **1a**. However, regarding their chemical properties, because of the lower ionization energy (*IE*) and the weaker bond strength of the Ge–Ge σ bond, the germanium analog is more reactive toward electrophiles. Thus, in dichloromethane containing a catalytic amount of tetracyanoethylene, **1c** undergoes oligomerization to give its higher homologs, such as 3,4,7,8,11,12-hexagermacyclododeca-1,5,9-triyne **2b** and 3,4,7,8,11,12,15,16-octagermacyclohexadeca-1,5,9,13-tetrayne **3b** (Chart 1).[20,21] In this paper we describe the

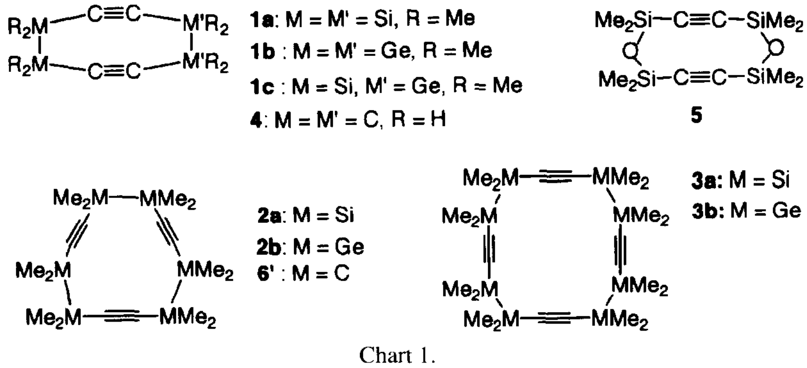


Chart 1.

Table 1. Crystal Data, Experimental Condition, and Details of Refinements

	1b	**2a**	**2b**
Crystal data			
Chemical formula	$C_{12}H_{24}Ge_4$	$C_{18}H_{36}Si_6$	$C_{18}H_{36}Ge_6$
Mr	458.67	421.01	688.01
Cell setting	Monoclinic	Trigonal	Trigonal
Space group	$P2_1/n$	$R\bar{3}c$	$R\bar{3}c$
a/Å	18.700(9)	12.6500(10)	12.882(2)
b/Å	6.364(2)	12.6500(10)	12.882(2)
c/Å	7.811(3)	31.251(5)	31.099(4)
β/°	91.42(4)	90	90
V/Å^3	929.3(6)	4330.9(8)	4469.3(11)
Z	2	6	6
D_x/Mg m^{-3}	1.639	0.969	1.534
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
λ/Å	0.71073	0.71073	1.54184
No. of reflections for cell parameters	25	25	24
θ range /°	16.4—17.5	16.1—17.0	28.1—34.9
μ/mm^{-1}	6.386	0.289	6.817
Temperature/K	293	293	293
Crystal form	Plate	Prism	Prism
Crystal size/mm	0.45 × 0.40 × 0.30	0.30 × 0.25 × 0.18	0.38 × 0.30 × 0.25
Color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC4
Data collection method	$2\theta-\omega$ scan	$2\theta-\omega$ scan	$2\theta-\omega$ scan
Scan width	$1.35+0.5\tan\theta$	$1.30+0.5\tan\theta$	$1.25+0.4\tan\theta$
Scan speed/° min^{-1}	8	4	4
Absorption correction	Numerical integration	Numerical integration	Numerical integration
T_{min}—T_{max}	0.146—0.256	0.954—0.967	0.144—0.321
No. of reflections			
Measured	2287	1059	878
Independent	2133	1047	833
With $I>2\sigma(I)$	1435	606	800
R_{int}	0.0253	0.0982	0.0235
θ_{max}/°	27.50	27.49	64.98
Range of h, k, l	$-24\leq h\leq 24, 0\leq k\leq 8, 0\leq l\leq 10$	$-14\leq h\leq 0, 0\leq k\leq 16, 0\leq l\leq 40$	$-12\leq h\leq 0, -13\leq k\leq 0, 0\leq l\leq 36$
Standard reflections	800, 020, 004	036,6−30,0−28	036,1−12,−102
Frequency of standard reflections	100	100	50
Intensity decay /%	4.98	4.29	3.96
Decay correction	Polynominal fitting	Polynominal fitting	Polynominal fitting
Refinement			
Refinement on	F^2	F^2	F^2
R ($F^2>2\sigma(F^2)$)	0.0448	0.0467	0.0428
R_w(all reflections)	0.1306	0.1195	0.1278
S	1.046	0.981	1.309
No. of reflections used in refinement	2133	1047	833
No. of parameters	86	44	38
H-atom treatment	Riding model	Riding model	Riding model with constrant on U_{iso}
Weight scheme[a]			
a, b	0.0670, 0.5829	0.0539, 0.000	0.058, 17.9822
$(\Delta/\sigma)_{max}$	0.000	0.000	0.001
$(\Delta/\rho)_{min}$,$(\Delta/\rho)_{max}$/eÅ^{-3}	−0.670,0.714	−0.165,0.206	−0.337,0.705
Extinction method	SHELXL	SHELXL	SHELXL
Extinction coefficient	0.0009(9)	0.0002(2)	0.00015(3)

[a] $w = 1/[\sigma^2(F^2)+(aP)^2+bP]$, where $P = (F_o^2+2F_c^2)/3$.

molecular structure of **1b** determined by the X-ray analysis together with those of **2b** and silicon analog **2a**. In addition, *IE*s of these sila- and germacyclic acetylenes **1a**, **1b**, **1c**, **2a**, **2b**, **3a**, and **3b** have been measured by the photoelectron spectroscopic method in the condensed phase.

Experimental

Materials. 3,4,7,8-Tetragermacycloocta-1,5-diyne **1b**, 3,4,7,8,11,12-hexasilacyclododeca-1,5,9-triyne **2a**, and 3,4,7,8,11,12-hexagermacyclododeca-1,5,9-triyne **2b** were prepared according to the reported methods.[1—3,20,21] The crystals of **1b** for the X-ray analysis were obtained by recrystallization from benzene and those of **2a** and **2b** were recrystallized from *n*-hexane.

X-Ray Structure Determination. The crystal data, as well as details concerning the data collection and the structure refinement are listed in Table 1. Intensity data were collected using Rigaku AFC-4 and AFC-5R diffractometers with graphite monochromators. Absorption corrections were applied numerically. Decay corrections were applied by the polynomial fitting of intensities of standard reflections. The structures were solved using the program SAPI91.[22] Hydrogen atoms were located geometrically, and refined by the riding model with U_{iso} for **1b** and **2a** and with constrained U_{iso} for **2b**. The structures were refined using a full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen. The final *R* values were 0.0448, 0.0467, and 0.0428 for 1435, 606, and 800 reflections with $I_0 > 2\sigma(I)$ for **1b**, **2a**, and **2b**, respectively. The final atomic parameters are given in Table 2.[23] Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[24] All computations were performed using the programs teXsan,[25] SHELXL-97,[26] and ORTEP II.[27]

Photoelectron Spectroscopy. The UV source (7.71 eV) emitted by dc glow discharge (1 kW, 200 mA) in pure hydrogen gas. The samples were prepared by casting thin films on small copper disc substrates. The noise current in this system can be diminished to 2×10^{-15} A. The inside of the collector is coated with a gold thin film.[28]

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors (U_{eq}) for Non-H Atoms

$$U_{\mathrm{eq}} = 1/3\sum_i\sum_j U_{ij}a_ia_j\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

Atom	*x*	*y*	*z*	U_{eq}/Å^2
(**1b**)				
Ge1	0.09970(4)	0.14132(11)	0.23872(8)	0.0469(2)
Ge2	0.11679(3)	0.24474(11)	−0.05676(8)	0.0454(2)
C11	0.0148(4)	−0.0285(11)	0.2234(8)	0.0514(16)
C12	0.0865(5)	0.3788(14)	0.3905(11)	0.074(2)
C13	0.1780(5)	−0.0330(16)	0.3271(13)	0.087(3)
C21	0.0370(4)	0.1220(10)	−0.1783(8)	0.0484(15)
C22	0.1151(4)	0.5481(12)	−0.0879(10)	0.0638(19)
C23	0.2037(4)	0.1241(13)	−0.1478(12)	0.072(2)
(**2a**)				
Si1	0.08323(7)	0.29482(7)	0.22671(3)	0.0545(3)
C1	0.1755(2)	0.2269(2)	0.24384(9)	0.0566(7)
C2	0.1773(4)	0.4646(3)	0.23090(16)	0.0924(12)
C3	0.0333(4)	0.2463(5)	0.17043(11)	0.0971(13)
(**2b**)				
Ge1	0.08339(6)	0.29655(6)	0.22544(2)	0.0650(4)
C1	0.1792(5)	0.2296(5)	0.24378(19)	0.0679(14)
C2	0.1794(7)	0.4707(6)	0.2290(3)	0.103(2)
C3	0.0323(9)	0.2397(10)	0.1674(2)	0.112(3)

Results and Discussion

The ORTEP drawings of **1b** and **2a** with the atomic numbering scheme are shown in Figs. 1 and 2, respectively. The molecular structure of **2b** is similar to that of **2a**. The bond distances and angles are given in Tables 3 and 4. Selected interatomic distances and bond angles of **1b**, **2a**, **2b**, and some cyclooctadiyne and cyclododecatriyne derivatives are listed in Table 5.

Structure of 1b. The molecules of **1b** have a crystallographic center of symmetry at the center of an 8-membered ring. The cyclooctadiyne ring is almost planar, as is that of its silicon analog **1a**.[13] In contrast, 4,9-dioxa-3,5,8,10-tetrasilacyclodeca-1,6-diyne **5**, oxygenation product of **1a**, has a chair-like conformation.[29] The C≡C bond length is 1.184(9) Å, which is almost the same length as those of **1a** (1.183 Å) and other cyclic acetylenes (Table 5). The Ge1–Ge2

Table 3. Bond Lengths (*l*) and Angles (*θ*) of **1b**

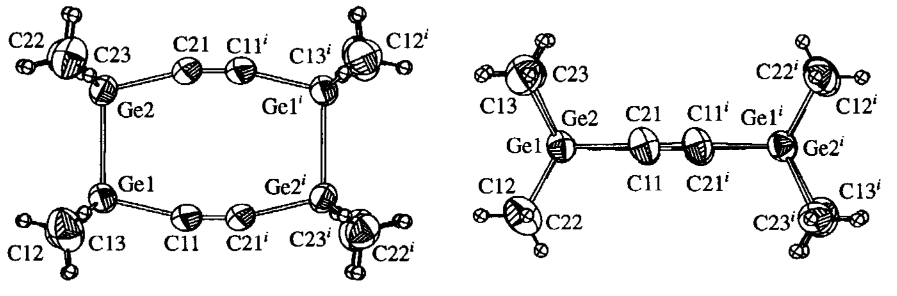
	l/Å		*l*/Å
Ge1–Ge2	2.4288(13)	Ge2–C22	1.946(8)
Ge1–C11	1.921(7)	Ge2–C23	1.948(7)
Ge1–C12	1.940(8)	C11–C21^i	1.184(9)
Ge1–C13	1.950(8)		
Ge2–C21	1.915(6)		
	θ/°		*θ*/°
C11–Ge1–C12	111.0(4)	C21–Ge2–C23	107.8(3)
C11–Ge1–C13	108.3(4)	C22–Ge2–C23	110.9(4)
C12–Ge1–C13	109.5(4)	C21–Ge2–Ge1	103.97(18)
C11–Ge1–Ge2	102.77(18)	C22–Ge2–Ge1	112.7(2)
C12–Ge1–Ge2	113.0(3)	C23–Ge2–Ge1	111.8(3)
C13–Ge1–Ge2	112.0(3)	C21^i–C11–Ge1	166.1(5)
C21–Ge2–C22	109.4(3)	C11^i–C21–Ge2	167.1(5)

Symmetry code *i*: −*x*, −*y*, −*z*.

Table 4. Bond Lengths (*l*) and Angles (*θ*) of **2a** and **2b**[a)]

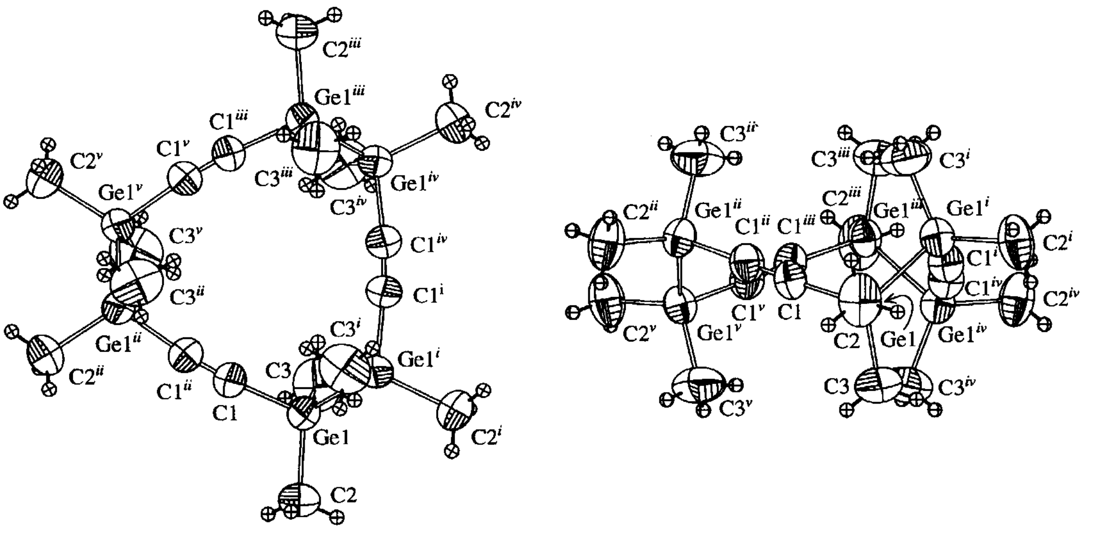
	2a *l*/Å	**2b** *l*/Å
M1–M1^i	2.3333(16)	2.4074(13)
M1–C1	1.841(3)	1.912(6)
M1–C3	1.866(4)	1.935(7)
M1–C2	1.869(3)	1.949(7)
C1–C1^{ii}	1.190(5)	1.190(11)
	θ/°	*θ*/°
C1–M1–M1^i	104.34(9)	104.03(18)
C3–M1–M1^i	111.04(16)	111.3(3)
C2–M1–M1^i	112.80(15)	112.8(3)
C1–M1–C3	108.03(17)	106.4(3)
C1–M1–C2	109.16(16)	108.7(3)
C3–M1–C2	111.1(2)	112.9(4)
C1^{ii}–C1–M1	174.84(15)	174.2(2)

a) M means Si and Ge for **2a** and **2b**, respectively. Symmetry code *i* : −*x*, *y*−*x*, 1/2−*z*; *ii* : *y*, *x*, 1/2−*z*.



(a) (b)

Fig. 1. ORTEP drawings with the atom-numebering of **1b**. The thermal ellipsoids for non-hydrogen atoms are drawn at 50% probability and the hydrogen atoms are drawn as spheres with a radius of 0.1 Å. (a) Top view and (b) projection viewed along the 8-membered ring. Symmetry code *i*: $-x$, $-y$, $-z$.



(a) (b)

Fig. 2. ORTEP drawings with the atom-numbering of **2b**. The thermal ellipsoids for non-hydrogen atoms are drawn at 50% probability and the hydrogen atoms are drawn as spheres with a radius of 0.1 Å. (a) Top view and (b) projection viewed along the 12-membered ring. Symmetry code *i*: $-x$, $y-x$, $1/2-z$; *ii*: y, x, $1/2-z$; *iii*: $x-y$, $-y$, $1/2-z$; *iv*: $-y$, $x-y$, z; *v*: $y-x$, $-x$, z.

Table 5. Comparison of the Interatomic Distances (l/Å) and Bond Angles (θ/°) for Cyclooctadiynes (**1a**, **1b**, and **4**) and Cyclododecatriynes (**2a**, **2b**, and **6**)

	1a$^{a)}$	**1b**	**4**$^{b)}$	**2a**	**2b**	**6**′(**6**)$^{c)}$
M–M	2.360	2.429	1.530	2.333	2.407	1.576(1.575)
M–C_{sp} $^{d)}$	1.841	1.918	1.459	1.841	1.912	1.455(1.455)
C≡C$^{d)}$	1.183	1.184	1.185	1.190	1.190	1.193(1.192)
M–M–C_{sp} $^{d)}$	103.9	103.4	110.8	104.3	104.0	109.4(112.1)
M–C≡C$^{d)}$	166.1	166.6	159.1	174.8	174.2	177.1(177.2)
C···C$^{e)}$	3.246	3.317	2.569	—	—	—

a) Refs. 13, 14, and 15. b) Ref. 29. c) Calculated by MOPAC-PM3 method.[38] d) Averaged values if two or more values exist in their strucrtures. e) Averaged transannular distances between C_{sp} and C_{sp}.

bond length of 2.4288(13) Å and the transannular distance, C11···C12, of 3.317(9) Å are much longer than those of cycloocta-1,5-diyne **4**,[30] but are only a little longer than those of **1a** by about 0.07 Å. These differences correspond to the differences of atomic radii. The M–M bond distances of **1a** and **1b** are elongated only by 0.03 Å as compared with the corresponding distances[31] of disilane (2.331 Å) and digermane (2.403 Å), respectively. The bond angles of M–C≡C in **1b** are 166.1(5) and 167.1(5)°. These values are comparable to that of **1a**, and the deviations from the linear bonds in sila- and germa-cyclooctadiynes are much less than that of carbon analog **4** (159.1°). These results show that the ring strain is released in different ways in these two types of cyclic acetylenes, cyclooctadiyne **4** and its higher group 14 element analogs **1a** and **1b**. Thus the carbon analog **4** releases the ring strain mainly by changing the bond angles (C≡C–C), in contrast to silicon and germanium analogs **1a** and **1b** in which the ring strains are released by the elongation of the M–M bond length with less deviations from linear M–C≡C bonds.

In crystals there are no significant intermolecular interactions, except for van der Waals' interactions.

Structures of 2a and 2b. The crystals of **2a** and **2b** are isomorphous to each other. The molecule has a crystallographic symmetry of $\bar{3}$. The molecules of **2a** and **2b** exist in chair-like conformations with almost linear fragments M–C≡C–M with the Ge1–C1–C1^{ii} angle of 174.84(15)° for **2a** and Si1–C1–C1^{ii} of 174.2(2)° for **2b** (*ii* is symmetry code, see Table 4). The bond lengths of M–M are 2.3333(16) and 2.4074(13) Å for **2a** and **2b**, respectively. These values are essentially the same as those of digermane and disilane.[31] As far as we are aware, no structural analysis of the carbon analog, cyclododeca-1,5,9-triyne (**6**)[32—37] or 3,3,4,4,7,7,8,8,11,11,12,12-dodecamethylcyclododeca-1,5,9-triynes (**6′**) has been reported, so the geometry of these compounds was obtained by means of MOPAC-PM3[38] method and the optimized conformation of **6′** was calculated to be chair-like as given in Fig. 3. To compare structural characteristics of these homologous cycles **6′** (**6**), **2a**, and **2b**, some bond lengths and angles are also summarized in Table 5. These structural features obtained for **2a** and **2b** suggest that distortion from planarity relieves the angle strain of the planar structures in **1a** and **1b**.

In crystals there are no significant intermolecular interactions, except for van der Waals' interactions.

Ionization Energies (*IE*s) by Photoelectron Spectroscopy in the Vacuum Ultraviolet Region. One of the intriguing properties of the 3,4-dimetala-1-butyne-1,4-diyl is its ability to show low *IE*.[20,21] Especially, bis(3,4-disila-1-butyne-1,4-diyl) **1a** gives a peak at 8.18 eV in its gas-phase photoelectron spectrum (cf. hexamethyldisilane 8.69 eV).[16,39] This can be readily ascribed to the planar geometry of **1a** which allows extremely efficient orbital overlap between Si–Si σ bond and C–C π bonds, as mentioned. In the 3,4-dimetala-1-butyne-1,4-diyl, the electronic properties such as *IE* are expected to be sensitive to the geometry of the ring system. In fact, bis(3,4-disila-1-butyne-1,4-diyl) **1a** shows lower *IE* in gas phase than that of tris(3,4-digerma-1-butyne-1,4-diyl) **2b**, which accommodates a chair-like conformation as shown in Fig. 2. Since in addition to **1a** and **1b**, the structures of higher homologs **2a** and **2b** were determined, *IE*s of all 3,4-dimetala-1-butyne-1,4-diyls obtained so far were measured under the same conditions, namely, in solid state by a retarding-field analyzer.[40] Figure 4 shows a typical photoelectron energy distribution curve (EDC) for the cast film of bis(3,4-disila-1-butyne-1,4-diyl) **1a** under the illumination photon energy (7.71 eV). The values of the retarding potential were plotted on the abscissa. The total photocurrent was also recorded on the chart simultaneously. From the photoelectron energy distribution of Fig. 4, the values of stopping voltage (V_0) and the saturation voltage (V_s) of the retarding potential for photoelectron were obtained. V_0 and V_s correspond to the collector voltage and the contact potential difference, respectively. From V_0 and V_s, the work function (φ) and the threshold energy (E_{th}) are estimated as $\varphi = \varphi_c - eV_s$, $E_{th} = h\nu - e(V_s - V_0)$, where φ_c is the work function of the collector, Aquadag.[40] The E_{th} values obtained are summarized in Table 6 and are lower than those observed from vertical *IE*s derived from gas-phase He I photoelectron spectra as shown.[16,20,21] Similar trends on *IE* values of oligogermanes and polygermanes are reported.[41,42] Although the errors inherent in the measurement of *IE*s in the solid are around 5 per cent,[40] close inspection of the table implies that as in the gas phase bis(3,4-dimetala-1-butyne-1,4-diyl)s **1a**—**c** having planar structures show lower *IE* values than those of their higher homologs **2a**, **b** and **3a**, **b**.

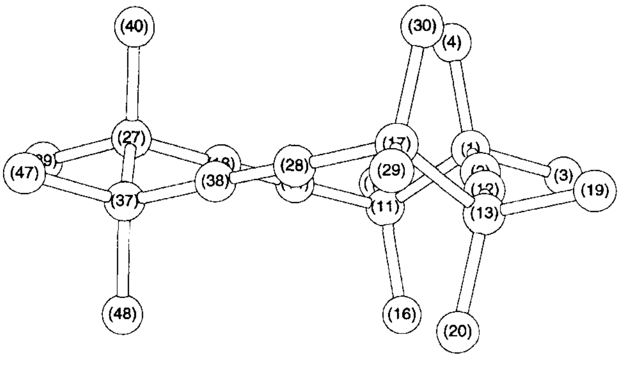


Fig. 3. MOPAC-PM3 optimized structure of **6′**. Hydrogen atoms are omitted for clarity.

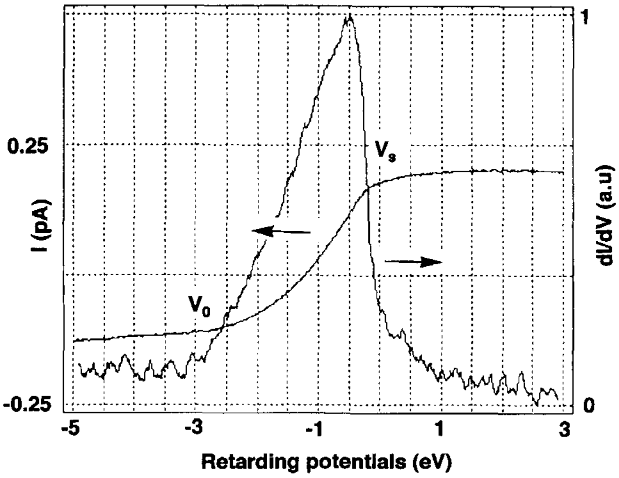


Fig. 4. The EDC for 3,4,7,8-tetrasilacycloocta-1,5-diyne **1a**: The current–voltage characteristics curve and its derivative for an incident photon energy of 7.71 eV.

Table 6. Ionization Energies (*IE*/eV) of Oligo(3,4-dimetala-1-butyne-1,4-diyl)s **1a**, **1b**, **1c**, **2a**, **2b**, **3a**, and **3b** in Condensed Phase

Compd	*IE*/eV	Compd	*IE*/eV	Compd	*IE*/eV
1a	4.91 (8.18)[a)]	**2a**	4.93 (8.45)[b)]	**3a**	5.00
1b	4.95 (8.00)[a)]	**2b**	4.99	**3b**	5.06
1c	4.95 (8.15)[a)]				

a) In vapor phase.[20,21] b) In vapor phase.[16]

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