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Polycarbodiimidogermylene: synthesis, characterization, properties and theoretical studies

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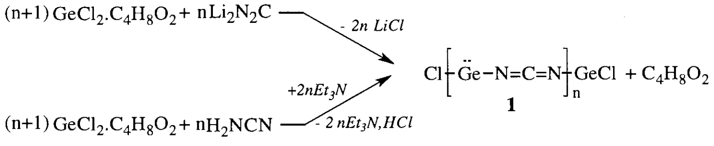
Abstract

Polycarbodiimidogermylene was prepared by transmetallation between dichlorogermylene, dioxane (**I**) and dilithium cyanamide, by transamination between bis(triethylgermyl)carbodiimide and (**I**), or by dehydrochloration between (**I**) and carbodiimide in the presence of triethylamine. The germylene structure was confirmed by its reactivity with 3,5-di-*t*-butylorthocatechol, which preserves the germylene structure, and with 3,5-di-*t*-butylorthoquinone, which leads to the expected spirogermane. The carbodiimide form was evident by its infrared spectrum, in agreement with DFT/B3LYP calculations. Geometry optimizations of isomers of the carbodiimide and cyanamide forms for $ClGe(NCNGe)_nCl$ ($n = 1-3$) confirm that the carbodiimide form is thermodynamically more stable by at least 10 kcal mol^{-1}. By the reaction of polycarbodiimidogermylene with dimethyldisulfide the number of terminal chlorine atoms in the polymer chains was found to be between 12 and 14 NCN groups per 2 chorines, as was further confirmed by elemental analyses. Polycarbodiimidogermylene is a semiconductor, having a volume conductivity of about 10^{-2} S cm^{-1}. Its UV spectrum shows absorptions between 650 and 2000 nm corresponding to transitions between 0.6 and 1.9 eV, confirming transitions in the forbidden gap.

Keywords: Polycarbodiimidogermylene; Semiconductors; Theoretical studies



Scheme 1.

1. Introduction

Recently there has been growing interest in metal 14 carbodiimides and cyanamides because of their potential applications [1–4]. In our studies of new germylcarbodiimides, we have already obtained polydimesitylgermylcabodiimides [5] which are non-conductors. In the hope of obtaining conducting polymers, we are examining polygermylene carbodiimides and we present our results here.

2. Results and discussion

The reaction of $GeCl_2$·dioxane with dilithium cyanamide, or cyanamide itself in the presence of triethylamine, led to a white powder of **1** (Scheme 1).

The same compound was also formed by an exchange reaction between bis(triethylgermyl)-carbodi-

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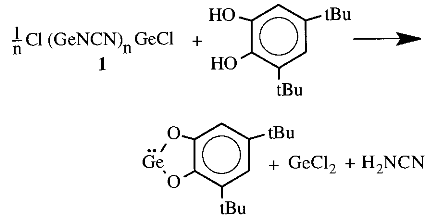
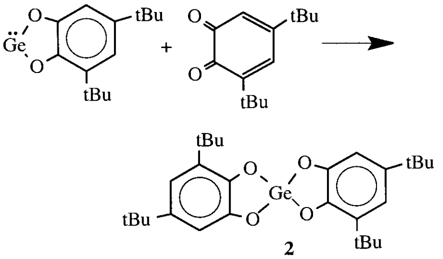
imide [6] and germylene dichloride (Eq. (1)). A similar compound, was also characterized in the thermal decomposition of bis(trimesitylgermylcarbodiimido) germylene [7].

$$(n+1)\,\mathrm{GeCl_2.C_4H_8O_2} + n\mathrm{Et_3GeNCNGeEt_3} \xrightarrow[-C_4H_8O_2]{} 2n\mathrm{Et_3GeCl} + \underset{\mathbf{1}}{\mathrm{Cl(GeNCN)_n GeCl}} \qquad (1)$$

The germylene structure was confirmed by its reaction with 3,5-di-*t*-butylcatechol, which gave the previously known stable 2-germylene(6,8-di-*t*-butyl)-4,5-benzo-1,3-dioxolane [8] (Eq. (2)) for which we found the same characteristics as in the literature [8]. As expected, further addition of 3, 5-di-*t*-butylorthoquinone to the latter led to the spirogermane **2** [8] (Eq. (3)). The terminal groups form an unstable unsymmetrical germylene which gave the expected symetrization [8] (Eq. (2)).



(2)



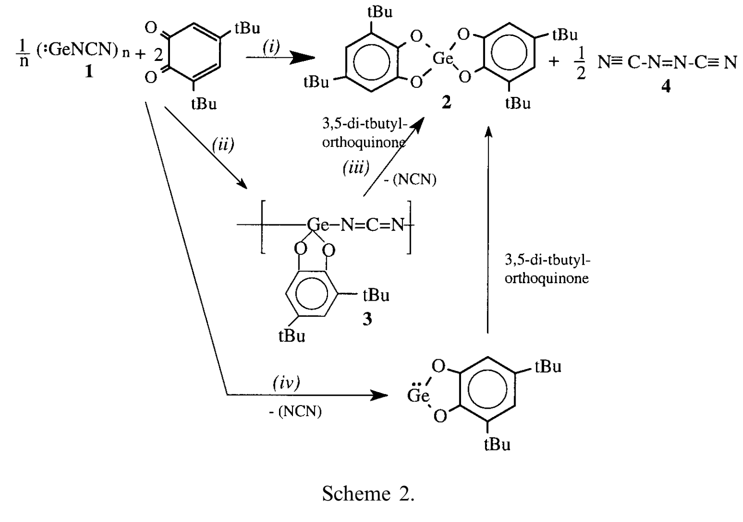
(3)

When polygermylene **1** was reacted with 3,5-di-*t*-butylorthoquinone in a 1:1 stoichiometry (Scheme 2, i), spirogermane **2** was the only product, with half of **1** remaining in suspension in the reaction mixture. In a 1:2 stoichiometry, **2** was quantitatively formed beside dicyanodiazene **4** [9,10]. This result is consistent with the high reactivity of germylenes towards 3,5-di-*t*-butylorthoquinone [8,11–13]. There are two possible ways of explaining the formation of **2** from **1** in this reaction (Scheme 2).

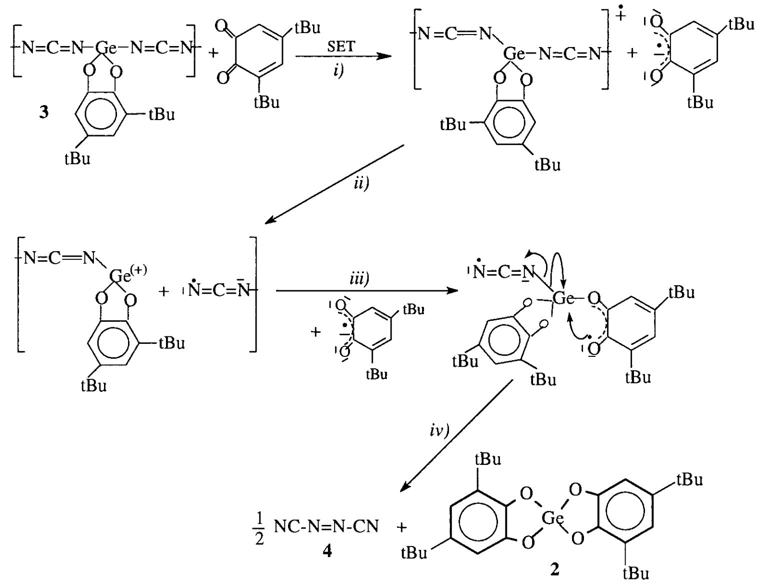
Actually, compound **3**, a polymer of germanium(IV) expected in the first step of the reaction by addition of quinone to $\mathrm{Ge_{II}}$ in **1**, cannot be isolated (Scheme 2, ii). As soon as reaction (ii) proceeds, the resulting **3** dissolves, facilitating a further addition of quinone to the Ge–N bonds of **3** (Scheme 2, iii). The other route (Scheme 2, iv), preserving the germylene structure in the presence of quinone, is less probable, with germanium(II) in **1** reacting faster with quinone than with Ge–N bonds [12,13].

The reaction between quinone and germanium nitrogen compounds usually proceeds by a single electron transfer in the first step of the reaction [11,13]. An ESR study of the reaction between **1** and 3,5-di-*t*-butylorthoquinone showed the characteristic doublet of the transitory *o*-semiquinonic species [13] formed in the first step of the reaction (Scheme 3, i). Duplication of cyanonitrene, eliminated (Scheme 3, iii) in the course of the reaction, led to dicyanodiazene **4**, which was characterized as in the literature [9,10].

A similar reaction was obtained between **1** and dimethyldisulfide (Eq. (4)), resulting in dicyanodiazene beside (methylthio)germanes. Of course, the main product of the reaction was tetra(methylthio)germane

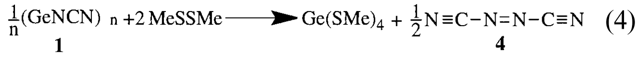


Scheme 2.

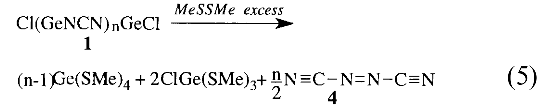


Scheme 3.

(Eq. (4)), but tris(methylthio)chlorogermane was also obtained (Eq. (5)) and the amount of this thiochlorogermane formed is a measure of the amount of terminal Ge–Cl groups in chains of **1**. It was found to be in the range 13–15% (Eq. (5)). This result leads to an average of two chlorine atoms for twelve to fourteen NCN groups.



$$\frac{1}{n}\underset{\mathbf{1}}{(\mathrm{GeNCN})}\,{}_n + 2\,\mathrm{MeSSMe} \longrightarrow \mathrm{Ge(SMe)_4} + \frac{1}{2}\underset{\mathbf{4}}{\mathrm{N{\equiv}C{-}N{=}N{-}C{\equiv}N}} \qquad (4)$$



$$\underset{\mathbf{1}}{\mathrm{Cl(GeNCN)_nGeCl}} \xrightarrow{MeSSMe\ excess} (n\text{-}1)\mathrm{Ge(SMe)_4} + 2\,\mathrm{ClGe(SMe)_3} + \frac{n}{2}\underset{\mathbf{4}}{\mathrm{N{\equiv}C{-}N{=}N{-}C{\equiv}N}} \qquad (5)$$

Unfortunately, polygermylene **1** does not melt and is insoluble in usual organic solvents and, therefore, we were unable to use a SEC (steric exclusion chromatography) analysis to determine the average molecular weight. Neither cyclic chains nor carbodiimide endings to the chains can be excluded. However, elemental analysis is roughly in favor of ClGe(NCNGe)$_{12}$Cl.

A powder diffractogram showed reflections, which means that **1** is at least partially microcrystalline.

An infrared spectrum of **1** shows the characteristic absorption $\nu_{\mathrm{N=C=N}}$ at 2105 cm^{-1}, confirming the carbodiimide structure, which we have already observed by X-ray diffraction of several germylcarbodiimide compounds [5–7], all absorbing around 2100 cm^{-1} in the infrared. For example, Mes$_3$GeN=C=NH exhibits the $\nu_{\mathrm{N=C=N}}$ absorption at 2122 cm^{-1}, while its less stable isomer Mes$_3$GeNH–C(N displays the $\nu_{\mathrm{C\equiv N}}$ absorption at 2198 cm^{-1} [7b].

To be certain about the carbodiimide structure of **1**, we undertook a theoretical study of ClGe(NCNGe)$_n$Cl ($n = 1$–4) using density functional theory (DFT) [14,15]. All calculations were performed with the GAUSSIAN 98 package of programs [16]. Both carbodiimide and cyanamide isomers were fully optimized. The former are depicted in Fig. 1 and the latter in Fig. 2. Selected geometrical parameters are presented in Tables 1 and 2. The nature of the calculated stationary points was determined by vibrational frequency analyses. All isomers identified have been found to be minima on their respective singlet energy potential surfaces.

Carbodiimidogermylenes (see Fig. 1) consist of twisted chains of C_2 symmetry in which the germanium atoms are linked by NCN units. The diimide fragments are nearly linear with N–C bond lengths in the usual range of 1.220–1.227 Å. The germanium centers are not in line with –N=C=N–, the C–N–Ge angles varying from 143.3 to 148.5° in the central part of the chains. These geometrical features closely resemble that obtained in the X-ray diffraction study of the bis(germyl)carbodiimide Mes$_3$Ge–N=C=N–GeMes$_3$ [6]. As expected, the valence angle at the germanium atom (N–Ge–N: 96°) is characteristic of germylene species. One can also notice that increasing the number of units in the framework does not alter the overall structure of the polymeric chain.

In order to compare with isomers of the cyanamide form, we attempted to optimize (–Ge–N–Ge–)$_n$ chains with dangling N–C≡N groups. We succeeded for $n = 1$ and 2 (see isomers (A) in Fig. 2). These isomers are

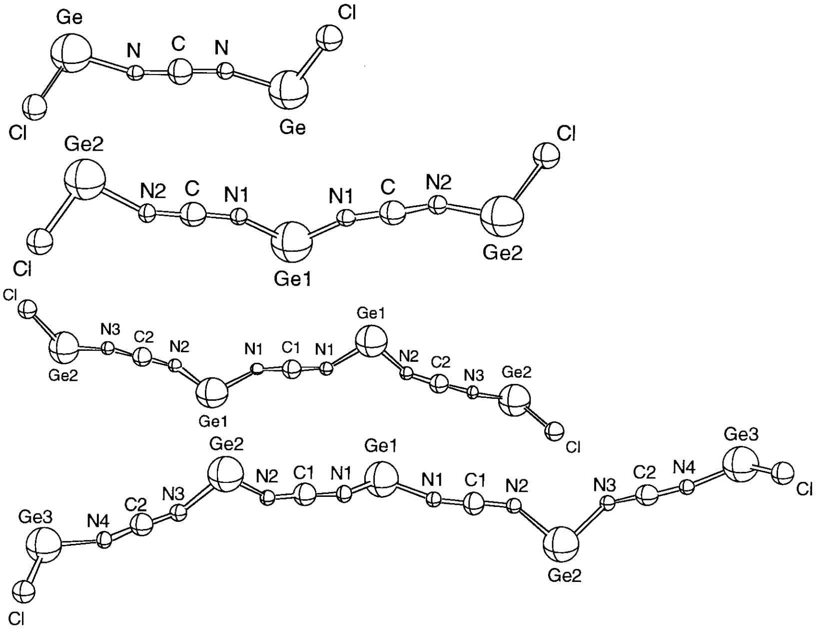


Fig. 1. DTF/B33LYP-optimized structures for the carbodiimide isomers of ClGe(NCNGe)$_n$Cl ($n = 1$–4).

characterized by two unequivalent C–N bonds, one corresponding to a single bond with a C–N distance of 1.347 Å and the other to a C≡N triple bond of 1.172 Å. Isomer A corresponding to $n = 1$ has a C_{2v} symmetry with the N1CN2 group as a twofold axis. Its planar geometry can be inferred from the delocalization of the N1 lone pair into the p vacant orbital of the germylenes. In the case $n = 2$, the two cyanamide groups are also nearly linear, but they are twisted along the –Ge–N–Ge–N–Ge– chain, so that this isomer A has only a C_2 symmetry. For $n = 3$, no structure with three cyanamide groups branched on a ···N–Ge–N··· quasi-linear chain can be optimized. The geometry optimization has led to a folded C_2 structure in which the central N1C1N2 group is close to a carbodiimide geometry (N1–C1: 1.264 Å and C1–N2: 1.204 Å), the two other ones clearly having a cyanamide geometry. All these distortions can be explained by the presence of various interactions in the π molecular system. In particular they are responsible for the short distance between the N2 and Ge2 atoms (2.310 Å), which is hardly longer than the classical Ge1–N1 and Ge2–N3 bonds (Table 2).

Although our purpose was not to achieve an exhaustive study of all the possible cyanamide isomers, we have to mention that, by complete loss of symmetry, most intriguing structures can be optimized (see isomers (B) in Fig. 2). Indeed one of the terminal germylenes rotates so that its empty p orbital can form a bonding interaction with the lone pair of a neighboring atom such as chlorine or nitrogen. For isomer B with $n = 1$, the resulting structure is characterized by a Ge2–Cl2 bond nearly orthogonal to the Ge2N1Ge1Cl1 plane and a surprisingly short distance between the Ge2 and Cl1 atoms (2.734 Å). In the same way, for isomer B with $n = 2$, the Ge1–Cl1 bond is nearly orthogonal to the Ge1N1Ge2N3C2N4 pseudo-ring with a short distance of 2.179 Å between the Ge1 and N4 atoms.

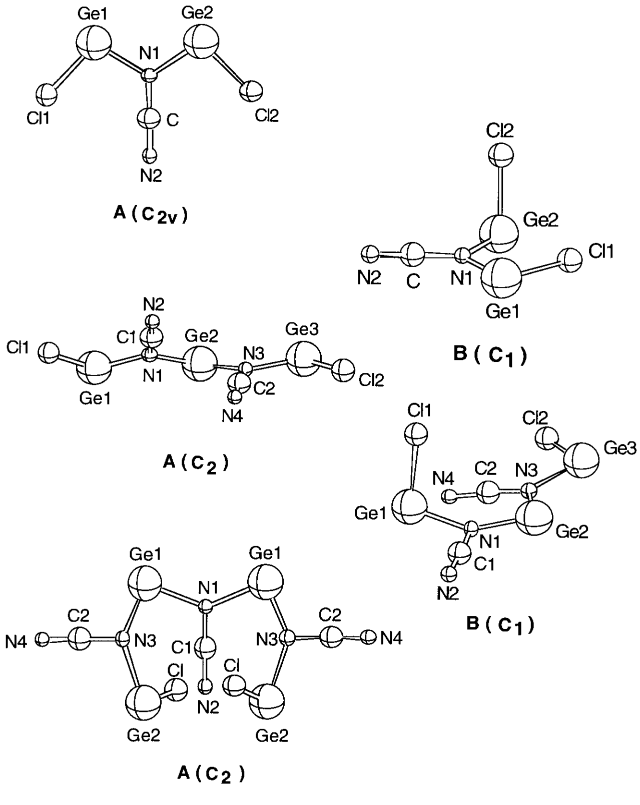


Fig. 2. DTF/B33LYP-optimized structures for the cyanide isomers of ClGe(NCNGe)$_n$Cl ($n = 1$–3).

Table 1
Selected geometrical parameters (Å and °) for the $ClGe(NCNGe)_nCl$ carbodiimide isomers optimized at the DFT/B3LYP level [a]

$n=1$		$n=2$		$n=3$		$n=4$	
C–N	1.221	C–N1	1.222	C1–N1	1.225	C1–N1	1.224
		C–N2	1.225	C2–N2	1.220	C1–N2	1.227
				C2–N3	1.227	C2–N3	1.220
						C2–N4	1.227
N–Ge	1.872	N1–Ge1	1.886	N1–Ge1	1.883	N1–Ge1	1.886
		N2–Ge2	1.870	N2–Ge1	1.889	N2–Ge2	1.882
				N3–Ge2	1.869	N3–Ge2	1.890
						N4–Ge3	1.869
C–N–Ge	158.5	C–N1–Ge1	146.9	C1–N1–Ge1	145.1	C1–N1–Ge1	144.4
		C–N2–Ge2	153.2	C2–N2–Ge1	148.5	C1–N2–Ge2	143.3
				C2–N3–Ge2	150.8	C2–N3–Ge2	147.7
						C2–N4–Ge3	150.0
N–C–N	180.0	N1–C–N2	177.2	N1–C1–N1	176.6	N1–C1–N2	176.8
				N2–C2–N3	178.6	N3–C2–N4	177.3
–	–	N1–Ge1–N1	95.9	N1–Ge1–N2	96.0	N1–Ge2–N2	96.0
						N2–Ge2–N3	96.0
Ge–Cl	2.256	Ge2–Cl	2.259	Ge2–Cl	2.260	Ge3–Cl	2.260
N–Ge–Cl	98.4	N2–Ge2–Cl	98.3	N3–Ge2–Cl	98.3	N4–Ge3–Cl	98.4

[a] See Fig. 1 for labeling of the atoms.

Table 2
Selected geometrical parameters (Å and °) for the $ClGe(NCNGe)_nCl$ cyanamide A and B isomers optimized at the DFT/B3LYP level [a]

$n=1$			$n=2$			$n=3$	
	Isomer A	Isomer B		Isomer A	Isomer B		Isomer A
N1–C	1.347	1.342	N1–C1	1.349	1.350	N1–C1	1.264
			N3–C2	1.349	1.303	N3–C2	1.351
C–N2	1.172	1.173	C1–N2	1.172	1.174	C1–N2	1.204
			C2–N4	1.172	1.186	C2–N4	1.174
Ge1–N1	1.957	1.873	Ge1–N1	1.959	2.141	Ge1–N1	2.048
Ge2–N1	1.957	2.055	Ge2–N1	1.945	1.874	Ge1–N3	1.894
			Ge2–N3	1.945	2.062	Ge2–N3	2.125
			Ge3–N3	1.959	1.955		
Ge1–Cl1	2.222	2.367	Ge1–Cl1	2.219	2.290	Ge2–Cl	2.272
Ge2–Cl2	2.222	2.252	Ge3–Cl2	2.219	2.228		
N1–C–N2	180.0	178.6	N1–C1–N2	177.3	177.9	N1–C1–N2	180.0
			N3–C2–N4	177.3	171.4	N3–C2–N4	177.9
Ge1–N1–Ge2	113.5	116.7	Ge1–N1–Ge2	113.0	137.5	Ge1–N1–Ge1	136.4
			Ge2–N3–Ge3	113.0	121.3	Ge1–N3–Ge2	140.5

[a] See Fig. 2 for labeling of the atoms.

Relative energies between the calculated isomers are listed in Table 3. It is clear that carbodiimidogermylenes are thermodynamically more stable than isomer A of the cyanamide form. As expected due to the presence of additional bonding interactions in cyanamide isomers (B), these isomers are more stable than isomers (A). However, carbodiimide isomers remain the most stable by about 10 kcal mol^{-1} for $n=1$ and 2.

Vibrational wavenumbers and infrared intensities calculated at the B3LYP level of theory, are presented in Table 4 for the N=C=N stretching modes of carbodiimidogermylenes ($n=1$–4). In all cases, these species display only one intense band corresponding to the N=C=N antisymmetric stretch. The calculated value of the vibrational frequency associated with this mode is in good agreement with the experimental result. Indeed,

Table 3
Relative energies (kcal mol^{-1}) for the ClGe(NCNGe)$_n$Cl isomers at the DFT/B3LYP level

Isomers	$n=1$	$n=2$	$n=3$
Carbodiimide	0.0	0.0	0.0
Cyanamide A	12.9	30.0	22.4
Cyanamide B	9.9	11.8	–

it decreases when n goes from 1 to 4, and tends toward the value observed in the infrared spectra of **1** (2105 cm^{-1}). Note, similar calculations on the cyanamide isomers (A) led to C≡N absorptions in the range 2250–2280 cm^{-1}, confirming the carbodimide structure of **1**.

Furthermore, there is a possibility of intermolecular interactions between the GeII of one carbodiimidogermylene and the nitrogen lone pair of another unit since such interactions are well known in germylene chemistry [11]. In **1**, such an interaction would lead to slight distortions of the N=C=N geometry (by about 0.04 Å) and therefore to a slight decrease of the frequency associated with the most intense N=C=N antisymmetric stretching mode. Calculations on [ClGe(NCNGe)$_n$Cl]$_2$ are in progress to more accurately evaluate this possible effect.

Polygermylene carbodiimide **1** is highly hygroscopic. A thin plate of compacted powder of **1** left at ambient atmosphere slowly accumulated water on the surface and became yellow due to germanium dihydroxide [17]. This hydrolysis (Eq. (6)) can be followed by infrared spectroscopy, by the appearance of the OH band and of the characteristic signals of cyanamide ($\nu_{OH} = 3405$ cm^{-1}, $\nu_{NH_2} = 3317$ and 3177 cm^{-1}, $\nu_{C\equiv N} = 2256$ cm^{-1}). Of course, the reaction leads eventually to GeO$_2$ according to Ref. [17], and cyanamide.

$$\underset{\mathbf{1}}{\mathrm{Cl(GeNCN)_nGeCl}} \xrightarrow{H_2O} \mathrm{(n+1)Ge(OH)_2 + 2H_3O^+Cl^- + nH_2NCN} \tag{6}$$

Table 5
Calculated excitation energy ΔE, wavelength λ and oscillator strength f for the vertical transition between the ^{1}A ground state and the ^{1}B excited state of the carbodiimide form of ClGe(NCNGe)$_n$Cl ($n = 1$–4)

n	$\Delta E_{1A\rightarrow 1B}$ (ev)	λ (nm)	$f \times 10^{-2}$
1	4.07	305	7.8
2	3.74	331	15.7
3	3.57	347	19.1
4	3.44	360	19.3

Preliminary results of a volume conductimetry for **1** gave a conductivity of 10^{-2} S cm^{-1}, in the range of semiconductors (10^{-6} to 1 S cm^{-1}) [18–24]. As semiconductors are characterized by transitions between the conduction band and the valence band, we examined **1** by reflectance UV spectrometry. In addition to an intense transition at 300 nm, we noted several absorptions within the range 650–2000 nm, which are lacking in non conducting germylcarbodiimides such as Mes$_3$GeNCNGeMes$_3$ or (Mes$_2$GeNCN)$_{n=3,4}$. Vertical electronic transitions were calculated using time-dependent density functional theory [16] for ClGe(NCNGe)$_n$Cl ($n = 1$–4). Only one transition has an oscillator strength greater than 0.01. It involves an excited configuration obtained by promoting electrons from the nitrogen lone pair orbitals to the vacant p orbitals of germylenes. The calculated excitation energies, the corresponding wavelengths and oscillator strengths are presented in Table 5. The calculated transition is located at 360 nm for $n = 4$ with an oscillator strength of 0.19, in good agreement with the observed one around 300 nm. With its ΔE of (3.4 eV in the same range as for SnO$_2$ [25], **1** belongs to the family of semiconductors having large forbidden gaps. However, transitions beyond 650 nm observed in the solid state cannot be obtained in our calculations carried out on non-interacting chains of carbodiimidogermylenes.

It seems that the conducting properties could be partly due to the alternation of metal atoms and –N=C=N– electron-rich group spacers, since for (SnNCN)$_n$ and [Ge$_{IV}$(NCN)$_2$]$_n$ [7a] we found conductivities in the range of 10^{-3} and 10^{-5} S cm^{-1}, respectively. There is no appreciable change in conductivity of **1**

Table 4
Calculated harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in km mol^{-1}) at the DFT/B3LYP level for the ClGe(NCNGe)$_n$Cl carbodiimide isomers

	Sym	$n=1$		$n=2$		$n=3$		$n=4$	
		Freq	Int	Freq	Int	Freq	Int	Freq	Int
N=C=N as stretch	b	2228	3633	2173	10084	2142	17946	2118	26992
	a	–	–	2238	300	2218	412	2192	378
	b	–	–	–	–	2240	608	2226	1299
	a	–	–	–	–	–	–	2237	48
N=C=N s stretch	a	1493	1	1475	0	1456	1	1455	18
	b	–	–	1470	2	1470	3	1449	1
	a	–	–	–	–	1471	1	1469	1
	b	–	–	–	–	–	–	1468	3

after small intervals of time. If oxidation occurs, it is not instantaneous.

Further investigations about the conductivity of our metalcyanamides including the variation of conductivity with temperature and theoretical studies are in progress.

3. Experimental

All reactions were carried out under nitrogen or argon and in dry solvents.

NMR spectra were recorded on Bruker AC80 (^{1}H) and AC 200 (^{13}C) spectrometers (δ ppm/TMS); IR spectra on a Perkin–Elmer 1600 FT IR. spectrometer; UV spectra on a Perkin–Elmer lambda 9 UV/VIS/NIR; mass spectra on a HP 5989 in the electron impact mode (70 eV) or on a Rybermag R10-10 spectrometer operating in the electron impact mode, or by chemical desorption (DCi/CH_4), or Fast Atom Bombardment (FAB, matrice: 2-nitrophenyl octyl ether NPOE). Melting points were measured on a Leitz microscope.

ESR experiments were done on a Bruker ER 200 instrument having an E.I.P. frequency meter.

*3.1. Preparation of **1***

3.1.1. By dehydrohalogenation between cyanamide and $GeCl_2$·dioxane

To a mixture of H_2NCN (0.05 g, 1.18 mmol) and $GeCl_2 \cdot C_4H_8O_2$ (0.27 g, 1.18 mmol) dissolved in 4 ml of THF was added at room temperature (r.t.) under stirring Et_3N (0.24 g, 2.36 mmol). After 2 h further stirring, THF was replaced by chloroform to dissolve triethylamine chlorohydrate. Polygermylene **1** was then filtered as a white–yellowish precipitate 0.10 g. Yield 77%. M.p. > 370°C. IR (Nujol mull): 2105 cm^{-1} (ν_{as} NCN). MS (FAB (NPOE), *m*/*z*): 676 [M$^+$, $n = 6$]. Compound **1** is insoluble in ether, THF, $CHCl_3$, CCl_4, benzene, toluene, dioxane, CH_3CN, DMSO and DMF

3.1.2. From dilithium cyanamide

Dilithium cyanamide, prepared at −70°C from H_2NCN (0.09 g, 2.15 mmol) in THF and ^{t}Buli (4.30 mmol, 2.53 ml at 1.7 M in pentane), was added under stirring at r.t. to $GeCl_2$·dioxane (0.50 g, 2.15 mmol) dissolved in 5 ml of THF. After 1.5 h the insoluble solid precipitated. Dioxane was identified in the solution by VPC and ^{1}H-NMR. The precipitate was washed three times with warm THF to eliminate LiCl, then filtered, leading to 0.21 g of **1**. Yield 87%.

3.1.3. By exchange from $Et_3GeNCNGeEt_3$

To $Et_3GeNCNGeEt_3$ [6] (0.43 g, 1.20 mmol) dissolved in 2 ml of THF was added $GeCl_2$·dioxane (0.27 g, 1.18 mmol) under stirring at r.t. After 2 h of stirring, the precipitate was filtered and washed twice with THF, yielding 0.08 g of **1**. Yield 61%. The filtrate was analyzed by VPC and VPC/MS showing quantitative formation of triethylchlorogermane, and disappearance of $Et_3GeNCNGeEt_3$. Anal. Calc. for: $ClGe(NCNGe)_{12}Cl$: C, 9.63; N, 22.47; Found: C, 9.64; N, 20.78%.

*3.2. Chemical characterization of **1***

To **1** (0.20 g, 1.77 mmol) in suspension in 3 ml of THF under stirring at r.t., was added a solution of 3,5-di-*t*-butylcatechol (0.39 g, 1.77 mmol) in 3 ml of THF. After 16 h, there was no remaining **1** and ^{1}H-NMR analysis confirmed the disappearance of 3,5-di-*t*-butylcatechol and the quantitative formation of 2-germylene(6,8-di-*t*-butyl)4,5-benzo-1,3-dioxolane by comparison with a pure sample of that germylene [8]. An equivalent of 3,5-di-*t*-butylorthoquinone (0.39 g, 1.77 mmol) in 4 ml of THF was added to the reaction mixture. After 4 h stirring at r.t., THF was replaced by 6 ml of benzene and H_2NCN was eliminated by centrifugation (0.061 g, yield 82%). The benzene phase was concentrated under vacuum and the residue washed twice with pentane, resulting in 0.71 g of pure **2** in agreement with [8], yield 78%.

*3.3. Reaction of **1** with 3,5 di-t-butylorthoquinone*

To **1** (0.05 g, 0.44 mmol) in suspension in 3 ml of THF at r.t. was added a solution of 3,5-di-*t*-butylorthoquinone (0.19 g, 0.88 mmol) in 2 ml of THF. After 18 h of stirring at r.t., evaporation of THF led to 0.24 g of an orange powder. ^{1}H-NMR analysis showed the characteristic signals of **2**, and mass spectrometry (Ei, 514 [M$^+$]) confirmed the parent ion of **2**. As **2** and **4** are both soluble (THF, benzene and $CHCl_3$) and insoluble (ether, pentane), in the same solvents, we were unable to separate them. However, **4** was easily characterized by IR and mass spectrometry (cf. literature [9,10]. IR. (Nujol mull): 2230 cm^{-1} (ν_{as}C(N), 1644 (ν N=N). MS (Ei, *m*/*z*,%): 40, 100% [M$^+$ − NCN]. The same experiment with half of the quinone led to the same results, but half of the starting amount of **1** remained with the final products.

3.4. ESR experiment

In a similar experiment, to a suspension of **1** (0.05 g, 0.44 mmol) in a 1:1 mixture of THF–toluene was added 3,5-di-*t*-butylorthoquinone (0.02 g, 0.08 mmol). The mixture was placed in the ESR spectrometer cavity at 2°C. The expected doublet of the *o*-semiquinonic transitory radical was observed at $g = 2.0219$ G; $a^{\mathrm{H}} =$ 3,4 G.

*3.5. Reaction of **1** with dimethyldisulfide*

To a suspension of **1** (0.27 g, 2.38 mmol) in 6 ml THF was added at r.t., under stirring, dimethyldisulfide (0.44 g, 4.76 mmol). After 18 h of stirring at r.t., THF was evaporated under vacuum yielding 0.46 g of a sticky orange residue. The residue, when treated with pentane, afforded 0.07g of a yellow powder of **4**, which was separated by centrifugation (yield 73%) and characterized as before by IR and mass spectrometry. The liquid phase, after evaporation of the solvents under 10 mm Hg allowed the characterization of $Ge(SMe)_4$ 87% [26] and $ClGe(SMe)_3$ 13%.

$Ge(SMe)_4$: ^{1}H-NMR ($CDCl_3$): δ_{ppm}, 2.23 (s, 12H, SMe).^{13}C-NMR ($CDCl_3$): δ_{ppm}, 11.08 (SMe). MS (Ei, *m*/*z*,%): 262, 1% [M^+]; 215, 11% [$M^+ - $Sme]; 121, 15% [$M^+ - 3$Sme]; 45, 100% [$HCS^+$].

$ClGe(SMe)_3$: ^{1}H-NMR ($CDCl_3$): δ_{ppm}, 2.30 (SMe).^{13}C-NMR ($CDCl_3$): δ_{ppm}, 11.55 (SMe). VPC/MS (Ei, *m*/*z*,%): 250, 4% [M^+]; 203, 12% [$M^+ - $Sme]; 156, 3% [$M^+ - 2$Sme]; 109, 25% [$M^+ - 3$Sme]; 45, 100% [$HCS^+$].

Another experiment led to yields in $Ge(SMe)_4$ 85% and $ClGe(SMe)_3$ 15%. Calc: $Cl(GeNCN)_{12}GeCl \rightarrow 11Ge(SMe)_4$ (85%) + $2ClGe(SMe)_3$ (15%); $Cl(GeNCN)_{14}GeCl \rightarrow 13\ Ge(SMe)_4$ (87%) + $2ClGe(SMe)_3$ (13%).

*3.6. Measurement of the electrical conductivity of **1***

A thin plate was obtained by pressing 0.18 g of **1** under 10 tons for 10 min. The volume conductivity measured was in the range of 10^{-2} S cm^{-1}.

*3.7. UV analysis of **1***

A thin plate of **1** (0.02 g) in KBr (0.20 g) was obtained by pressing the mixture under 10 tons for 10 min. This plate was analyzed by UV reflectance. The strongest absorption was observed around 300 nm (257, 289, 316 nm) and weaker ones were at 656, 1542, 1708, 2034 nm. These absorptions do not exist in $Mes_3GeNCNGeMes_3$ [6] and $(Mes_2GeNCN)_{n=3,4}$ [5], which are not electrical conductors.

*3.8. Hydration of **1***

The previously prepared thin plate when left in moist air, slowly formed a bulky drop on its surface. The plate slowly changed from white to the yellow color of $Ge(OH)_2$, and gradually darkened to light brown [17]. The IR spectrum of a KBr disk of **1** when examined before and after exposure to moist air showed the appearance of $\nu_{OH} = 3405$ cm^{-1}, and the characteristic bands of H_2NCN: $\nu_{NH_2} = 3317$ and 3177 cm^{-1}, $\nu_{NCN} = 2256$ cm^{-1}.

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