

A theoretical study of linear germacyanogen isomers

Mingjae Huang, Ming-Der Su*

School of Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, ROC

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Abstract

The structures of all possible linear isomers of Ge-containing cyanogens were optimized at MP2, B3LYP, and QCISD levels of theory. At all levels of theory, the most stable isomer was found to be GeNCN, while for cyanogen itself, the most stable isomer is well known to be NCCN. Our theoretical results predict that the order of stability of the acyclic germacyanogens is GeNCN > GeNNC > NGeCN > NGeNC. The difference between the order of stability among germacyanogen and cyanogen isomers is rationalized, taking into account the position of the unpaired electron on nitrogen in the GeN radical, and that on carbon in the CN radical. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, a large number of theoretical and experimental studies have dealt with the structures, spectra, and heats of formation of three linear isomers NCCN (cyanogen), CNCN (isocyanogen), and CNNC (diisocyanogen) [1–14]. It was found that their order of stability is NCCN > CNCN > CNNC. These three cyanogen isomers can be regarded as products of different types of pairing of the two constituent CN radicals. Therefore, one may use a simple valence bond theory to explain the order of their stability.

It has been proved that in the CN radical $:C\equiv\dot{N}$ has much less weight than $\cdot C\equiv N$: [15]. That is to say, the unpaired electron is located preferentially on the carbon rather than on the nitrogen. It is natural to suppose that, during the dimerization of the CN radicals, the preferred geometry of the adduct is that in which the unpaired electrons can form a single bond. For this reason, the most stable cyanogen isomer should be NCCN, the second NCNC, and the least stable CNNC.

Likewise, if carbon is replaced by silicon, then it can be regarded as silacyanogen with a chemical formula CSiN₂. It has been theoretically proved that the stability of the acyclic structures is SiNCN > SiNNC >

NSiCN > NSiNC [16]. By analogy with the cyanogen and silacyanogen isomers, the germanium-substituted cyanogens can be characterized by the general formula CGeN₂. In fact, germanium lies below carbon and silicon in the periodic table; hence it might be possible to find new species such as germacyanogen in the laboratory. However, to the best of our knowledge, the existence of cyanogen's germanium analogues, which are formally the products of addition of CN and GeN radicals, have not yet been reported.

In an attempt to provide information on the molecular structures and spectroscopic properties of the CGeN₂ species, as well as their relative stability, we have examined the CGeN₂ potential energy surface using both ab initio and density function theory (DFT). In this paper, we shall, therefore, provide accurate molecular parameters and spectroscopic data to guide experimental studies on these species.

2. Computational methods

Geometry optimization was performed using Møller–Plesset second-order perturbation theory (MP2) [17]. DFT was carried out using the exchange potentials of Becke [18], the correlation functional of Lee, Yang, and Parr (B3LYP) [19], and the quadratic configuration interaction calculations with singles and doubles sub-

* Corresponding author. Fax: +886-7-321-5339

E-mail address: midesu@cc.kmu.edu.tw (M.-D. Su).

stitutes [20]. 6–311+G(d,p) and 6–311++G(2df,2p) basis sets were used for optimizations with the B3LYP, MP2, and QCISD methods. Furthermore, the 6–311++G(3df,2pd) basis set was used for QCISD(T) single-point calculations on QCISD geometries. All calculations were carried out using the GAUSSIAN-98 program package [21].

3. Results and discussion

To highlight the questions that formed the basis for this study, it is perhaps worthwhile to discuss briefly the electronic structures of the CN and GeN radicals. It is well established that the doublet CN radical has two electronic states. One is a $^2\Pi$ state, which has a lone pair of electrons on carbon [15]. The other is a $^2\Sigma^+$ state, which only has a single nonbonding electron on carbon. The same situation also applied to the doublet GeN radical. According to our QCISD/6–311+G(2d,p) computations, the $^2\Sigma^+$ state of CN is 14 kcal mol $^{-1}$ more stable than the $^2\Pi$ state. On the contrary, the $^2\Pi$ state of GeN is calculated to be 37 kcal mol $^{-1}$ more stable than the $^2\Sigma^+$ state. In other words, in the CN radical the $\cdot\text{C}\equiv\text{N}$: valence structure dominates over $:\text{C}=\ddot{\text{N}}\cdot$, while in the GeN radical $:\text{Ge}=\ddot{\text{N}}\cdot$ has much more weight than $\cdot\text{Ge}\equiv\text{N}$:. This strongly implies that the order of stability of linear germacyanogen isomers can be understood from the position of the unpaired electron in the diatomic molecules. Based on the above discussion, one may easily see that the preferred resonance structure for the CN radical is the one that has an unpaired electron localized at carbon. That is to say, $\cdot\text{C}\equiv\text{N}$: is ‘good’, while $:\text{C}=\ddot{\text{N}}\cdot$ is ‘bad’. Therefore, one may obtain the following scheme:

- (1) $:\text{N}=\text{C}\cdot\cdot\text{C}\equiv\text{N}$: Best
- (2) $:\text{N}=\text{C}\cdot\cdot\ddot{\text{N}}=\text{C}$:
- (3) $:\text{C}=\ddot{\text{N}}\cdot\cdot\ddot{\text{N}}=\text{C}$: Worst

Indeed, all the previous computational results support this simple scheme [1–14]. Likewise, for the case of GeN, the preferred diatomic radical structure should be

the one that has an unpaired electron localized at N. Simply speaking, $:\text{Ge}=\ddot{\text{N}}\cdot$ is ‘good’, while $\cdot\text{Ge}\equiv\text{N}$: is ‘bad’. As a result, one may predict the sequence of stability of the isomers to be as follows:

- (1) $:\text{Ge}=\ddot{\text{N}}\cdot\cdot\text{C}\equiv\text{N}$: Best
- (2) $:\text{Ge}=\ddot{\text{N}}\cdot\cdot\ddot{\text{N}}=\text{C}$:
- (3) $:\text{N}=\text{Ge}\cdot\cdot\text{C}\equiv\text{N}$:
- (4) $:\text{N}=\text{Ge}\cdot\cdot\ddot{\text{N}}=\text{C}$: Worst

Actually, as shown in Table 1, all our calculated results confirm this prediction. That is to say, the thermodynamic stability for the acyclic germacyanogen isomers should decrease in the order: GeNCN (1) > GeNNC (2) > NGeCN (3) > NGeNC (4). Moreover, it is interesting to note that the energy difference between GeNCN (1) and both the third stable NGeCN (3) and the least stable NGeNC (4) isomer appears to depend strongly on the level of theory used. For instance, NGeCN (3) is 56 kcal mol $^{-1}$ above GeNCN (1) with the MP2 method, while their energy difference at the B3LYP and QCISD levels of theory reaches 81 and 69 kcal mol $^{-1}$, respectively. Again, NGeNC (4) is less stable than GeNCN (1) by 92 kcal mol $^{-1}$ at the B3LYP level, whereas MP2 and QCISD methods predict this energy difference to be 76 and 80 kcal mol $^{-1}$, respectively. Furthermore, it has to be mentioned here that structures (2) and (3) each have one ‘bad’ valence structure, but our theoretical results predict the former (GeNNC) to be more stable than the latter (NGeCN). The reason for this may be due to the fact that germanium is reluctant to form singly bonded compound with carbon [22,23].

To determine the stability or possible reactivity of some molecular systems, it is advisable to determine homolytic bond dissociation energies for the weakest bonds in the molecule. It is obvious that this bond should be the one between GeN and CN radicals. It is well known that for accurately computing molecular energies, computational methods that include electron correlations are necessary. As one can see in Table 1, the QCISD(T) level computed the GeN–CN bond dissociation

Table 1
Total energies of the most stable isomer (a.u.) and relative energies of other isomers (kcal mol $^{-1}$) of linear germacyanogen

Method/basis set	GeNCN, E_{total}	GeNNC, ΔE	NGeCN, ΔE	NGeNC, ΔE	GeN+NC, ΔE
B3LYP/6–311+G(d,p)	–2224.637428	48.4	81.3	93.1	148.3
B3LYP/6–311++G(2df,2p)	–2224.646049	47.5	80.5	91.5	148.7
MP2/6-311+G(d,p)	–2222.642915	49.6	55.5	76.6	183.7
MP2/6–311++G(2df,2p)	–2222.733367	49.3	57.3	76.4	189.2
QCISD/6–311+G(2d,p)	–2222.679317	48.6	69.5	80.5	199.2
QCISD(T)/6–311++G(3df,2pd)//QCISD/6–311+G(2d,p)	–2222.782634	48.5	67.3	78.8	141.5

Table 2
Structural parameters for linear germacyanogen isomers computed at five levels of theory

	B3LYP/6-311+G(d,p)	B3LYP/6-311++G(2df,2p)	MP2/6-311+G(d,p)	MP2/6-311++G(2df,2p)	QSISD/6-311+G(2d,p)
<i>Ge=N-C≡N</i>					
Ge=N(Å)	1.685	1.681	1.695	1.693	1.685
N-C(Å)	1.291	1.289	1.309	1.302	1.309
C≡N(Å)	1.168	1.166	1.186	1.181	1.167
<i>Ge=N-N=C</i>					
Ge=N(Å)	1.684	1.680	1.706	1.702	1.683
N-N(Å)	1.274	1.272	1.284	1.278	1.298
N=C(Å)	1.185	1.180	1.201	1.194	1.178
<i>N≡Ge-C≡N</i>					
N≡Ge(Å)	1.641	1.638	1.690	1.689	1.670
Ge-C(Å)	1.882	1.877	1.887	1.884	1.907
C≡N(Å)	1.158	1.154	1.184	1.178	1.160
<i>N≡Ge-N=C</i>					
N≡Ge(Å)	1.645	1.642	1.666	1.667	1.677
Ge-N(Å)	1.813	1.804	1.825	1.818	1.823
N=C(Å)	1.185	1.179	1.194	1.188	1.183

tion energy to be 142 kcal mol⁻¹. This energy is relatively high and should ensure stability of the GeNCN (1) species. Therefore, it should be observable experimentally as was previously suggested.

Structural parameters for the acyclic germacyanogen isomers are presented in Table 2. The geometries for each species is very similar, regardless of the chosen theoretical method. It is interesting to point out that for the most stable GeNCN (1) isomer B3LYP/6-311+G(d,p) and QCISD/6-311+G(2d,p) geometries are almost identical, except for the N-C bond length. However, a detailed comparison of GeNCN (1) geometries shows that, the MP2 method gave slightly longer Ge-N and C-N bond distances, while the B3LYP method generated a slightly shorter N-C bond distance (see Table 2).

The B3LYP theoretical vibrational frequencies, IR intensities, and dipole moments for the germacyanogen isomers are summarized in Table 3. As demonstrated previously [24,25], the vibrational spectra for small molecular systems computed with the B3LYP DFT method are much closer to the experimental values than

with almost any other ab initio method. Thus, we expect that this hybrid DFT method should also produce reliable vibrational spectra for these germacyanogen isomers. It is intriguing to find that the highest-frequency vibration for all four isomers is predominantly the C≡N stretch contribution, and its value reflects changes in the C≡N bond lengths. For instance, as seen in Tables 2 and 3, the highest values of the $\omega_1(\text{C}\equiv\text{N})$ frequency occur for the GeNCN and NGeCN isomers. Correspondingly, these two isomers have the shortest C≡N equilibrium bond length.

In short, our computational results have demonstrated that the order of stability of germacyanogen isomers predicted using the simple valence structure rule is consistent with that predicted by quantum mechanical methods. Besides this, all the germacyanogen species studies in this work are calculated to possess large dipole moments (see Table 3). Thus, a relatively stable compound with a GeNCN pattern should exist and be possible to isolate for experimental observations. Furthermore, it is believed that our theoretical calculations provide reliable information for the species for

Table 3
Theoretical vibrational frequencies (cm⁻¹), IR intensities (km mol⁻¹), and dipole moments (Debye) for acyclic germacyanogen isomers computed with the B3LYP method by using 6-311G+(d,p) basis set

Mode (symmetry)	GeNCN	GeNNC	NGeCN	NGeNC
$\omega_1(\Sigma)$	2249 (81.0)	2109 (120.0)	2269 (13.4)	2089 (439.0)
$\omega_2(\Sigma)$	1407 (85.5)	1385 (59.8)	1032 (2.3)	1010 (9.8)
$\omega_3(\Sigma)$	552 (24.4)	546 (23.4)	476 (18.7)	511 (45.6)
$\omega_4(\Pi)$	546 (25.3)	415 (14.1)	259 (4.2)	151 (0.0)
$\omega_5(\Pi)$	141 (1.8)	150 (2.9)	77 (7.5)	75 (13.4)
Dipole moment	6.355	5.335	1.286	1.559

which experimental data are still unknown, and could also assist experimental studies on germacyanogen chemistry.

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References

- [1] T. van der Does, F. Bickelhaupt, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 936.
- [2] O. Grabant, C.A. deLange, R. Mooyman, T. van der Does, F. Bickelh, *Chem. Phys. Lett.* 155 (1989) 221.
- [3] F. Stroh, M. Winnewisser, *Chem. Phys. Lett.* 155 (1989) 21.
- [4] J.W.G. Seibert, M. Winnewisser, B.P. Winnewisser, *J. Mol. Spectrosc.* 180 (1996) 26.
- [5] N.N. Haese, R.C. Woods, *J. Chem. Phys.* 73 (1980) 4521.
- [6] M.T. Nguyen, *Chem. Phys. Lett.* 157 (1989) 430.
- [7] K.K. Sunil, J.H. Yates, K.D. Jordan, *Chem. Phys. Lett.* 171 (1990) 185.
- [8] L.S. Cederbaum, F. Tarantelli, H.-G. Weikert, M. Scheller, H. Köel, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 761.
- [9] P. Botschwina, P. Sebal, *Chem. Phys.* 141 (1990) 311.
- [10] P. Botschwina, *Chem. Phys. Lett.* 255 (1994) 480.
- [11] C.D. Sherrill, H.F. Schaefer, *J. Chem. Phys.* 100 (1994) 8920.
- [12] P.J. Botschwina, *Chem. Phys.* 99 (1993) 6217.
- [13] Y.H. Ding, X.R. Huang, Z.S. Li, C.C. Sun, *J. Chem. Phys.* 108 (1998) 2024.
- [14] Y. Ding, Z. Li, X. Huang, C. Sun, *J. Chem. Phys.* 113 (2000) 1745 (and references therein).
- [15] B.T. Luke, J.A. People, M.-B. Krogh-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar, P.V.R. Schleyer, *J. Am. Chem. Soc.* 108 (1986) 270.
- [16] I.S. Ignatyev, H.F. Schaefer, III, *J. Chem. Phys.* 107 (1997) 5776.
- [17] C. Møller, M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [18] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [19] C. Lee, W. Yang, R.G. Parr, *Phys. Rev.* 37 (1988) 785.
- [20] J.A. Pople, M. Head-Gordon, K. Raghavachari, *J. Chem. Phys.* 87 (1987) 5968.
- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
- [22] H.-Y. Liao, M.-D. Su, S.-Y. Chu, *Inorg. Chem.* 39 (2000) 3522.
- [23] H.-Y. Liao, M.-D. Su, S.-Y. Chu, *Chem. Phys. Lett.* 341 (2001) 122.
- [24] B.S. Jursic, *Int. J. Quantum Chem.* 64 (1997) 263.
- [25] B.S. Jursic, *J. Mol. Struct. (Theochem.)* 394 (1997) 15.