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Generation and characterization of ionic and neutral selenocumulene $HC_3Se^{+/\bullet}$ by tandem mass spectrometry and computational study

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Abstract

Dissociative electron ionization (70 eV) of diphenyl diselenide [$(C_6H_5Se)_2$] generates *m/z* 117 ions of composition [H, C_3, $^{80}Se]^+$. The collision-induced dissociation (CID) mass spectrum of these ions are consistent with the selenocumulene connectivity $HCCCSe^+$. Neutralization–reionization mass spectrum (NRMS) of these structurally characterized ions confirmed that the corresponding neutral analog, hitherto unknown hetero cumulene, HCCCSe, is stable in the rarefied gas phase. The relative, dissociation, and isomerization energies for the ions and neutrals studied at B3LYP/6-31G(d,p) and B3LYP/6-311+G (2d,p) levels are used to support and interpret the experimental results.

Keywords: Selenocumulene; Collision-induced dissociation; Neutralization–reionization; Computational chemistry

1. Introduction

Over the past few years small organoselenium molecules have attracted a great deal of attention from both experimentalists and theoreticians due to their importance as building blocks in organic synthesis and reactive intermediates in the synthesis of selenium containing molecules [1–8]. Some of these molecules have been reported to play an important role as metabolic intermediates of anti-carcinogenic activity in biological pathways [9,10], hence they are related to systems of biological importance. These selenides are also of special interest and importance from the view point of atmospheric chemistry as 25% of atmospheric selenium exists in the vapor phase which can undergo photolysis and other chemical reactions with hydroxyl radicals, nitrate radicals, and ozone leading to depletion of these compounds in the atmosphere [11]. Following the reports on the detection of selenium element in interstellar clouds [12], it is possible that small selenium molecules might occur in the stellar environment. The synthesis and isolation of these molecules in condensed phase is very difficult because of their high reactivity and propensity to undergo polymerization or dissociation [1,13–17]. For these reasons there exist only few reports in the literature concerning with the spectroscopic detection of these molecules, viz., selenoacetaldehyde and selenoformaldehyde [18].

Amongst the experimental methods neutralization–reionization mass spectrometry (NRMS) [19–22] has been established as a powerful and versatile technique for investigating highly reactive elusive radicals or molecules, including polycarbon oxides [23,24] and sulfides [25–28]. There are very few reports available in the literature on the experimental generation of elusive selenium containing molecules, which are of fundamental importance as discussed above. Gerbaux et al. have generated and characterized ionic and neutral $RCNSe^{\bullet+}$ [29] and pyridine *N*-selenide [30] by NRMS. Schroeder et al. have demonstrated that ionic and neutral C_6H_4 $[XTeY]^{\bullet+}$ (X, Y = S, Se) is a viable species in the gas phase [31]. Recently, Wang et al. have produced C_nSe^- anions in the gas phase by laser ablation of mixed selenium and carbon powders and characterized them by collision-induced dissociation (CID). They have concluded from their experimental and theoretical study at ROHF and B3LYP/6-31G* levels that these anions have linear structure and even numbered are much more stable than those with an odd number [32]. In the present work, we report on the successful generation and characterization of the

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ionic and neutral polycarbon selenide, $HC_3Se^{+/\bullet}$ by NRMS in combination with theoretical calculations. Recently, its oxygen and sulfur analogs, $HC_3O^{+/\bullet}$ [23] and $HC_3S^{+/\bullet}$ [28], which are important in interstellar space chemistry [33] have been successfully characterized by tandem mass spectrometry and theoretical calculations.

2. Experimental and theoretical methods

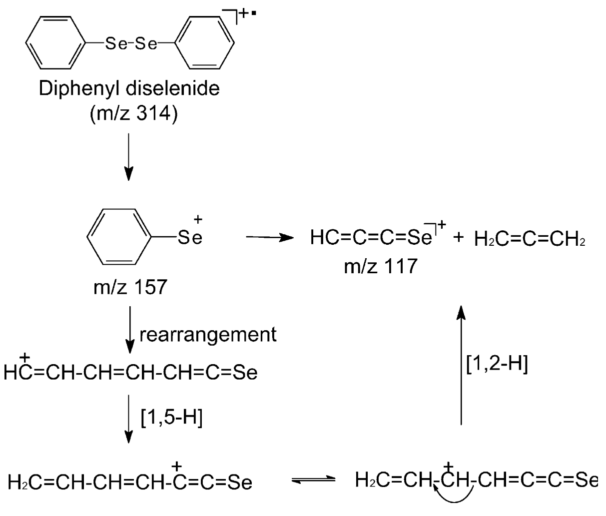
The mass spectrometric experiments were performed on VG Micromass Autospec M mass spectrometer of E_1BE_2 geometry [34] (E denotes an electric sector, and B a magnetic sector). The instrument has two collision chambers (Cls-2 and Cls-3) and an intermediate deflector electrode, all in the third field-free region (between E_1B and E_2).

Diphenyl diselenide was commercially available and used without further purification. The sample was introduced into the ion source using the direct insertion probe under the following conditions: source temperature, 200 °C; electron energy, 70 eV; trap current, 200 μA; acceleration potential, 7 kV. Accurate mass measurements of *m/z* 117 and *m/z* 115 ions from diphenyl diselenide were obtained at a resolution of $m/\Delta m = 5000$ (10% valley definition), using the data system. The CID mass spectra were recorded by mass selecting the beam of *m/z* 117 ions using E_1B (MS-1), with 7 keV translation energy and allowing collision with oxygen in the collision cell Cls-3; the resulting ions were analyzed by scanning E_2 (MS-2). The MS^3 experiments were performed by allowing the precursor ions to dissociate in the FFR-1 (preceding E_1) and transmitting the fragment ions formed there into the FFR-3, where a CID spectrum was obtained using Cls-3. The NR experiments were conducted by mass selecting the beam of *m/z* 117 and *m/z* 115 ions with E_1B (MS-1) and neutralizing them in Cls-2 with xenon. The remaining ions were deflected away from the beam of neutrals by means of a deflector electrode (+5 kV). The neutral beam was reionized in Cls-3 with O_2 target gas and the resulting ions were recorded by scanning E_2. The spectra shown are accumulations of 10–15 scans.

Structures and energies of the HC_3Se ions and neutrals pertinent to this study, connecting transition states and dissociation products were probed by B3LYP/6-31G(d,p) [35] and B3LYP/6-311+G(2d,p) as implemented in Gaussian 98, revision A.9 [36]. Stationary points were characterized as either minima (all real frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedure. The minima connected by given transition structures were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were used as a zero-point correction for the electronic energies. Spin unrestricted calculations were used for all open shell systems and the spin contamination was not found to be high (0.75–0.76) for doublets. The geometries obtained by the density functional methods have been further refined by using a larger basis set, 6-311+G(2d,p).

3. Results and discussion

EI mass spectrum (70 eV) of diphenyl diselenide [37a] shows a fairly abundant peak at *m/z* 117 (35% of base peak) corresponding to the most abundant isotopic composition [37b] of $[C_3, H, {}^{80}Se]^+$ ions whose elemental compositions has been confirmed by high resolution measurements and isobaric impurities were not detected. From the observed fragmentation pattern, we propose a selenocumulene structure $\mathbf{1a}^+$ for the ion at *m/z* 117. Formation of these ions from *m/z* 157 ($C_6H_5{}^{80}Se^+$), as evidenced from the metastable ion spectrum, involves the loss of an allene ($H_2C{=}C{=}CH_2$) molecule. This process appears to be triggered by an initial isomerization of $C_6H_5Se^+$ ions to a linear structure followed by successive 1,5-H and 1,2-H migrations accompanying the cleavage of the C_3–C_4 bond as depicted in Scheme 1. Other plausible isomeric structures are $\mathbf{1b}^+$ and $\mathbf{1c}^+$.



Scheme 1.

The CID mass spectrum (Fig. 1a) of *m/z* 117 ($HC_3{}^{80}Se^+$) ions displays abundant peaks at *m/z* 116 (loss of $H^\bullet$), *m/z* 104 (loss of $CH^\bullet$), *m/z* 92 (loss of $C_2H^\bullet$), *m/z* 80 (loss of $C_3H^\bullet$), and *m/z* 37 (loss of Se) corresponding with the fragment ions $C_3Se^{\bullet+}$, $C_2Se^{\bullet+}$, $CSe^{\bullet+}$, $Se^{\bullet+}$ and $HC_3{}^+$, respectively. Compared to the CID mass spectra of the polycarbon oxides, HC_3O^+ and HC_4O^+, which do not show a peak at *m/z* 16 ($O^{\bullet+}$), the $Se^{\bullet+}$ ions are now forming the second most abundant peak after *m/z* 116. This can be attributed to the difference in ionization energy between selenium and oxygen [IE (Se) = 9.75 eV versus IE (O) = 13.6 eV]. The appearance of ${}^{80}Se^{+\bullet}$ as abundant fragment ion is very much similar to the CID spectrum of selenium containing ions, $RCNSe^{\bullet+}$ [29] and pyridine *N*-selenide [30]. A low abundant peak at *m/z* 25 (loss of CSe) corresponding to the C_2H^+ ion is also present in the spectrum. The narrow peak at *m/z*

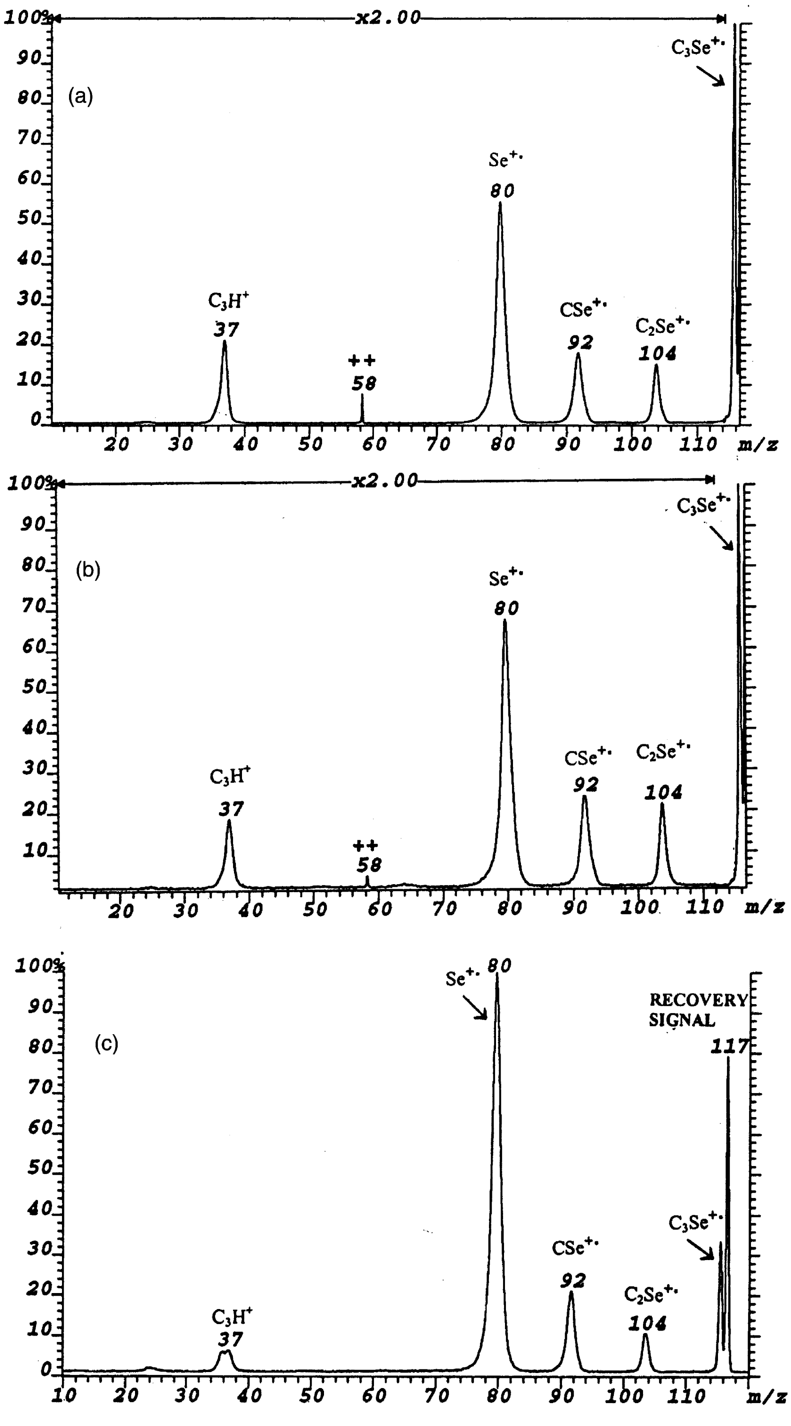


Fig. 1. (a) MIKES-CID spectrum (O_2, 70% T) of *m/z* 117 ions, (b) MIKES-CID (O_2, 70% T) spectrum (MS^3 of metastably generated *m/z* 117 ions in the FFR-1) from *m/z* 157 ions and (c) NR spectrum (Xe, 70% T/O_2, 70% T) of *m/z* 117 ions from diphenyl diselenide.

58 corresponds to the doubly charged *m/z* 117 ions which results from the charge stripping process $117^+ \rightarrow 117^{2+} \rightarrow 116^{2+} + H^\bullet$. All these structure indicative fragment ions are consistent with the selenocumulene structure $HCC_2{}^{80}Se^+$ (**1a**$^+$). This proposal is supported by the CID spectrum of *m/z* 115 ions corresponding with the second most abundant isotopic peak of elemental composition $HC_3{}^{78}Se^+$ ions (Fig. 2a). It can be noted that the spectrum now displays peaks at *m/z* 102, *m/z* 90 and *m/z* 78 corresponding with $^{78}SeC_2{}^{\bullet+}$, $^{78}SeC_2{}^{\bullet+}$, $^{78}Se^{\bullet+}$, ions, respectively.

Loss of allene and Se are the dissociations of the metastable *m/z* 157, $C_6H_5Se^+$ ions and the internal energy content of the resulting *m/z* 117 ions is expected to be lower than the source generated ions. Our theoretical calculations, as will be discussed later, predict **1a**$^+$ ions to be the most stable structure and, therefore, the metastably generated *m/z*

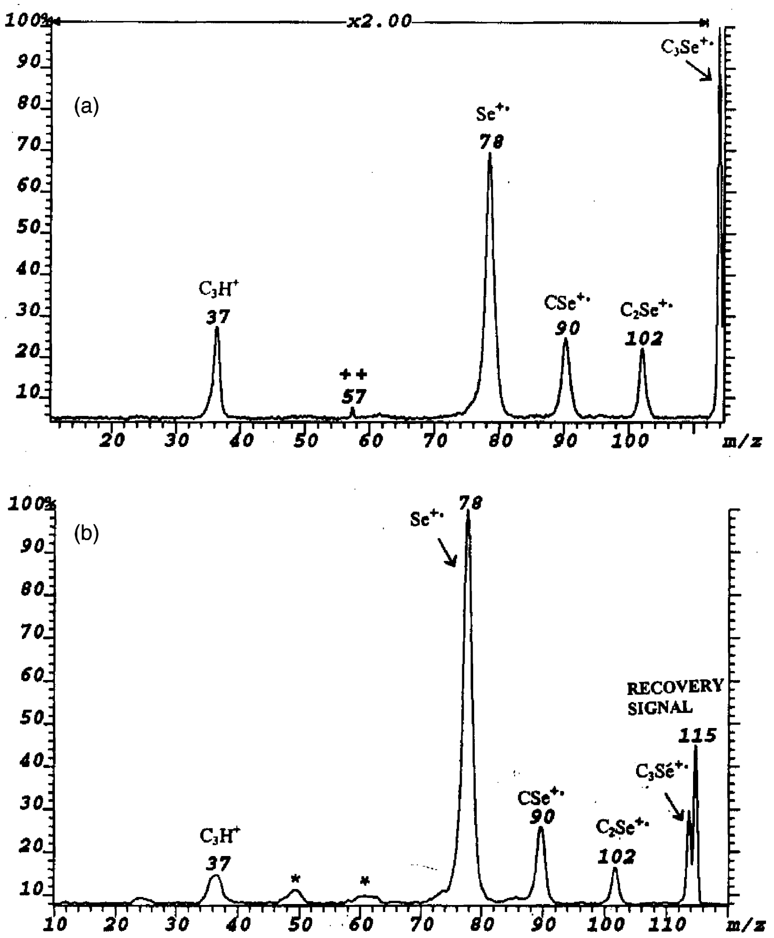


Fig. 2. (a) MIKES-CID spectrum (O_2, 70% T) of *m*/*z* 115 ions and (b) NR spectrum (Xe, 70% T/O_2, 70% T) of *m*/*z* 115 ions from diphenyl diselenide. *Artifact signals.

117 ions from the *m*/*z* 157 precursor ion may well represent isomerically pure ions **1a**$^+$. The CID spectrum of these ions is presented in Fig. 1b. The spectrum is very closely similar to that of Fig. 1a except for the decreased abundance of the doubly charged ion. Thus, the results of MS^3 experiment further strengthens the purity of **1a**$^+$ ions.

In line with the experimental results, our theoretical calculations presented in the Table 1 and the potential energy diagram of Fig. 3 show that all the three isomeric ions **1a**$^+$, **1b**$^+$, and **1c**$^+$ are minima on the potential energy surface and separated from each other by substantial energy barriers. Ion **1a**$^+$ is the most stable having a linear structure with C∝v symmetry (Fig. 4). Ion **1b**$^+$ is the second most stable structure followed by **1c**$^+$, which are less stable than **1a**$^+$ by 56 and 83 kcal mol^{-1}, respectively (Table 1). The energy barriers for isomerization from **1a**$^+$ → **1b**$^+$ is 63 kcal mol^{-1}, **1a**$^+$ → **1c**$^+$, 109 kcal mol^{-1}, and **1b**$^+$ → **1c**$^+$, 103 kcal mol^{-1}, while **1b**$^+$ → **1a**$^+$ and **1c**$^+$ → **1a**$^+$ requires fairly low, 7 and 26 kcal mol^{-1}, respectively. Thus, it is likely that most of the *m*/*z* 117 ions are formed with the structure **1a**$^+$ and significant contribution of **1b**$^+$ and **1c**$^+$ can be ruled out. Further support for this proposal follows from the absence of peaks in the CID mass spectrum (Fig. 1a) at *m*/*z* 105 and *m*/*z* 93 corresponding with the HC_2Se^+ (loss of C) and $HCSe^+$ (loss of C_2), which are expected for the structures **1b**$^+$ and **1c**$^+$, respectively. The calculated dissociation energies for various fragmentation

Table 1
Total (a.u.) and relative energies (kcal mol^{-1}) of (H, C_3, Se) ions calculated using B3LYP/6-31G(d,p) and B3LYP/6-311+G(2d,p) methods

Species	B3LYP/6-31G(d,p) (+ZPC)	B3LYP/6-311+G(2d,p) (+ZPC)
1a$^+$ (C_v^*)	−2513.872031 (0.0)	−2516.069498 (0.0)
1b$^+$ (C_s)	−2513.782172 (56.3)	−2515.97876 (56.9)
1c$^+$ (C_1)	−2513.738762 (83.6)	−2515.936318 (83.5)
TS1a$^+$ → **1b**$^+$ (C_1)	−2513.771711 (63.0)	−2515.968251 (63.5)
TS1a$^+$ → **1c**$^+$ (C_s)	−2513.697281 (109.6)	−2515.895048 (109.4)
TS1b$^+$ → **1c**$^+$ (C_s)	−2513.706884 (103.6)	−2515.904899 (103.2)
$C_3Se^{\bullet+}$ (a) + $H^\bullet$	−2513.649828 (139.4)	−2515.847955 (139.0)
$C_3Se^{\bullet+}$ (b) + $H^\bullet$	−2513.603416 (168.5)	−2515.807730 (164.2)
$C_2Se^{\bullet+}$ + $CH^\bullet$	−2513.515756 (223.5)	−2515.716683 (221.3)
$CSe^{\bullet+}$ + $C_2H^\bullet$	−2513.571414 (188.6)	−2515.778195 (182.7)
$Se^{\bullet+}$ + $C_3H^\bullet$	−2513.582036 (181.9)	−2515.796446 (171.3)
C_3H^+ + Se	−2513.575053 (186.3)	−2515.784305 (178.9)
C_2H^+ + CSe	−2513.442117 (269.7)	−2515.674381 (248.0)

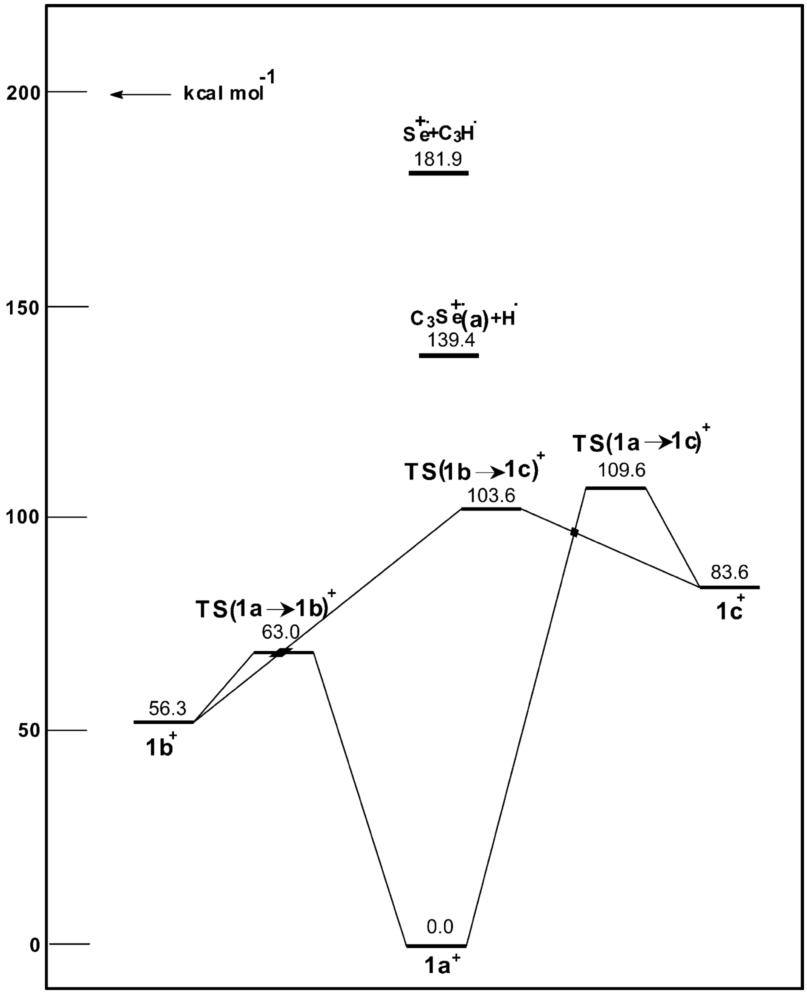


Fig. 3. Potential energy diagram from B3LYP/6-31G(d,p) for the rearrangement and dissociation reactions of ions **1a**$^+$ to **1c**$^+$.

channels are also found to be in total agreement with the fragment ion abundances in the CID mass spectrum (Table 1). For example, the most abundant peak in the CID mass spectrum at *m*/*z* 116 (loss of H$^\bullet$) corresponds to the fragmentation channel of the lowest dissociation energy and the lowest abundant peak of *m*/*z* 25 with highest energy dissociation channel. Based on all these experimental results combined together with the computational calculations, we propose that for energetic and entropic reasons most of the ions will have the selenocumulene structure, **1a**$^+$.

The neutralization–reionization (NR) mass spectrum of the ions **1a**$^+$ (Fig. 1c) displays a fairly abundant recovery signal at *m*/*z* 117 (80% of the base peak) and resembles the CID spectrum of Fig. 1a. This indicates that vertical neutralization of **1a**$^+$ ions yields corresponding neutral species that are stable on the NR experimental time scale of microseconds and have retained HC_3Se^+ connectivity. This proposal is supported by the NR spectrum of *m*/*z* 115 ions (Fig. 2b) corresponding with the composition $HC_3\,^{78}Se^+$ ions. The spectrum is identical with that of *m*/*z* 117 ions (Fig. 1c), in the way that now the spectrum exhibits all $^{78}Se^+$ containing ions instead of $^{80}Se^+$ ions. That the NR spectra are closely similar to the CID spectra indicates that the fragment ions in the NR spectra are mostly due to collisional reionization process.

These experimental results are also in line with the theoretical calculations (Figs. 5 and 6, Table 2), which predict that **1a** is the global minimum and stable with respect

Table 2
Total (a.u.) and relative energies (kcal mol^{-1}) of (H, C_3, Se) neutrals calculated using B3LYP/6-31G(d,p) and B3LYP/6-311+G(2d,p) methods

Species	B3LYP/6-31G(d,p) (+ZPC)	B3LYP/6-311+G(2d,p) (+ZPC)
1a$^\bullet$ (C_s)	−2514.137545 (0.0)	−2516.342223 (0.0)
1b$^\bullet$ (C_s)	−2514.109777 (17.4)	−2516.312809 (18.4)
1c$^\bullet$ (C_1)	−2514.073394(40.2)	−2516.28185(37.8)
TS1a$^\bullet$ → **1b**$^\bullet$ (C_1)	−2514.048025 (56.1)	−2514.254622 (55.3)
TS1a$^\bullet$ → **1c**$^\bullet$ (C_s)	−2514.014848 (76.9)	−2516.220959 (76.0)
TS1b$^\bullet$ → **1c**$^\bullet$ (C_s)	−2514.030265 (67.3)	−2516.234571 (67.5)
$C_3Se + H^\bullet$	−2514.017966 (75.0)	−2516.222595 (75.0)
$C_2Se + CH^\bullet$	−2513.850377 (180.2)	−2516.06003 (177.0)
$CSe + C_2H^\bullet$	−2513.969194 (105.6)	−2516.1817 (100.7)
$Se + C_3H^\bullet$	−2513.910282 (142.6)	−2516.129168 (133.6)

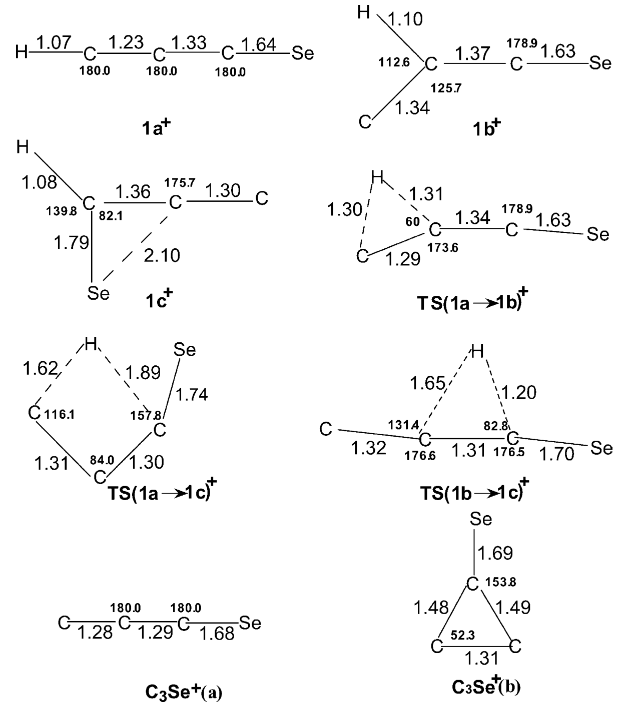


Fig. 4. Selected optimized geometries [B3LYP/6-31G(d,p)] of ionic HC$_3$Se$^+$, **1a**$^+$, its isomers, **1b**$^+$ and **1c**$^+$, connecting transition states and isomers of C$_3$Se$^+$, bond lengths in angstrom, bond angles in degrees.

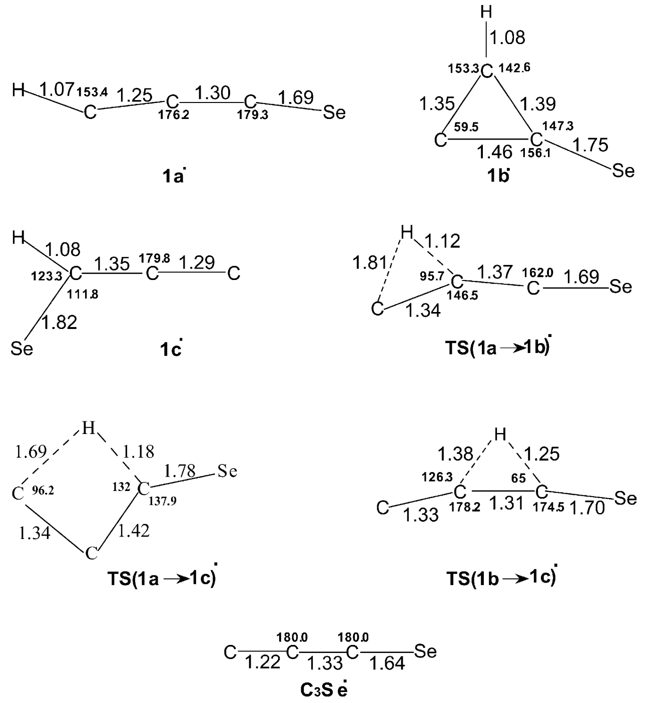


Fig. 6. Selected optimized geometries [B3LYP/6-31G(d,p)]of neutral HC$_3$Se$^\bullet$, **1a**$^\bullet$, its isomers, **1b**$^\bullet$ and **1c**$^\bullet$, connecting transition states and fragment ion C$_3$Se$^\bullet$ bond lengths in angstrom, bond angles in degrees.

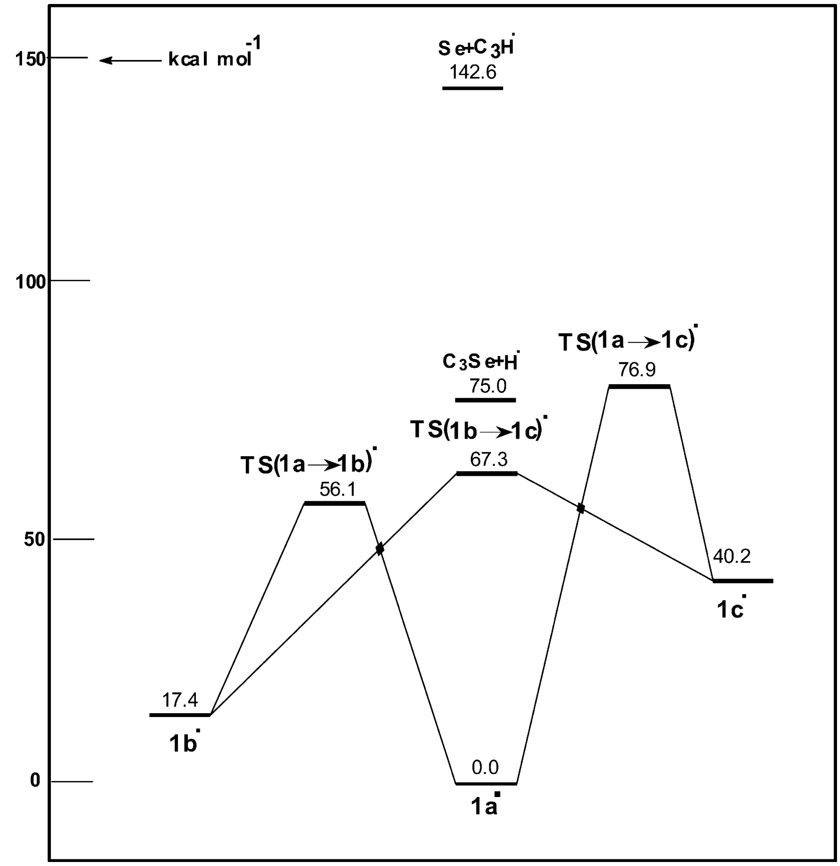


Fig. 5. Potential energy diagram from B3LYP/6-31G(d,p) for the rearrangement and dissociation reactions of neutral **1a**$^\bullet$ to **1c**$^\bullet$.

to dissociation. Similar to the oxygen analog CCHCO, CCHCSe (**1b**$^\bullet$) is unstable and undergoes ring closure to yield the cyclic isomer (*cyclo*-C_3H)-Se, which is predict to lie 17 kcal mol^{-1} higher in energy than **1a**$^\bullet$. In contrast to the cation relative stabilities, **1c**$^\bullet$ is found to be only 40 kcal mol^{-1} less stable than **1a**$^\bullet$. Both **1b**$^\bullet$ and **1c**$^\bullet$ are separated from **1a**$^\bullet$ by substantial energy barriers of 56 and 77 kcal mol^{-1}, respectively, which rules out the likely isomerization of **1a**$^\bullet$ → **1b**$^\bullet$ and **1a**$^\bullet$ → **1c**$^\bullet$. While the cation **1a**$^+$ is linear, the radical **1a**$^\bullet$ has a bent structure with C_s symmetry. This is expected to produce Frank–Condon effects for vertical neutralization and reionization processes. It can be noted that the calculated vertical ionization of the neutral (IE_v) requires only 0.3 eV (7 kcal mol^{-1}) more than the adiabatic process and vertical neutralization of thermalized HC_3Se^+ ions differ by 0.1 eV (2 kcal mol^{-1}) from adiabatic process. Thus, the minimum excess Frank–Condon energy of $HC_3Se^\bullet$ is only 7 kcal mol^{-1} which is insufficient to induce any fragmentation or isomerization as the threshold energy of dissociation or isomerization lies very high in energy. This scenario is very much similar to that of $HC_3O^\bullet$ radical [23]. Thus, our theoretical calculations confirm that the neutral $HC_3Se^\bullet$ is a viable species in the rarefied gas phase.

4. Conclusion

From the combined results of mass spectrometric experiments and theoretical calculations at B3LYP/6-31G(d,p) and B3LYP/6-311+G(2d,p) levels, it is proposed that dissociative electron ionization of diphenyl diselenide yields [H, C_3, Se]$^+$ ions of the connectivity $HCCCSe^+$. CID mass spectra of source and metastably generated [H, C_3, Se]$^+$ ions are used to deduce the selenocumulene connectivity. NR experiments confirm the theoretical prediction that neutral selenocumulene, $HC_3Se^\bullet$ is a stable species in the gas phase.

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(b) Selenium has six isotopes and their abundances are: ^{74}Se: 0.87, ^{76}Se: 9.02, ^{77}Se: 7.58, ^{78}Se: 23.52, ^{80}Se: 49.82 and ^{82}Se: 9.19. The abundance of *m*/*z* 116 in the EI mass spectrum of diphenyl diselenide is negligible (<1%), hence, isotopic contributions to *m*/*z* 117 are ruled out.