Iminoethenethiones, $RN{=}C{=}C{=}S$: Characterization by Neutralization–Reionization Mass Spectrometry and G2(MP2) Theory

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Abstract: (Methylimino)ethenethione (**2**) and iminoethenethione (**4**) are stable molecules on the microsecond time scale of neutralization–reionization mass spectrometry experiments. The corresponding radical cations were generated by fragmentation of thiazolopyrimidinedione molecular ions $\mathbf{1}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$. Iminoethenethione (**4**) does not tautomerize to thioformyl cyanide (H–CS–CN, **5**) under the wall-less conditions of the MS experiment, but it does so under FVP conditions when generated from isoxazolones **6**. Thioformyl cyanide was unequivocally identified by IR and mass spectra. The structures and stabilities of **2**, **4**, and $\mathbf{4}^{\cdot+}$ were investigated by ab initio calculations at the G2(MP2) level of theory. Both **2** and **4** are predicted to have a singlet ground state, in contrast to $O{=}C{=}C{=}S$, for which a triplet state is preferred. The singlet–triplet gaps are approximately 40 kJ mol^{-1}. In agreement with experimental findings, both iminoethenethiones are calculated to be thermodynamically and kinetically stable species, lying in energy wells with at least a 100 kJ mol^{-1} barrier to dissociation into HNC (or CH_3NC) + CS. The IR and UV spectra and ionization energies of **2** and **4** are predicted. The iminoethenethione radical cation ($\mathbf{4}^{\cdot+}$) is found to be the global minimum on the $C_2HNS^{\cdot+}$ potential energy surface and stable toward all possible fragmentations: the most favorable fragmentations into $H^{\cdot}$ + $NCCS^{+}$ and HNC + $CS^{\cdot+}$ are in accord with the mass spectrometric observations.

1. Introduction

Whereas the odd-membered cumulenes of the type $X{=}C{=}C{=}C{=}Y$ are relatively stable albeit highly reactive molecules,[2-5] the even-membered analogs, $X{=}C{=}C{=}Y$, are extremely unstable and very little known. C_2O_2 is predicted by theory to possess a triplet ground state,[6] and all attempts to detect it experimentally have failed so far.[7] However, C_2S_2 has been well characterized by neutralization–reionization (NR)[8] and collisional activation (CA)[8,9] mass spectrometry, as well as matrix isolation IR and UV spectroscopy.[9,10] Even though it is still not certain whether the ground state of C_2S_2 is singlet or triplet,[6,9,10] this molecule survives generation in flash vacuum pyrolysis (FVP) reactions up to 1000 °C with short contact times, but it polymerizes in the neat state above 60 K.

The thioxoethenone radical cation, $OCCS^{\cdot+}$, has been generated in a mass spectrometer, and the existence of the neutral OCCS was established by NRMS experiments.[11] Similar attempts to detect neutral OCCO[7f,g] and RNCCO[12] were negative.

Here we report the successful generation of iminoethenethione, $HN{=}C{=}C{=}S$, and its methyl derivative, $CH_3N{=}C{=}C{=}S$, in NRMS experiments, as well as theoretical calculations, using G2(MP2) theory, in support of the experimental interpretations.

2. Results

$CH_3N{=}C{=}C{=}S$ (2). The (Methylimino)ethenethione radical cation ($\mathbf{2}^{\cdot+}$) was generated in a mass spectroscopic retro-

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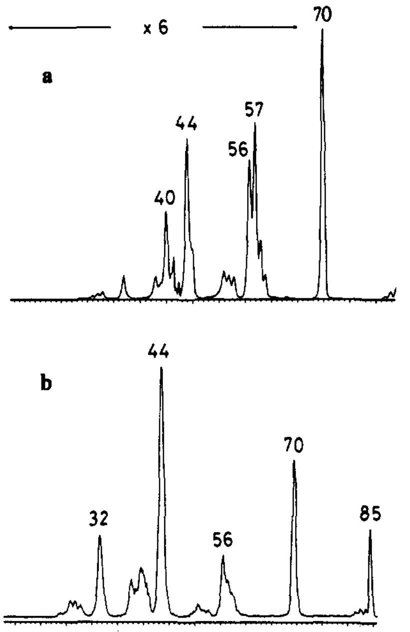
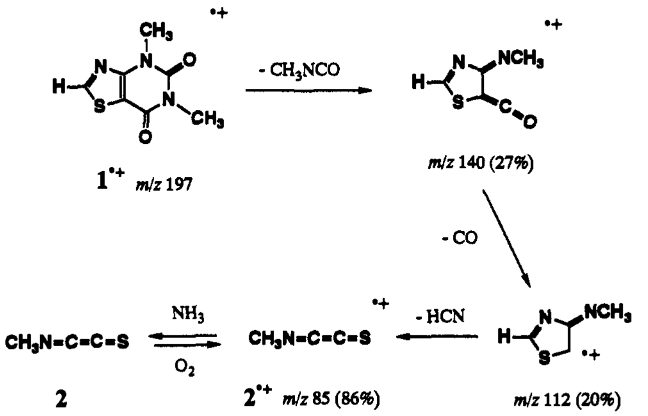


Figure 1. (a) CA mass spectrum of $CH_3N{=}C{=}C{=}S^{\cdot+}$ ions ($2^{\cdot+}$) (m/z 85) from $1^{\cdot+}$. (b) Neutralization–reionization mass spectrum (NH_3/O_2) of these ions.

Scheme 1



Diels–Alder reaction of the intense molecular ion[13] of 4,6-dimethylthiazolo[4,5-*d*]pyrimidine-5,7-dione ($1^{\cdot+}$), which, on loss of methyl isocyanate, generates an ion at m/z 140 (relative intensity 27%). This, in turn, eliminates CO to give m/z 112 (20%) and then HCN to furnish the desired ion $2^{\cdot+}$, m/z 85 (86%) (Scheme 1).

The CA spectrum of these m/z 85 ions (Figure 1a) features an intense peak due to loss of $CH_3^{\cdot}$ ($NCCS^+$, m/z 70), corresponding to a low-energy simple bond cleavage. Other important fragment ions corroborating the structure are m/z 56 ($C_2S^{\cdot+}$), 44 ($CS^{\cdot+}$), and 32 ($S^{\cdot+}$). The connectivity NCCS is further illustrated in an MS/MS/MS experiment (Figure 2), in which the CA spectrum of the m/z 70 ion features a very intense peak due to $CS^{\cdot+}$. The fragmentation to $CS^{\cdot+}$ + CN (ΔH_f° = 1803 kJ mol^{-1}) is preferred over CS + $CN^{\cdot+}$ (2062 kJ mol^{-1}).[14]

The neutralization–reionization mass spectrum of the $CH_3NCCS^{\cdot+}$ ions (Figure 1b) features an abundant recovery signal for survivor ions (m/z 85), thus demonstrating stability of the neutral **2** on the microsecond time scale of the NRMS experiment. The good agreement between the CA and NR mass spectra indicates that ion and neutral possess the same connectivity. Thus, it is concluded that CH_3NCCS (**2**) is a stable molecule in the gas phase, resisting decomposition into CH_3NC and CS.

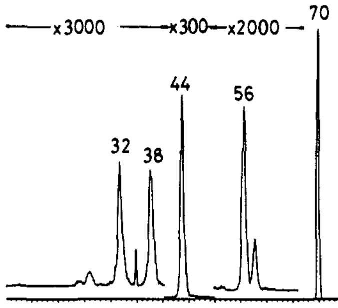


Figure 2. MS/MS/MS experiment on m/z 85 ions from $1^{\cdot+}$. A beam of mass-selected m/z 85 ions collides with He; the so-produced m/z 70 ions are mass-selected and then collided with oxygen to produce the CA spectrum.

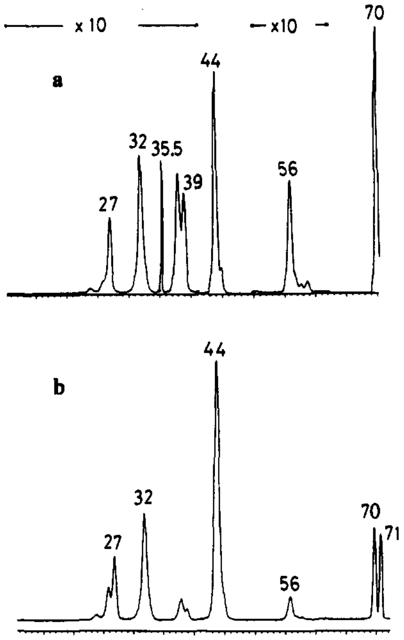
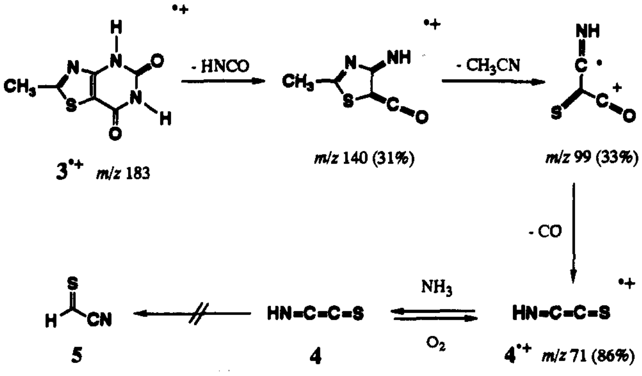


Figure 3. (a) CAMS of $HN{=}C{=}C{=}S^{\cdot+}$ ions ($4^{\cdot+}$) (m/z 71) from $3^{\cdot+}$. (b) NRMS of these ions.

Scheme 2



$HN{=}C{=}C{=}S$ (4). The iminoethenethione radical cation ($4^{\cdot+}$) was generated in a similar manner from the thiazolopyrimidinedione $3^{\cdot+}$ (Scheme 2). Here, the sequence of eliminations is HNCO, CH_3CN, and CO, giving ions at m/z 140 (31%), 99 (33%), and 71 (86%). The m/z 71 ion ($HNCCS^{\cdot+}$, $4^{\cdot+}$) shows very intense losses of $H^{\cdot}$ (giving $NCCS^+$, m/z 70, identical with the NCCS ion described above) and HNC (to $CS^{\cdot+}$, m/z 44) in the CA spectrum (Figure 3a) (these fragmentations are seen already in the absence of the collision gas, O_2). Again, the fragmentation to HNC + $CS^{\cdot+}$ rather than $HNC^{\cdot+}$ + CS is in agreement with the thermochemistry (1569 and 1674 kJ mol^{-1}, respectively)[14] and the calculations reported in section 3. A significant contribution of azirinethione ions ($16^{\cdot+}$) is less likely on the basis of the CA spectrum (Figure 3a).

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Table 1. Relative Abundances of Fragments in CA (O_2) Mass Spectra of Isomeric $C_2HNS^{\bullet+}$ Ions (*m/z* 71)

	m/z^a															
ion	70	59	58	57	56	46	45	44	39	38	35.5	32	27	26	25	24
HNCCS$^{\bullet+}$ (**4**$^{\bullet+}$)	1885	5	3	8	68		166	1465	57	68	*100*	75	41	4		1
HCSCN$^{\bullet+}$ (**15**$^{\bullet+}$)^b	2114	5	44	14	17		279	1357	71	83	41	*100*	24	7		
HCNCS$^{\bullet+}$ (**13**)^c	2260	7	36	21	30		199	1481	80	84	54	*100*	32	7		
HCCNS$^{\bullet+}$ (**14**$^{\bullet+}$)^d	1041	1	8	5	4	*100*	261	411	30	27	12	42	2	1	1	<1
H-CS-CN$^{\bullet+}$ (**5**$^{\bullet+}$)	949	2	5	13	15		311	321	39	39	8	*100*	7	6	2	1

^{a} *m/z* 70, 45, and 44 excluded from the normalization. ^{b} From methyl thiocyanate, CH_3SCN, by loss of 2 H. ^{c} From methyl isothiocyanate, $CH_3N{=}C{=}S$, by loss of 2 H. ^{d} From acetonitrile sulfide,^{3} $CH_3C{\equiv}NS$, by loss of 2 H.

The HNCCS connectivity is further confirmed by the characteristic loss of NH (giving $CCS^{\bullet+}$, *m/z* 56) and by comparison with the CA spectra of isomeric ions generated by loss of 2H from methyl thiocyanate (CH_3SCN), methyl isothiocyanate ($CH_3N{=}C{=}S$), acetonitrile sulfide ($CH_3C{\equiv}NS$), and thioformyl cyanide, H–CS–CN (**5**) (Table 1). These isomers show very pronounced differences, indicating a lack of interconversion of the ions. In particular, only the HCCNS ion generated from $CH_3C{\equiv}NS$ features a strong signal due to $NS^{\bullet+}$ at *m/z* 46. These differences are retained in the NR mass spectra of the five isomers, which all show significant recovery signals. The NRMS of $HN{=}C{=}C{=}S^{\bullet+}$ (**4**$^{\bullet+}$) is shown in Figure 3b. It is of interest to note that, in an NRMS with Me_2NH/O_2, the intensity of the molecular ion, *m/z* 71, is significantly enhanced relative to that of the NH_3/O_2 experiment. This may be attributed to the closeness of the ionization energies of HNCCS (calculated 8.43 eV; Table 2) and dimethylamine (experimental 8.23 eV;[14] calculated 8.38 eV). The NRMS experiments demonstrate that the neutral molecule $HN{=}C{=}C{=}S$ (**4**) is stable on the microsecond time scale in the rarefied gas phase of the mass spectrometer. The question of spin multiplicity of **4** is addressed in section 3. Most notably, it does not tautomerize to thioformyl cyanide (**5**) in this wall-less experiment. In contrast, such tautomerization does take place in FVP experiments as demonstrated below.

In analogy with the method used by us to generate $S{=}C{=}C{=}S$,[9] we prepared the isoxazolones **6** and subjected them to mass spectrometry and flash vacuum pyrolysis. The normal mass spectrum of **6b** (400 °C) shows only a weak peak at *m/z* 71 (13%), but mass selection followed by CAMS demonstrates that this ion has the HNCCS (**4**$^{\bullet+}$) structure (Figure 4a).[15] The *m/z* 71 signal becomes stronger on increasing the temperature of the FVP oven directly attached to the ion source, reaching a relative intensity of *ca.* 20% at 800 °C, but the CA mass spectra clearly show that the ion structure has changed (Figure 4b) (this is true already at 600 °C). The presence of a strong signal at *m/z* 45 (HCS), in addition to that at *m/z* 44 (CS), suggested that isomerization to thioformyl cyanide (**5**) had taken place (Table 1), and this was confirmed by infrared spectroscopy as described below. Analogous results were obtained on FVP of **6a**.

Table 2. Calculated Total (hartrees) and Relative Energies (kJ mol^{-1}) of HNCCS$^{\bullet+}$ (**4**$^{\bullet+}$), HNCCS (**4S**), CH_3NCCS (**2S**), and Related Species^a

			energy	
species	sym	state	tot.	rel^b
HNCCS$^{\bullet+}$ (**4**$^{\bullet+}$)	C_s	$^2A'$	–528.688 00	0
HNCCS$^{\bullet+\,c}$	C_s	$^2A'$	–528.676 75	29.5
H–CS–CN$^{\bullet+}$ (**5**$^{\bullet+}$)	C_s	$^2A'$	–528.680 36	20.1
HCNCS$^{\bullet+}$ (**13**$^{\bullet+}$)	C_s	$^2A'$	–528.662 95	65.7
TS: **4**$^{\bullet+}$ → **5**$^{\bullet+}$ (**10**$^{\bullet+}$)	C_s	$^2A'$	–528.530 34	413.9
HNCCS (**4S**)	C_s	$^1A'$	–528.986 44	0
NHCCS^d	C_s	$^1A'$	–528.962 86	61.9
H–CS–CN (**5S**)	C_s	$^1A'$	–529.037 06	-132.9
TS: **4S** → **5S** (**10**)	C_s	$^1A'$	–528.876 44	288.8
TS: **4S** → HNC + CS (**11**)	C_s	$^1A'$	–528.940 90	119.6
HSCCN (**12S**)	C_s	$^1A'$	–528.976 57	24.9
HCNCS (**13S**)	C_s	$^1A'$	–528.961 64	65.1
HCCNS (**14**)	C_s	$^1A'$	–528.946 63	104.5
HCSCN (**15**)	C_s	$^1A'$	–528.955 81	80.4
$\overline{\mathrm{CHNC}}{=}\mathrm{S}$ (**16**)	C_s	$^1A'$	–528.985 71	1.9
$\overline{\mathrm{NHCC}}{=}\mathrm{S}$ (**17**)	C_s	$^1A'$	–528.936 86	130.2
HNCCS (**4T**)	C_s	$^3A''$	–528.971 21	40.0
H–CS–CN (**5T**)	C_s	$^3A''$	–528.974 99	30.1
HSCCN (**12T**)	C_1	^3A	–528.946 58	104.6
HCNCS (**13T**)	C_s	$^3A''$	–528.945 54	107.4
H(N)CCS (**18T**)	C_s	$^3A''$	–528.934 02	137.6
CH_3NCCS (**2S**)	C_1	^1A	–568.205 99	0
CH_3NCCS (**2T**)	C_1	^3A	–568.189 72	42.7
CH_3–CS–CN (**19**)	C_s	$^1A'$	–568.272 67	–175.0
TS: **2S** → **19** (**20**)	C_s	$^1A'$	–568.076 99	338.7
TS: **2S** → CH_3NC + CS (**21**)	C_1	^1A	–568.165 75	105.7
HNCCS (**4**$^{2+}$)	$C_{\infty v}$	$^1\Sigma^+$	–528.175 39	
H–CS–CN (**5**$^{2+}$)	C_s	$^1A'$	–528.033 13	
HNCC (S)	C_s	$^1A'$	–131.147 56	
HNCC (T)	C_s	$^3A''$	–131.143 96	
HNCC$^{\bullet+}$	$C_{\infty v}$	$^2\Pi$	–130.793 93	
NCCS$^{\bullet}$	C_s	$^2A'$	–528.385 81	
NCCS$^+$	$C_{\infty v}$	$^1\Sigma^+$	–528.096 40	
CCS (S)	$C_{\infty v}$	$^1\Sigma^+$	–473.621 10	
CCS (T)	$C_{\infty v}$	$^3\Sigma^-$	–473.636 12	
CCS$^{\bullet+}$	$C_{\infty v}$	$^2\Pi$	–473.265 45	
HCN	$C_{\infty v}$	$^1\Sigma^+$	–93.282 49	
HNC (S)	$C_{\infty v}$	$^1\Sigma^+$	–93.260 50	
HNC (T)	C_s	$^3A'$	–93.086 44	
HNC$^{\bullet+}$	$C_{\infty v}$	$^2\Sigma^+$	–92.780 09	
CH_3CN	C_{3v}	$^1A_1$	–132.519 83	
CH_3NC	C_{3v}	$^1A_1$	–132.483 27	
CS (S)	$C_{\infty v}$	$^1\Sigma^+$	–435.705 59	
CS (T)	$C_{\infty v}$	$^3\Pi$	–435.571 47	
CS$^{\bullet+}$	$C_{\infty v}$	$^2\Sigma^+$	–435.285 97	
NH (S)	$C_{\infty v}$	$^1\Sigma^+$	–55.075 53	
NH (T)	$C_{\infty v}$	$^3\Sigma^-$	–55.140 03	
NH$^{\bullet+}$	$C_{\infty v}$	$^2\Pi$	–54.648 27	
S (S)	K_h	^1P	–397.601 93	
S (T)	K_h	^3P	–397.646 99	
S$^{\bullet+}$	K_h	^2P	–397.199 99	
H$^{\bullet}$	K_h	^2S	–0.500 00	

^{a} G2(MP2) E_0 energies. ^{b} Relative to HNCCS$^{\bullet+}$ (**4**$^{\bullet+}$), HNCCS (**4**), and CH_3NCCS (**2**) for $C_2HNS^{\bullet+}$, C_2HNS, and C_3H_3NS species, respectively. ^{c} Corresponding to vertical ionization of HNCCS (**4S**). ^{d} Corresponding to vertical transition of HNCCS$^{\bullet+}$ (**4**$^{\bullet+}$).

Thioformyl Cyanide, H–CS–CN (5). The definitive identification of thioformyl cyanide required access to its IR and mass spectra. Previous attempts to obtain these were unsuccessful.[16a] However, we successfully generated **5** by FVP of allyl cyanomethyl sulfide (**9**) and monitored the reaction by both MS and IR spectroscopy. The mass spectrometric monitoring showed the molecular ion of **9** (*m/z* 113) disappearing as the FVP temperature increased from 325 to 600 °C. Concurrently, ions due to propene (*m/z* 42) and **5** (*m/z* 71) increased in intensity over the range 400–800 °C. The mass spectra are reported in the Experimental Section. The Ar matrix IR spectrum of **5** was obtained under the same conditions.[16b] The mass and IR spectra of **5** together

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(15) The electron ionization mass spectrum of **6b** recorded as a function of FVP temperature shows the molecular ion (*m/z* 246) rapidly decreasing, and disappearing at *ca.* 700 °C. At the same time, *m/z* 202, corresponding to loss of CO_2, increases, reaching at maximum at 700 °C. The CA spectrum of the *m/z* 202 ion is dominated by a peak at *m/z* 142 having the structure $PhN{=}C{=}C{=}C{=}NH^{\bullet+}$ according to comparison with previous investigations of this ion from other sources.[4e] Above 700 °C the *m/z* 202 ion rapidly decreases, and signals at *m/z* 103 (PhCN), 44 (CO_2), 28 (C_2H_4), and 71 increase in intensity.

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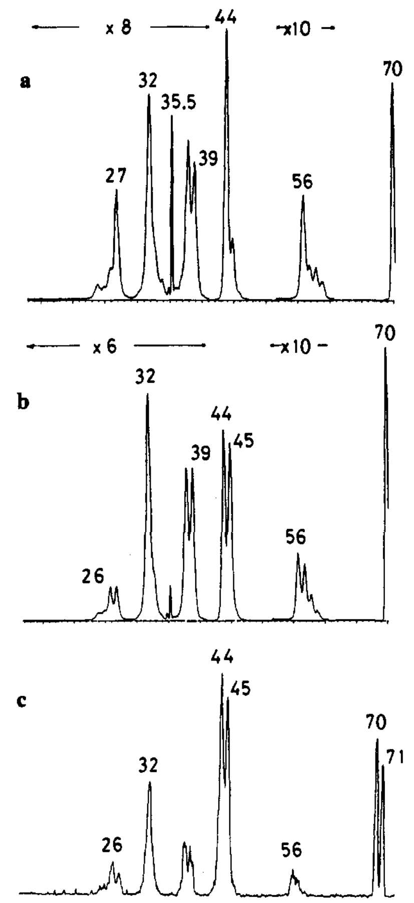
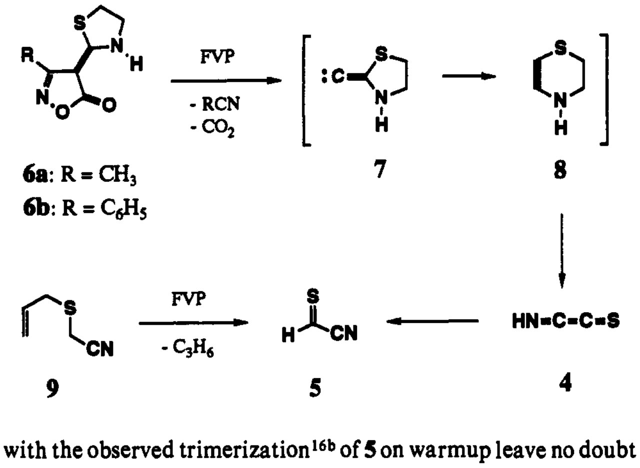


Figure 4. (a) CAMS (O_2) of m/z 71 ions from the EI mass spectrum of **6a** at 400 °C. (b) CAMS (O_2) of the m/z 71 ions from the FVP of **6b** at 600 °C. The CA (He) spectrum is virtually identical; also the CA (He) and CA (O_2) spectra obtained at 800 °C are virtually identical with the one shown. (c) NRMS (NH_3/O_2) of m/z 71 [H–CS–CN (**5**)] from experiment b.

Scheme 3



with the observed trimerization[16b] of **5** on warmup leave no doubt as to its structure.

FVP of **6a** with Ar matrix isolation of the products for IR spectroscopy revealed the formation of CO_2, CH_3CN, C_2H_4, and **5**, the last identified by direct comparison with authentic samples produced from **9**. This experiment indicates that **4** is produced in a mechanism analogous to that for C_2S_2 formation,[9] i.e. via intermediates such as **7** and **8** (Scheme 3). However, **4** undergoes rapid tautomerization to **5** due to wall collisions under FVP conditions. The tautomerization **4** → **5** is not an intramolecular sigmatropic shift, for calculations indicate a very high barrier for such a process (section 3). For this very reason, HN═C═C═S is observable in the mass spectrometry experiments where no wall collisions take place.

3. Theory

Method and Results. Standard ab initio molecular orbital calculations[17] were carried out using the GAUSSIAN 92 series of programs.[18] The structures and energies of C_2HNS, $C_2HNS^{\cdot+}$, C_2HNS^{2+}, and C_3H_3NS were investigated by the Gaussian-2 [G2(MP2)] theory. The G2(MP2) method, described in detail elsewhere,[19] is a composite procedure based effectively on QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G* energies (evaluated by making certain additivity assumptions) together with zero-point vibrational and isogyric corrections. In the G2(MP2) theory, the basis-set extension energy corrections are obtained at the MP2 level.[19a] Calculated MP2/6-31G* geometries for $C_2HNS^{\cdot+}$, C_2HNS, and C_3H_3NS isomeric structures and transition structures are displayed in Figure 5, with corresponding G2(MP2) energies presented in Table 2. Harmonic vibrational frequencies and infrared intensities of the singlet and triplet iminoethenethiones (**2** and **4**) calculated at the HF/6-31G* and MP2/6-31G* (with frozen-core approximation) levels, using analytical second derivatives, are collected in Table 3. The MP2/6-31G* frequencies were scaled by a factor of 0.9427 to account for their average overestimation at this level of theory.[20] The vertical transition energies of iminoethenethiones, given in Table 4, were calculated via the configuration interaction with singles (CIS) method[21] using the 6-311++G(2df,2p) basis set,[17] based on the MP2/6-31G* geometries. Spin-restricted calculations were used for closed-shell systems and spin-unrestricted for open-shell systems.

Structure and Stability of HN═C═C═S$^{\cdot+}$. We are not aware of any theoretical calculation on the iminoethenethione radical ion (**4**$^{\cdot+}$). It is the lowest-energy structure of the $C_2HNS^{\cdot+}$ ion. H–CS–CN$^{\cdot+}$ (**5**$^{\cdot+}$) and HCNCS$^{\cdot+}$ (**13**$^{\cdot+}$) lie close in energy, 20 and 66 kJ mol^{-1} above **4**$^{\cdot+}$. **4**$^{\cdot+}$ is predicted to have a shallow W-shaped skeleton (Figure 5). It has somewhat localized C≡N and C═S bonds (1.182 and 1.532 Å, respectively). This cumulene ion is predicted to be thermodynamically stable with respect to all possible fragmentations. (Figure 6). The lowest-energy pathway corresponds to the loss of a hydrogen atom (241 kJ mol^{-1}). Dissociation of **4**$^{\cdot+}$ into HNC + CS$^{\cdot+}$ is also favorable (372 kJ mol^{-1}). In agreement with the mass spectral results reported in section 2, all other fragmentation processes are considerably higher in energy (>500 kJ mol^{-1}). Rearrangement of **4**$^{\cdot+}$ to the thioformyl cyanide radical cation (**5**$^{\cdot+}$), via a four-center transition **10**$^{\cdot+}$ (Figure 5), requires a sizable barrier of 414 kJ mol^{-1}. Hence, **4**$^{\cdot+}$ is calculated to be a stable species in the gas phase, in excellent agreement with the experimental observation.

Adiabatic (IE_a) and vertical (IE_v) ionization energies of HNCCS (**4S**) were calculated at the G2(MP2) level, which is able in general to reproduce ionization energies to within 0.1 eV.[19,22] The predicted IE_a and IE_v values of **4S** are 8.12 and 8.43 eV, respectively (Table 2). The large difference between IE_a and IE_v (0.31 eV) is attributed to the large change in molecular geometry upon ionization (see discussion below).

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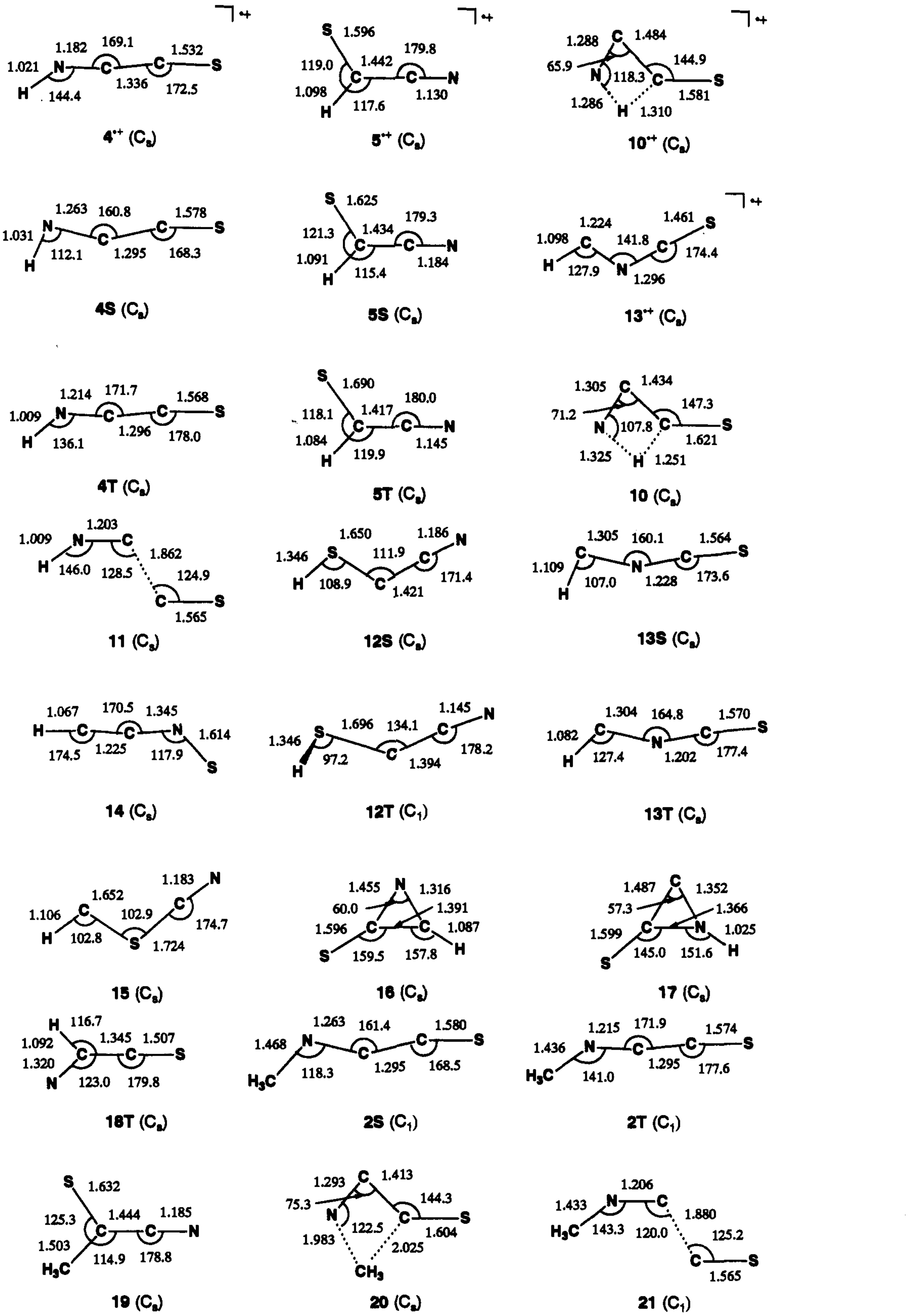

Figure 5. Optimized geometries (MP2/6-31G*) of $C_2HNS^{•+}$, C_2HNS, and C_3H_3NS isomeric structures and transition structures (bond lengths in angstroms and bond angles in degrees).

Relative Energies of C_2HNS Isomers. Several isomeric C_2-HNS structures were considered on both the singlet and triplet surfaces. Thioformyl cyanide, H–CS–CN (**5S**), is the global minimum on the C_2HNS potential energy surface. Singlet iminoethenethione, HN=C=C=S (**4S**), an isoelectronic analogue of thioxoethenone (O=C=C=S),[11] is the second-lowest-energy isomer of C_2HNS, 133 kJ mol^{-1} above **5S**. The triplet $^3A''$ state of HNCCS (**4T**) is very close in energy, 40 kJ mol^{-1} above the singlet (**4S**). This result is in sharp contrast to the oxygen analogue, O=C=C=S, where the triplet is favored over the singlet by 19 kJ mol^{-1} at the G2(MP2) level,[23] significantly less than the previously reported value (110 kJ mol^{-1} at HF/6-31G*+ZPVE level).[11] Other linear-chain isomers, HSCCN (**12S**), HCNCS (**13S**), HCCNS (**14**), and HCSCN (**15**), are

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(23) Wong, M. W.; Wentrup, C. To be published.

Table 3. Calculated IR SPectral Data for Singlet and Triplet Iminoethenethiones (**2** and **4**)

		mode frequency[a]		intensity[b]	
		HF/6-31G*	MP2/6-31G*[c]	HF/6-31G*	MP2/6-31G*[c]
		Singlet $CH_3N{=}C{=}C{=}S$ (**2S**)			
A	ν_1	3303	3199 (3015)	15	6
	ν_2	3301	3197 (3013)	20	12
	ν_3	3217	3094 (2917)	51	28
	ν_4	2332	2064 (1946)	2	5
	ν_5	1674	1554 (1465)	343	62
	ν_6	1632	1539 (1450)	0	6
	ν_7	1627	1510 (1423)	5	27
	ν_8	1577	1469 (1385)	95	31
	ν_9	1270	1181 (1114)	3	0
	ν_{10}	1193	1108 (1045)	2	0
	ν_{11}	1071	1007 (949)	31	10
	ν_{12}	735	703 (663)	4	22
	ν_{13}	611	531 (501)	3	3
	ν_{14}	555	454 (428)	20	25
	ν_{15}	288	271 (256)	2	1
	ν_{16}	240	215 (203)	9	6
	ν_{17}	147	132 (125)	4	2
	ν_{18}	143	123 (116)	0	1
		Triplet $CH_3N{=}C{=}C{=}S$ (**2T**)			
A	ν_1	3333	3213 (3029)	26	11
	ν_2	3299	3173 (2992)	19	17
	ν_3	3226	3093 (2916)	83	51
	ν_4	2183	2479 (2337)	419	27
	ν_5	1705	1696 (1599)	328	356
	ν_6	1644	1555 (1466)	6	5
	ν_7	1628	1549 (1461)	11	3
	ν_8	1584	1502 (1416)	291	65
	ν_9	1261	1197 (1128)	88	6
	ν_{10}	1194	1182 (1115)	1	1
	ν_{11}	1062	1059 (998)	28	9
	ν_{12}	639	665 (627)	11	8
	ν_{13}	516	470 (443)	90	4
	ν_{14}	441	417 (393)	9	18
	ν_{15}	245	275 (259)	60	0
	ν_{16}	194	139 (131)	1	0
	ν_{17}	101	134 (126)	43	1
	ν_{18}	59	64 (60)	2	3
		Singlet $HN{=}C{=}C{=}S$ (**4S**)			
A′	ν_1	3678	3391 (3196)	22	2
	ν_2	2349	2057 (1939)	28	0
	ν_3	1619	1475 (1390)	310	50
	ν_4	1238	1160 (1093)	198	223
	ν_5	748	714 (673)	18	0
	ν_6	364	319 (300)	9	0
	ν_7	250	228 (214)	3	3
A″	ν_8	628	661 (623)	0	17
	ν_9	225	207 (196)	3	0
		Triplet $HN{=}C{=}C{=}S$ (**4T**)			
A′	ν_1	3798	3710 (3498)	143	261
	ν_2	2006	2569 (2421)	180	74
	ν_3	1531	1646 (1551)	91	370
	ν_4	829	851 (802)	746	103
	ν_5	690	710 (669)	28	91
	ν_6	463	463 (436)	88	0
	ν_7	215	207 (195)	7	3
A″	ν_8	449	432 (408)	1	3
	ν_9	197	135 (128)	0	7

[a] In cm^{-1}. [b] In km mol^{-1}. [c] Scaled values (by a factor of 0.9427)[20] are given in parentheses.

calculated to have higher energy than **4S**, by 25, 65, 105, and 80 kJ mol^{-1}, respectively (Figure 5 and Table 2). The cyclic CHNC=S structure (**16**) has an energy similar to that of **4S**, while the cyclic CNHC=S structure (**17**) is predicted to have high energy (Figure 5, Table 2). For the singlet nitrene H(N)CCS (**18S**), calculations at both HF/6-31G* and MP2/6-31G* levels indicate that this structure rearranges spontaneously to the cyclic structure **16**.

We have considered several isomers on the triplet C_2HNS potential energy surface: HNCCS (**4T**), H-CS-CN (**5T**), HSCCN (**12T**), HCNCS (**13T**), and H(N)CCS (**18T**) (Figure 5). As on the singlet surface, thioformyl cyanide (**5T**) is the lowest-energy structure. However, it lies 163 kJ mol^{-1} above the global minimum (**5S**). The triplet HNCCS (**4T**) lies close in energy, 10 kJ mol^{-1} above **5T**, while the energies of other triplet structures, **12T**, **13T**, and **18T**, are not competitive (Table 2).

Table 4. Calculated Vertical Transition Energies (eV) of Singlet and Triplet Iminoethenethiones (**2** and **4**)[a,b]

	$CH_3N{=}C{=}C{=}S$ (**2**)		$HN{=}C{=}C{=}S$ (**4**)	
	singlet (**2S**)	triplet (**2T**)	singlet (**4S**)	triplet (**4T**)
T1	0.90 (0.000)	2.99 (0.000)	0.79 (0.000)	2.98 (0.000)
T2	4.56 (0.001)	3.28 (0.013)	4.56 (0.001)	3.35 (0.006)
T3	4.94 (0.131)	3.71 (0.000)	5.06 (0.110)	3.77 (0.000)
T4	5.66 (0.357)	4.75 (0.391)	5.74 (0.198)	4.83 (0.323)
T5	6.42 (0.002)	5.06 (0.000)	6.57 (0.014)	5.12 (0.000)
T6	6.58 (0.230)	5.40 (0.001)	6.83 (0.002)	5.54 (0.001)
T7	6.84 (0.255)	5.50 (0.075)	7.04 (0.010)	5.62 (0.064)
T8	7.00 (0.007)	5.64 (0.003)	7.15 (0.755)	5.86 (0.002)
T9	7.16 (0.075)	5.84 (0.002)	7.34 (0.008)	5.86 (0.005)
T10	7.38 (0.001)	5.97 (0.000)	7.56 (0.593)	6.13 (0.001)

[a] CIS/6-311++G(2df,2p)//MP2/6-31G* values. [b] Oscillator strengths are given in parentheses.

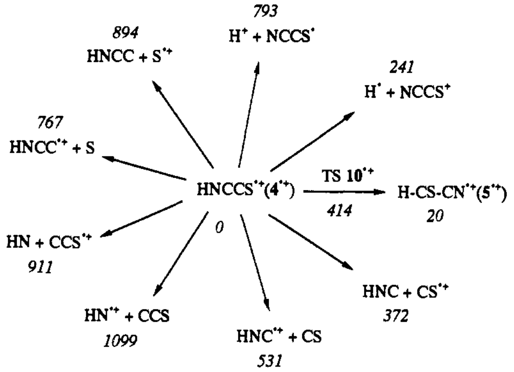

Figure 6. Dissociation and rearrangement reactions of $HNCCS^{\cdot+}$ ($4^{\cdot+}$). The relative energies [G2(MP2) values, in kJ mol^{-1}] are in italics.

Geometrical Structure of HN=C=C=S. As with other X=C=C=Y systems,[8-11] both **4S** and **4T** are characterized by short central C—C bond length (1.295 and 1.296 Å, respectively, Figure 5), somewhat between a typical C=C double and C≡C triple bond. For comparison, the experimental CC bond lengths in ethylene and acetylene are 1.339 and 1.203 Å, respectively.[24] Note that the electrons of the N=C=C=S skeleton in **4S** are considerably more delocalized than those of the corresponding radical cation ($4^{\cdot+}$). The C—N and C—S bond distances are longer (by 0.04–0.05 Å), while the C—C bond length is shorter (by 0.04 Å).

Stability of HN=C=C=S. In order to assess the stability of singlet iminoethenethione (**4S**), we have considered several fragmentation and rearrangement pathways. The energy requirement for these reactions are summarized in Figure 7. The energetically most favorable fragmentation reaction of **4S**, the loss of CS, is calculated to be slightly endothermic, by 53 kJ mol^{-1}. On the other hand, the energy requirement for other dissociation reactions of **4S**, leading eventually to NH, S, or H˙, are significantly higher in energy, 552, 513, and 264 kJ mol^{-1}, respectively. The dissociation of **4S** to HNC + CS is calculated to have a significant activation barrier of 120 kJ mol^{-1}, via transition structure **11** (Figure 5). Note that the product of this reaction, HNC, can rearrange to the more stable isomer, HCN. The "nonlinear" dissociation to HCN is predicted to be slightly exothermic by 4 kJ mol^{-1}. The calculated reaction barrier for the rearrangement of HNC to HCN is 125 kJ mol^{-1} [G2(MP2) value]. For the triplet HN=C=C=S (**4T**), the spin-allowed

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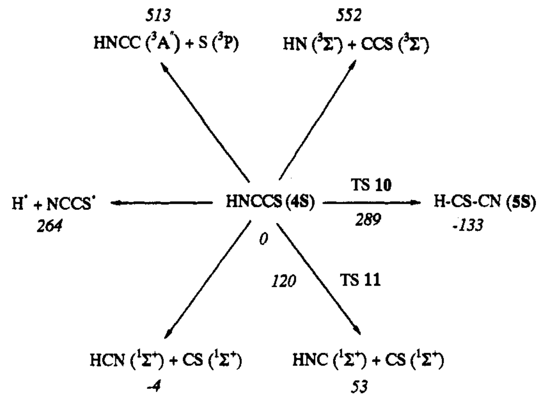

Figure 7. Dissociation and rearrangement reactions of singlet HNCCS (4S). The relative energies [G2(MP2) values, in kJ mol^{-1}] are in italics.

dissociations to HNC ($^1\Sigma^+$) + CS ($^3\Pi$) and HNC ($^3\Pi$) + CS ($^1\Sigma^+$) are quite endothermic, by 366 and 470 kJ mol^{-1}, respectively.

Although singlet HN=C=C=S (4S) is characterized by a short C—C bond (1.295 Å), the calculated dissociation energy is rather small (53 kJ mol^{-1}). Likewise, $^1\Sigma^+$ O=C=C=S is calculated to have a short C—C equilibrium distance (1.288 Å, MP2/6-31G*), but the dissociation of OCCS to CO + CS is predicted to be exothermic by 68 kJ mol^{-1} [G2(MP2) value].[23] Similar findings have been reported for $^3\Sigma^-$ C_2O_2 and C_2S_2.[6a,b] Thus, the general correlation between bond length and bond strength does not hold for the X=C=C=Y systems.

As pointed out in the previous section, thioformyl cyanide (5S) is calculated to be more stable than 4S by 133 kJ mol^{-1}. However, rearrangement of 4S to 5S, via a 1,3-hydrogen shift, involving a four-centre transition structure **10** (Figure 5), requires a high activation barrier (289 kJ mol^{-1}), even larger that those required for the fragmentations to HNC + CS and H˙ + NCCS˙ (Figure 7). Hence, iminoethenethione (4S) is confirmed to be a thermodynamically and kinetically stable species in the gas phase.

Since the neutralization in an NR experiment is a vertical process,[25] it is instructive to calculate the energy of the vertically neutralized species (NE_v). The theoretical results of Figure 8 predict that vertical neutralization of ground-state $HNCCS^{\cdot+}$ ($4^{\cdot+}$) should lead to neutral HNCCS (singlet) molecules with 62 kJ mol^{-1} internal energy. Although this is a large value, due to a large change in geometry in going from $HNCCS^{\cdot+}$ to HNCCS (4S), it is significantly less than the energy required (133 kJ mol^{-1}) for the dissociation of 4S to HNC + CS. Hence, our calculated results are consistent with the experimental observation of iminoethenethione in the neutralization–reionization mass spectrum.

Structure and Stability of CH_3N=C=C=S. As with the parent compound (**4**), (methylimino)ethenethione (**2**) is predicted to have a singlet ground state. The singlet–triplet gap is 43 kJ mol^{-1}. The calculated N—C, C—C, and C—S bond lengths in 2S and 2T (Figure 5) are almost identical to those calculated for 4S and 4T, respectively. Fragmentation of 2S to CH_3NC + CS is calculated to be slightly endothermic (by 51 kJ mol^{-1}) and inhibited by a significant activation barrier of 106 kJ mol^{-1}, via transition structure **21** (Figure 5). Like HNCCS (4S), the cyano isomer CH_3-CS-CN (**19**) is significantly more stable than 2S, by 175 kJ mol^{-1}. However, tautomerization of 2S to **19**, via transition structure **20** (Figure 5), requires a large activation barrier of 339 kJ mol^{-1}. Therefore, 2S is calculated to be an observable species in the gas phase, in excellent accord with the experimental finding.

The $HNCCS^{2+}$ Dication. It is interesting to note that a very strong signal for charge-stripped ions (*m/z* 35.5), corresponding to iminoethenethione dications (4^{2+}), appeared in the CAMS of

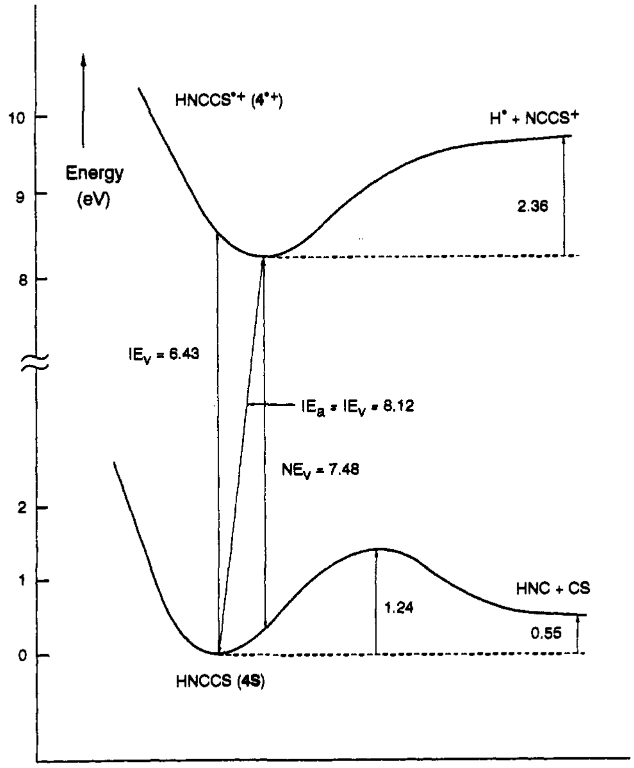

Figure 8. Schematic potential energy surfaces for the fragmentation of HNCCS (4S) and HNCCS$^{\cdot}$ (4^+) showing neutralization and ionization processes.

6a (Figure 4a). The charge-stripping peak of thioformyl cyanide dications (5^{2+}) is significantly smaller (Figure 4b). Consistent with these experimental observations, $HNCCS^{2+}$ (4^{2+}) is considerably more stable than H-CS-CN^{2+} (5^{2+}), by 374 kJ mol^{-1}. 4^{2+} is predicted to have a linear skeleton, in contrast to the W-shaped skeleton of the corresponding neutral (**4**) and monocation ($4^{\cdot+}$). It has a tightly bound geometry: the calculated C—N and C—S bond lengths are 1.163 and 1.510 Å, respectively, significantly shorter than normal C≡N and C≡S triple-bond lengths. Similar findings have been reported for many multiply-charged ions.[26] The strong preference for the linear structure (4^{2+}) over the nonlinear isomer (5^{2+}) is attributed to minimizing electrostatic repulsion between the positive charges which lie mainly on the terminal H and S atoms;[27] the calculated Mulliken charges are 0.57 and 0.98, respectively. Fragmentation reactions of 4^{2+} to H^+ + $NCCS^{\cdot+}$ and $HNC^{\cdot+}$ + CS^+ are calculated to be endothermic by 207 and 287 kJ mol^{-1}, respectively. Thus, the iminoethenethione dication is calculated to be a thermodynamically stable species, in excellent agreement with its observation in CAMS.

IR and UV Spectra. IR and UV spectroscopy are important techniques for the identification of cumulenes such as S=C=C=S.[9,10] To facilitate future spectroscopic characterization of iminoethenethiones (**2** and **4**) in the gas phase or low-temperature matrices, we report the calculated IR and UV spectra of both the singlets and triplets. The IR spectra were calculated at both HF/6-31G* and MP2/6-31G* levels (Table 3). First, we note that the correlated (MP2) IR intensities are significantly different from the HF values for 4S and 4T. For instance, ν_4 of 4T is 8 times more intense than ν_3 at the HF level but ν_4 becomes a weaker band than ν_3 at the MP2 level. A recent study on the cumulenes RN=C=C=C=O has shown that incorporation of electron correlation is essential for the correct prediction of the

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[25] For reviews see: (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513. (d) Plisner, M.; Flammang, R. *Chim. Nouv.*. **1990**, *8*, 893.

[26] For examples, see: (a) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1990**, *94*, 638. (b) Wong, M. W.; Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Chem. Phys.* **1989**, *91*, 2971. (c) Radom, L.; Gill, P. M. W.; Wong, M. W.; Nobes, R. H. *Pure Appl. Chem.* **1988**, *60*, 183.

[27] For reviews, see: (a) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 132. (b) Radom, L.; Wong, M. W.; Gill, P. M. W. *Adv. Mass Spectrom.* **1989**, 702.

relative intensities of cumulenic stretching frequencies.[4c] Our best predicted frequency values of iminoethenethiones (Table 3) were obtained by scaling the MP2/6-31G* values with a factor of 0.9427, a value derived from an extensive comparison of 122 molecules.[20] The characteristic feature of the IR spectra of iminoethenethiones is the moderate absorption band of the C=S stretching mode, e.g. ν_5 in **2** and ν_3 in **4**. The calculated IR spectra of the singlets (**2S** and **4S**) show clear differences from the spectra predicted for the triplets (**2T** and **4T**). Although the C—S bond lengths in the singlets are similar to those of triplets, the triplet CS stretches are considerably more intense and higher in frequency (by 150 cm^{-1}) than those of the corresponding singlets (Table 3). Likewise, the central C—C bond lengths in the singlets and triplets are very similar, but the corresponding CC stretching bands (ν_4 in **2** and ν_2 in **4**) are significantly different: the singlets are almost infrared inactive and have higher frequency (by 400 cm^{-1}) than the triplets. Thus, singlet and triplet iminoethenethiones can be distinguished from each other by their IR spectra.

The first ten transition energies of **2** and **4** were calculated using the configuration interaction including all singly excited configurations (CIS) approach,[21] with the 6-311++G(2df,2p) basis set (Table 4). The calculated UV spectra of **2S** and **4S** show several strong absorption bands, which correspond to $\pi \rightarrow \pi^*$ transitions, while there is only one strong absorption band predicted for **2T** and **4T** (at 4.75 and 4.83 eV, respectively). The lowest transition energy (T1) of **2S** and **4S** corresponds to a transition from the ground state to a low-lying excited state, $^1A''$ and ^1A, respectively.

4. Conclusions

The iminoethenethione radical cations $\mathbf{2}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ are very stable in the gas phase. The neutral cumulenes **2** and **4** are formed in NRMS experiments and are long-lived on the microsecond time scale under the wall-less conditions. However, when generated by FVP of **6**, **4** isomerizes to thioformyl cyanide (**5**) due to wall collisions. Matrix isolation of N-substituted iminoethenethiones should be feasible, and further experiments toward this goal will be reported in due course. Thioformyl cyanide (**5**) was definitively identified by its IR and (high resolution) mass spectra. Ab initio calculations, using G2(MP2) theory, confirmed the stabilities of the iminoethenethiones (**2** and **4**), which lie in an energy well of ~100 kJ mol^{-1} with respect to CS loss. Both **2** and **4** are predicted to have a singlet ground state. Direct tautomerization of RNCCS to R–CS–CN, e.g. **4S** → **5S**, is calculated to have a high activation barrier (~300 kJ mol^{-1}). $\mathbf{4}^{\cdot+}$ is predicted to be the global minimum of the $C_2HNS^{\cdot+}$ potential energy surface and stable toward all possible fragmentations.

5. Experimental Section

The electron ionization (EI), collision activation (CA), and neutralization–reionization (NR) mass spectra were recorded on a six-sector double VG Analytical AutoSpec 6F spectrometer (VG Analytical, Manchester, U.K.) of geometry $E_1B_1E_2E_3B_2E_4$ (E electric sector; B magnetic sector).[28] In the CA experiments, a beam of fast ions (8 keV) is mass selected in the first three sectors ($E_1B_1E_2$) and subjected to collisional activation with O_2 (80% transmission) or in some experiments with helium. In the NR experiments, neutralization of the ions with NH_3 (80% T) precedes reionization with O_2 (also 80% T). Nonneutralized ions remaining in the neutralization step were eliminated by floating the calibration ion source inserted between the two cells at 9 kV. The spectra were recorded by scanning E_3 and collecting the ions in the fourth field-free region. Spectra shown in the figures result from the average of 20 (CA) or 100 (NRMS) scans corresponding to a 0.5- or 2.5-min acquisition time, respectively.

The mass spectrometer was fitted with an FVP oven as previously described.[29] Simple EI mass spectra were recorded on a Kratos MS25RFA spectrometer, also fitted with a pyrolysis oven as previously described.[9] The pyrolysis equipment for FVP/matrix isolation was as previously reported.[9]

4,6-Dimethylthiazolo[4,5-*d*]pyrimidine-5,7-dione (**1**)[30] and 2-methylthiazolo[4,5-*d*]pyrimidine-5,7-dione (**3**)[31] were prepared according to the literature.[32] Acetonitrile sulfide ($CH_3C{\equiv}NS$) was generated from 1,3,4-oxathiazol-2-one as previously described.[33] Methyl thiocyanate and methyl isothiocyanate were commercial samples (Aldrich Chemical Co.). Thioformyl cyanide (**5**) was generated from allyl cyanomethyl sulfide (**9**) as previously described.[16b]

4-[Bis(methylthio)methylene]-3-methylisoxazol-5(4*H*)-one. A solution of 3 g (30 mmol) of 3-methylisoxazol-5(4*H*)-one in 12 mL of dry DMSO was treated with 6.0 g (60 mmol) of triethylamine followed by 2.5 g (33 mmol) of carbon disulfide. The flask was stoppered, and the solution was stirred for 1 h at room temperature and then cooled in ice. After methyl iodide (9.4 g, 66 mmol) was added dropwise, the yellow solution was allowed to stir at 0 °C for 30 min before ice was added, which caused the formation of a yellow precipitate. The solid was collected by filtration and washed thoroughly with water. Recrystallization from dry acetonitrile gave 4.0 g (65%): mp 92–94 °C; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3 H, Me), 2.72 (s, 6 H, 2 SMe); ^{13}C NMR ($CDCl_3$) δ 15.6, 19.2, 21.9, 111.1, 158.2, 166.9, 181.7; IR (KBr) 1718, 1709, 1684, 1547 cm^{-1}; MS *m/z* 203 (M^+, 96), 188 (12), 156 (100), 145 (43), 128 (14), 116 (14), 100 (42), 97 (55). Anal. Calcd for $C_7H_9NO_2S_2$: C, 41.3; H, 4.47; N, 6.90. Found: C, 40.90; H, 4.46; N, 6.88.

4-(2-Aza-5-thiacyclopentylidene)-3-methylisoxazol-5(4*H*)-one (6a). A suspension of 2-aminoethanethiol hydrochloride (0.56 g, 5.0 mmol) in 20 mL of THF was treated with triethylamine (0.50 g, 5.0 mmol). After 1 h of stirring, 4-[bis(methylthio)methylene]-3-methylisoxazol-5(4*H*)-one (1.30 g, 5.0 mmol) was added to the mixture, which was then refluxed for 3 h. After cooling and evaporation of the solvent, the solid residue was digested with water, filtered off, and then washed with water and methylene chloride to give 0.60 g (65%) of pure **6a**. An analytical sample was prepared by recrystallization from ethanol: mp 225–230 °C; ^1H NMR (DMSO-d_6) δ 2.16 (s, 3 H, Me), 3.46 (t, *J* = 8 Hz, 2 H, SCH_2), 3.94 (t, *J* = 8 Hz, 2 H, NCH_2); ^{13}C NMR (DMSO-d_6) δ 13.27, 29.61, 50.06, 85.07, 157.86, 169.49, 172.54; IR (KBr) 3257, 1677, 1576, 1543 cm^{-1}; MS *m/z* 184 (M^+, 100), 167 (10), 142 (7), 126 (10), 60 (12); HRMS *m/z* 184.0308, calcd for $C_7H_8N_2O_2S$ 184.030 65. Anal. Calcd for $C_7H_8N_2O_2S$: C, 45.64; H, 4.38; N, 15.21. Found: C, 45.53; H, 4.30; N, 15.31.

4-(2-Aza-5-thiacyclopentylidene)-3-phenylisoxazol-5(4*H*)-one (6b). A suspension of 2-aminoethanethiol hydrochloride (0.56 g, 5.0 mmol) in 20 mL of THF was treated with triethylamine (0.50 g, 5.0 mmol). After 1 h of stirring, 4-[bis(methylthio)methylene]-3-phenylisoxazol-5(4*H*)-one (1.30 g, 5.0 mmol) was added to the mixture, which was then refluxed for 20 h. After cooling and evaporation of the solvent, the solid residue was dissolved in dichloromethane (40 mL) and the solution washed with water (4 × 20 mL). The organic layer was dried over sodium sulfate, the solvent evaporated, and the solid recrystallized from THF to give 0.7 g (67%) of **6b**: mp 194–195 °C; ^1H NMR ($CDCl_3$) δ 3.29 (t, *J* = 8 Hz, 2 H, SCH_2), 4.02 (t, *J* = 8 Hz, 2 H, NCH_2), 7.51–7.39 (m, 5 H, Ph), 9.29 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 30.4, 49.1 86.9, 128.5, 128.9, 129.0, 130.2, 161.9, 170.9, 174.1; IR (KBr) 3219, 1688, 1583, 1516 cm^{-1}; MS *m/z* 246 (M^+, 99), 203 (10), 142 (53), 128 (26), 117 (30), 103 (73), 77 (78), 44 (72). Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.0; H, 3.87; N, 11.30. Found: C, 58.4; H, 4.03; N, 11.30.

FVP/IR Spectroscopy of 6a. FVP of **6a** at 900 °C (10^{-5} mbar) with Ar matrix isolation of the products at 18 K allowed the detection of the five strongest IR absorptions of thioformyl cyanide[16b] at 2221, 1320, 1103, 889, and 824 cm^{-1}. Other bands in the spectrum could be attributed to acetonitrile (2293, 2257, 1449, 1411, 1376, 1042, and 919 cm^{-1}), ethene (1440 and 954 cm^{-1}), and carbon disulfide (1528 cm^{-1}).

Mass Spectrum of Thioformyl Cyanide (5). Allyl cyanomethyl sulfide (**9**) was subjected to FVP over the temperature range 300–800 °C in the oven directly attached to the ion source of the Kratos mass spectrometer.[9] Ion intensities were plotted as ion current vs total ion current. The molecular ion of **9** (*m/z* 113) decreased, and those of propene (*m/z* 42) and **5** (*m/z* 71) increased smoothly from 325 to 600 °C. Little change

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took place at higher temperatures. Electron ionization (EI) mass spectrum of **9** (300 °C): *m/z* 113 (27), 71 (5), 70 (5), 73(35), 45 (47), 44 (3), 42 (10), 41 (100), 39 (45). EI mass spectrum of **5** plus propene (700 °C): *m/z* 71 (90), 70 (85), 45 (25), 44 (20), 42 (60), 41 (100), 39 (65). HRMS: *m/z* 70.9830, calcd for HC_2NS 70.982 97.

The Ar matrix IR spectrum of **5** was as previously reported.[16b]

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