

Formation of the heterocumulene anion SCCCN^- by a cyano migration from the radical anion of 1,2-dicyanoethylenedithiolate †

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The anionic heterocumulene SCCCN^- was generated in the gas phase by collisional activation of the radical anion of 1,2-dicyanoethylenedithiolate. The mechanism of this reaction, as well as the structures of neutral and anionic products, was investigated by hybrid density functional theory (DFT) calculations. Dissociation to form SCCCN^- and SCN is proposed to occur by a radical directed cyano migration reaction, with calculations suggesting this is the lowest energy fragmentation pathway available to the precursor anion. In contrast, the even-electron protonated 1,2-dicyanoethylenedithiolate anion fragmented by loss of HCN .

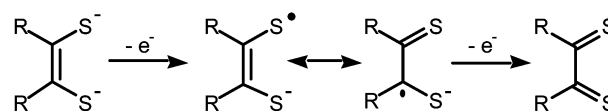
Introduction

Astrophysicists have detected more than 120 molecular species over a range of galactic media including diffuse interstellar clouds, dark clouds and circumstellar envelopes.^{1–3} The detection of previously unknown species such as cumulenes (*e.g.* C_nH and C_nH_2) and heterocumulenes (*e.g.* C_nE , HC_nE ; $\text{E} = \text{O}, \text{N}, \text{Si}$) has prompted chemists to attempt their synthesis in the laboratory.^{4–7} Given that some interstellar clouds have very low pressures and temperatures (*e.g.* number densities as low as $1\text{--}100$ molecules cm^{-3} , and temperatures below 100 K) gas-phase techniques have proven ideal for their study. For example, approaches involving neutralisation reionisation mass spectrometry, flash vacuum pyrolysis or supersonic molecular beams have been particularly successful in the generation of a number of cumulene and heterocumulene type species.^{4–8} Potential interstellar species can also be explored in the laboratory under temperature and pressure conditions similar to those of interstellar regions, thus providing insights into their formation and reactivity.^{9,10} In conjunction with these experimental approaches, high-level *ab initio* and density functional theory calculations have provided insights into the structure, spectroscopy and reactivity of these species.^{7,11–13}

The present study describes the generation of the heterocumulene anion SCCCN^- by collisional activation of the radical anion of 1,2-dicyanoethylenedithiolate, mnt^- ($\text{mnt}^- = \text{A}$; $\text{mnt}^{2-} = \text{maleonitriledithiolate} = 1,2\text{-dicyanoethylenedithiolate} = [\text{S}_2\text{C}_2(\text{CN})_2]^{2-}$). Related alkylated heterocumulene species SCCCNAr have been prepared previously by flash vacuum pyrolysis of suitable precursors.^{14,15} The radical equivalent SCCCN has also been prepared very recently in a supersonic molecular beam as part of the series SC_nN ($n = 1\text{--}7$).¹⁶ These species were studied by a combination of microwave spectroscopy and high-level *ab initio* calculations.

Dithiolene ligands are relevant in the context of the mononuclear molybdenum and tungsten containing enzymes, which are important in the global metabolism of carbon, nitrogen and sulfur.¹⁷ A common feature of these enzymes is the presence of a pterin cofactor coordinated to the metal centre through a dithiolene unit. The dithiolene unit of the pterin ligand is thought to be important in modulating the redox chemistry of the metal centre at the active site of the enzyme,¹⁷ and the

non-innocence of these ligands in metal/ligand based redox processes has been emphasised.¹⁸ With regard to free dithiolenes, three different redox-levels are available (Scheme 1): (i) the reduced dianionic ene-1,2-dithiolate (dithiolene) form; (ii) the one-electron oxidised radical form and (iii) the fully oxidised 1,2-dithione form which is neutral. The radical anion **A** of the present study corresponds to the one-electron oxidised form, for which two distinct resonance forms are conceivable (Scheme 1, $\text{R} = \text{CN}$).



Scheme 1

Experimental

Synthesis

The free ligand $\text{Na}_2(\text{mnt})$ as well as the metal-complexes $(\text{Bu}_4\text{N})_2[\text{MoO}_2(\text{mnt})_2]$ and $(\text{Et}_4\text{N})_2[\text{WO}_2(\text{mnt})_2]$ were prepared by standard literature procedures.^{19–21}

Mass Spectrometry

Mass spectrometry experiments were conducted using a modified Finnigan LCQ quadrupole ion trap mass spectrometer equipped with a Finnigan electrospray ionisation source. Tetraalkylammonium salts of $[\text{MO}_2(\text{mnt})_2]^{2-}$ were sprayed from acetonitrile (0.1 mg mL^{-1}) while $\text{Na}_2(\text{mnt})$ was sprayed from $90 : 10$ MeCN : H_2O . Electrospray solutions were pumped into the electrospray source at approximately 3 $\mu\text{L min}^{-1}$. Typical electrospray source conditions involved needle potentials of 4.0 kV and heated capillary temperatures of 200 °C. Mass selection and collisional activation were carried out using standard isolation and excitation procedures²² using the 'advanced scan' function of the LCQ software.

Theoretical calculations

Structures were optimized using the hybrid B3LYP density functional theory method^{23,24} and the modest $6\text{-}31\text{+G}^*$ basis set within the GAUSSIAN98 suite of programs.²⁵ Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by frequency calculations. Zero-point energies were corrected by the empirical scaling factor of 0.9804 ²⁶ and added to the

† Dedicated to Professor John H. Bowie on the occasion of his 65th Birthday and in recognition to his pioneering work on the gas phase chemistry of anions.

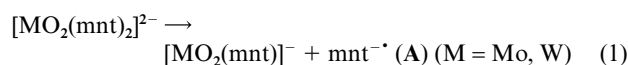
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total electronic energy. Minima connected by a given transition state were confirmed by inspection of the imaginary frequency using the MOLDEN package²⁷ and by intrinsic reaction coordinate calculations.^{28,29}

Results and discussion

(a) Fragmentation reactions of the radical anion of dicyanoethylenedithiolate

Electrospray ionization of the salts $(\text{Bu}_4\text{N})_2[\text{MoO}_2(\text{mnt})_2]$ or $(\text{Et}_4\text{N})_2[\text{WO}_2(\text{mnt})_2]$ in MeCN produced abundant signal of the dianions $[\text{MO}_2(\text{mnt})_2]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$). Collisional activation of these dianions resulted in one-electron oxidation of a dianionic mnt^{2-} ligand and its loss as the radical anion **A** (eqn. 1, data not shown). The complementary anion $[\text{MO}_2(\text{mnt})]^-$ was also observed, apparently generated by one-electron reduction of the metal centre in the corresponding redox half reaction. Generation of the radical anion **A** by this intramolecular redox reaction is conceptually very similar to the generation of peptide radicals by collisional activation of peptide-metal complexes.^{30–32}



The radical anion **A** (m/z 140) can also be generated directly by electrospray ionization of the sodium salt of its dianionic reduced form $\text{Na}_2(\text{mnt})$. Strong signals for the radical anion **A** (m/z 140) and its protonated form (m/z 141) were observed. However the dianionic form mnt^{2-} (m/z 70) was not observed. This might be due to its oxidation during the electrospray process, or its inherent instability with respect to electron autodetachment.³³

Collisional activation of the radical anion **A** yielded the cumulene SCCCN^- (m/z 82, relative abundance 100%) as the major ionic product with loss of radical SCN . Considerably weaker signals were observed for S_2^- from loss of neutral dicyanoacetylene NCCCCN (m/z 64, $\approx 2\%$) and SCN^- from loss of neutral SCCCN (m/z 58, $\approx 4\%$) (Fig. 1).

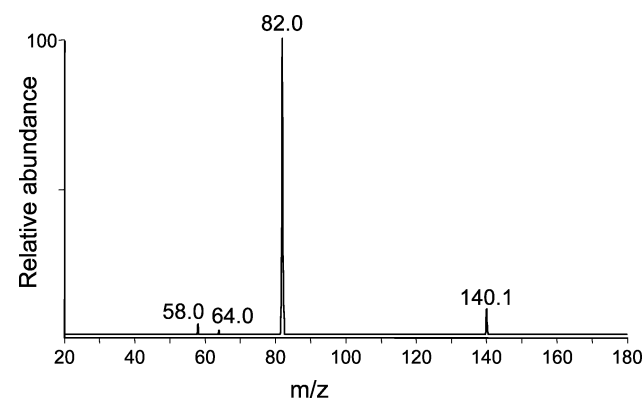


Fig. 1 Collisional activation of the radical anion of 1,2-dicyanoethylenedithiolate (**A**) (m/z 140) to generate the heterocumulene anion SCCCN^- (m/z 82).

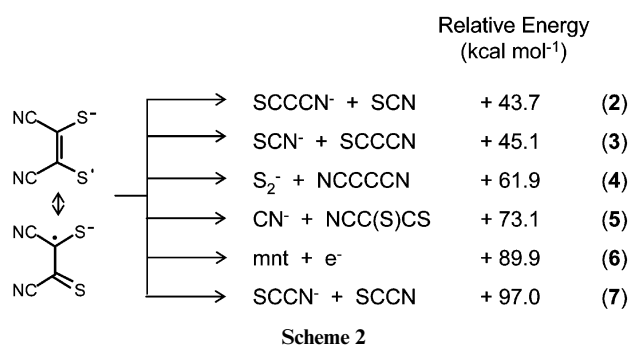
The formation of the major product ion SCCCN^- requires intramolecular migration of a CN unit from carbon to sulfur, and could conceptually occur through either charge or radical driven mechanisms. In order to investigate these possibilities further, the fragmentation of the protonated 1,2-dicyanoethylenedithiolate anion $[\text{mnt}^{2-} + \text{H}^+]^-$ was examined. This anion can be considered a hydrogen atom adduct of **A**. In contrast with its radical counterpart, collisional activation of $[\text{mnt}^{2-} + \text{H}^+]^-$ yielded $[\text{S}_2, \text{C}_3, \text{N}]^-$ as the major ionic product (m/z 114, 100%) arising from loss of neutral HCN (data not shown). The product anion $[\text{S}_2, \text{C}_3, \text{N}]^-$ might correspond to the

acetylene type species $\text{NC-C}\equiv\text{C-S-S}^-$ or the thioketene $\text{S}=\text{C}=\text{C}(\text{CN})\text{S}^-$. Importantly, no SCCCN^- is observed in fragmentation of $[\text{mnt}^{2-} + \text{H}^+]^-$. This different fragmentation channel in the even-electron analogue might suggest that fragmentation of **A** to form SCCCN^- occurs by a radical driven mechanism.

The radical anion **A** and its even electron analogue $[\text{mnt}^{2-} + \text{H}^+]^-$ exhibited markedly different fragmentation properties. Importantly, the cumulene anion SCCCN^- is not observed for the even electron species, with dominant loss of HCN occurring instead. Further insight into the mechanism, energetics and structures relevant to the formation of SCCCN^- was provided by theoretical calculations using hybrid density functional theory.

(b) Theoretical calculations on the mechanism of formation of SCCCN^-

Hybrid DFT calculations were used to investigate a number of possible decomposition pathways for the radical anion **A**. The calculated endothermicity for each of these pathways is detailed in Scheme 2 (eqns 2–7).



These data suggest that formation of the cumulene anion SCCCN^- is the least endothermic dissociation channel (eqn. 2, 43.7 kcal mol⁻¹). However, formation of the complementary species SCN^- and SCCCN is calculated to be only slightly higher in energy (eqn. 3), as a consequence of the very similar electron affinities of SCCCN (3.55 eV) and SCN (3.49 eV).[§] This is consistent with a small amount of SCN^- being observed experimentally upon collisional activation of **A** (Fig. 1). The peak intensities of SCCCN^- and SCN^- are consistent with relative electron affinities calculated for their neutral counterparts, and with previous observations that small differences in electron affinity can result in more significant differences in peak intensity for competing reaction channels.³⁴

The disulfur radical anion S_2^- (m/z 64) is the only other ionic product observed. Fragmentation of **A** to form S_2^- and neutral dicyanoacetylene is calculated to be endothermic by 62 kcal mol⁻¹ (eqn. 4), approximately 20 kcal mol⁻¹ more endothermic than formation of SCCCN^- . These calculations are consistent with the experimental observation of S_2^- as a very minor product only.

Both the cyanide anion CN^- (eqn. 5) and products arising from the symmetrical dissociation of **A** to form the complementary anion-radical pair SCCN^- and SCCN (eqn. 7) are not observed experimentally. To rationalize this, we have calculated the former reaction to be endothermic by approximately 73 kcal mol⁻¹ (eqn. 5) and the latter pathway to be endothermic by 97 kcal mol⁻¹ for the singlet anion ($^1\text{A}' \text{SCCN}^-$), while dissociation to the triplet anion ($^3\Sigma \text{SCCN}^-$) is only slightly less

[§] The average absolute uncertainty in electron affinities calculated using the B3LYP method has been found to be ± 0.2 eV (J. C. Reinstra-Kiracofe, G. S. Tschumper, H. F. Schaefer III, S. Nandi and G. B. Ellison, *Chem. Rev.*, 2002, **102**, 231–282). However, the precision would be expected to improve further when comparing the relative EA's of two homologues (such as SCN and SC_3N) calculated at the same level of theory.

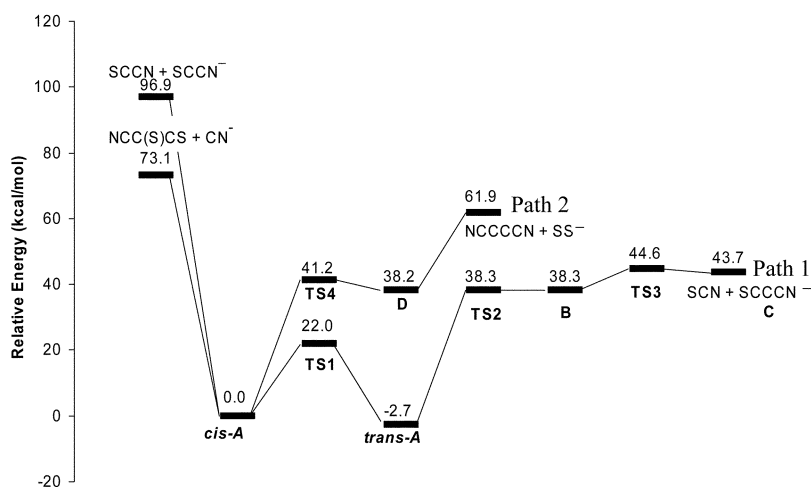


Fig. 2 B3LYP/6-31+G* energy diagram for the fragmentation of the radical anion of dicyanoethylenedithiolate. Energies are relative to *cis-A*.

endothermic (*ca.* 91 kcal mol⁻¹). In all cases, the reactions are considerably less favoured than formation of the major products SCCCN⁻ and SCN⁻, consistent with the fact that CN⁻ and SCCN⁻ are not observed experimentally.

Finally, the adiabatic electron detachment energy of the *cis* isomer of **A** (*cis-A*) is calculated to be 89.9 kcal mol⁻¹ (eqn. 6), considerably more endothermic than formation of SCCCN⁻. This suggested that electron detachment is unlikely to occur in these experiments.

Theoretical calculations were used to provide further insight into the mechanism of formation of the ionic products SCCCN⁻, SCN⁻ and S₂⁻ generated upon collisional activation of **A**. Dissociation of **A** to form SCCCN⁻ requires migration of a cyano moiety to the sulfur of the neighbouring carbon of the ethylene unit, and this migration is expected to proceed from *trans-A*. This is calculated to be 2.7 kcal mol⁻¹ more stable than *cis-A*, with a *cis-trans* isomerization barrier of 22 kcal mol⁻¹ (**TS1**) separating these isomers (Fig. 2). This barrier is substantially lower than *cis-trans* isomerization barriers for typical alkenes (62–65 kcal mol⁻¹),³⁵ however it is consistent with: (a) the relatively long “ethylene” bond in the optimised structure of **A** (*ca.* 1.44 Å *cf.* 1.32 Å in ethylene); (b) reduced barriers observed for other cyano-substituted ethylenes;³⁶ and (c) the two different resonance structures possible for the reduced thioketene form of **A** (Scheme 1). The unpaired electron in both *cis-* and *trans-A* is delocalised within the π-bonding system of each molecule, resulting in ground states of ²B₁ and ²A_u for these isomers of C_{2v} and C_{2h} symmetry, respectively.

Migration of a cyano moiety to the sulfur of the adjacent carbon is predicted to occur through **TS2** to the cyclic intermediate **B**, which lies 38.3 kcal mol⁻¹ higher in energy than *cis-A*. Interestingly, transition state **TS2** and intermediate **B** have ²A' ground electronic states, with the single unpaired electron in the σ-framework of the molecule. This contrasts with the ²A_u ground state of *trans-A*, where the unpaired electron is located in the π-framework of the molecule, and suggests that the rearrangement *trans-A* → **B** is accompanied by surface crossing.³⁷ The lowest energy excited state of *trans-A* containing the unpaired electron in the σ-framework is approximately 23.3 kcal mol⁻¹ higher in energy than the ground state. This is significantly lower than the energy required to access **TS2**, suggesting this excited state might be accessible, and that this reaction might occur on an excited state potential energy surface.

Ring-opening of the cyclic intermediate **B** by carbon–carbon bond cleavage such that the migrating cyano moiety remains bound to sulfur proceeds through **TS3**, which is 6 kcal mol⁻¹ higher in energy than **B** (Fig. 2). This ring opening is followed by dissociation to the products SCCCN⁻ (**C**) and SCN. The alternative products SCN⁻ and SCCCN are also expected to result from the cyclic intermediate **B**.

The ²A' ground-state of intermediate **B** and transition states **TS2** and **TS3** suggest that migration of CN from carbon to sulfur involves the unpaired electron, and consequently this reaction is best described as migration of a cyano radical. A related gas-phase migration involving CN transfer has been reported previously in the formation of [C(CN)₃]⁻ from the radical anion [(NC)₂C–O–C(CN)₂]⁻.³⁸ This migration was proposed to occur by a charge-driven internal nucleophilic S_Ni pathway, in contrast to the radical driven process proposed for the present rearrangement.

The optimised structures *cis-* and *trans-A*, intermediates **B** and **C**, as well as transition state structures **TS1**, **TS2** and **TS3** are provided in Fig. 3. The geometry of the product anion SCCCN⁻ (**C**) is similar to that of its oxygenated analogue OCCCCN⁻,³⁹ with the obvious exception of the C–S bond, which is 1.64 Å long compared with the 1.22 Å C–O bond. The calculated bond lengths for SCCCN⁻ are consistent with the possible resonance structures S=C=C=C=N⁻ ↔ S–C=C=C=N.

The final product observed from collisional activation of **A** is the radical ion S₂⁻ (*m/z* 64, Fig. 1), which occurs with loss of neutral dicyanoacetylene (eqn. 4). This reaction is calculated to be approximately 18 kcal mol⁻¹ more endothermic than formation of SCCCN⁻ (eqn. 4). Calculations suggested that this reaction proceeds through transition state **TS4** with rupture of a carbon–sulfur bond and sulfur–sulfur bond formation to yield intermediate **D**. Dissociation of intermediate **D** to generate dicyanoacetylene NC–C≡C–CN and the disulfur radical anion S₂⁻ requires approximately 24 kcal mol⁻¹. This pathway is approximately 17 kcal mol⁻¹ above the highest energy point on the potential energy surface for formation of SCCCN⁻ (**TS3**), consistent with the experimental observation that only a very small amount of S₂⁻ is formed. This reaction also appears to involve surface crossing from the ²B₁ ground state of *cis-A* (unpaired electron in π-framework) to the ²A' ground state of **TS4** (unpaired electron in σ-framework). The lowest energy excited state of *cis-A* with the unpaired electron in the σ-framework is calculated to be only 6.1 kcal mol⁻¹ higher in energy than the ²B₁ ground state, consistent with this excited state being accessible and the possibility of this reaction occurring on an excited state potential energy surface.

Conclusions

The radical anion of 1,2-dicyanoethylenedithiolate was generated in the gas-phase by collisional activation of the metal-complexes [M^uO(mnt)₂]²⁻ (M = Mo, W). This radical anion fragmented predominantly by loss of radical SCN to yield the heterocumulene anion SCCCN⁻. Theoretical calculations suggested this decomposition occurred by radical-directed migration of a cyano moiety from carbon to a sulfur of the

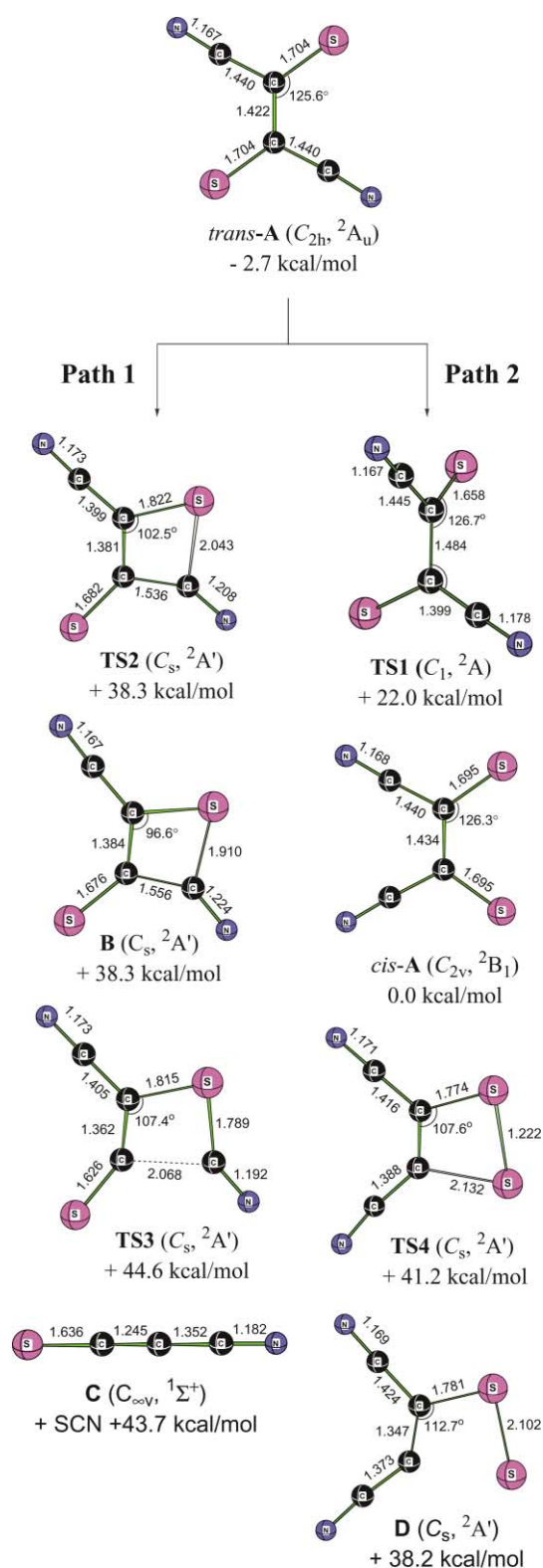


Fig. 3 Structures of the intermediates and transition states for the fragmentation of the radical anion A to yield SCCCN⁻ (Path 1) and S₂ (Path 2).

neighbouring carbon in the ethylene unit. This reaction was calculated to be endothermic by approximately 46 kcal mol⁻¹, and represented the lowest energy decomposition pathway. In contrast, the even electron protonated 1,2-dicyanoethylene-dithiolate anion fragmented predominantly by loss of HCN.

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