The Laboratory Generation of Potentially Interstellar Cumulenes $S(C_n)S$ ($n = 2-6$) and Their Radical Cations

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The title compounds are generated and characterized in the gas phase by tandem mass spectrometry (neutralization-reionization mass spectrometry); it is demonstrated that both *even*- and *odd*-numbered polycarbon disulfides $S(C_n)S$ ($n = 2-6$) are stable species. The elusiveness of the even-numbered analogues (n = 2, 4, 6) in the condensed phase must be due to facile intermolecular reactions.

Linear and/or quasi-linear molecules with polycumulated double bonds of the general structure $C(C_n)Y$ (X, Y: lone electron pair, H_2, O, S; $n \geq 2$) have recently attracted considerable interest[1]. This is partly due to the unique spectroscopic and chemical properties of these species, some of which are believed to play a crucial role in the genesis of interstellar organic compounds.

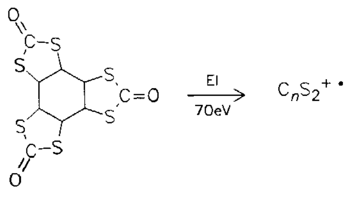
Unfortunately, quite a few of these molecules have such a high reactivity that they cannot even be produced as a transient due to their high *inter*molecular reactivity. This is especially true for cumulenes containing an *even* number of carbon atoms, these molecules are believed to be considerably less stable than their *odd*-numbered analogues[1b,2]. This "instability", however, does not reflect an intrinsic property since under appropriate conditions, e. g. in the diluted gas phase, several of these cumulenes could easily be generated. For sulfur-containing cumulenes, typical examples include: $:C=C=S$[3], $O=C=C=S$[12], $S=C=C=S$[4], $S=C=C=C=C=S$[3]. All these — and many other elusive molecules — became recently accessible from the corresponding cation radicals by using the powerful method of neutralization-reionization mass spectrometry (NRMS)[5].

Here we report on the successful gas-phase generation and characterization of the whole series of cumulenes $S(C_n)S$ (n = 2, 3, 4, 5, 6) and their corresponding cation radicals by using NRMS. In view of the fact that C_3S_2 is already known for nearly a century[6], the present findings together with the previously reported[3,4] successful generation of the even-numbered species $S(C_2)S$ and $S(C_4)S$ clearly support the view that the elusiveness of $S(C_n)S$ does not reflect an inherent stability of these molecules; in the gas phase, irrespective of the "even/odd problem"[2], they are perfectly stable.

Electron impact ionization (70 eV)[7] of 2*H*,5*H*,8*H*-benzo[1,2-*d*:3,4-*d*':5,6-*d*'']tri(1,3-dithiol)-2,5,8-trione[8] (**1**) affords as quite abundant fragments the complete series of $C_nS_2^{+\bullet}$ (Scheme 1). The base peak in the EI spectrum of **1** corresponds to $C_6S_6^{+\bullet}$, which upon neutralization gives rise to the most interesting benzotri(1,2-dithiet)[9].

The mass selection of a given $C_nS_2^{+\bullet}$ species using *B*(1)*E*(1) in a tandem experiment[10], followed by collisional activation[11] of the 8-keV translational energy beam with oxygen as collision gas (80% transmission, *T*), afforded collisional activation (CA) mass spectra which clearly reflect the connectivity of the species of interest. Typical fragments, for example for $C_6S_2^{+\bullet}$, are due to losses of a sulfur atom, the elimination of C_nS (n = 1, 2, 3), the formation of $C_n^{+\bullet}$ ($n = 1-6$), and charge stripping to generate a doubly-charged ion (Scheme 2). Carbon atom extrusion processes, i. e. losses of neutral C_n, are of minor importance (Table 1).

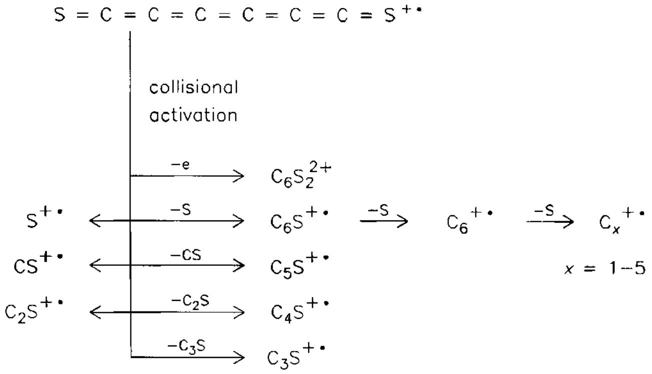
Scheme 1



1

n	m/z	% rel. Intensität
2	88	60
3	100	65
4	112	55
5	124	75
6	136	50

Scheme 2



For the remaining cumulenes $C_nS_2^{+\bullet}$ ($n = 2-5$) an identical fragmentation pattern, though with varying intensities, is observed (Table 1). The base peak in the CA spectra of $C_nS_2^{+\bullet}$ ($n = 2-6$) invariably corresponds to the loss of CS.

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Table 1. Collisional activation mass spectra of $C_nS_2^{+\bullet}$ [a]

m/z	$C_6S_2^{+\bullet}$ 136	$C_5S_2^{+\bullet}$ 124	$C_4S_2^{+\bullet}$ 112	$C_3S_2^{+\bullet}$ 100	$C_2S_2^{+\bullet}$ 88
124	2				
112	2	2			
104	6				
100	3	2	<1		
92	100	18			
88		3	1	5	
80	4	100	12		
76			3	4	7
72	<1				
68	23	8	100	55	
64				26	5
62		21			
60	4	1			
56	3	7	20	100	35
50				27	
48	2	3	<1		
44	2	6	9		100
36	<1	2	2		
32	<1	2	3		10
24	<1	<1	<1		2
12	<1	<1	<1		<1

[a] Intensities are expressed in % of the base peak intensity. The intensity of the mass-selected precursor ion $C_nS_2^{+\bullet}$ is excluded.

If the mass-selected $C_nS_2^{+\bullet}$ species are subjected to an NRMS experiment (xenon 80% T/oxygen 80% T), one obtains in all cases very abundant recovery signals; moreover, the fragmentation pattern is often close if not identical with the one observed in the CA mass spectra. The fact that the relative intensities of the ion signals in the NR (Table 2) and the CA mass spectra do not exactly match is due to reionization of neutral fragments generated by either collision-induced dissociation (in the collision cell) of $C_nS_2^{+\bullet}$ or, alternatively, by fragmentation of a fraction of the C_nS_2 molecules prior to reionization. In any case, there cannot possibly exist any doubt that cumulenes of the general formula $S{=}(C_n){=}S$ ($n = 2-6$) are stable species in the gas phase[12].

Table 2. Neutralization-reionization mass spectra of $C_nS_2^{+\bullet}$ [a]

m/z	$C_6S_2^{+\bullet}$	$C_5S_2^{+\bullet}$	$C_4S_2^{+\bullet}$	$C_3S_2^{+\bullet}$
136	100*			
124	<1	100*		
112	<1	<1	72*	
104	18			
100	2	<1	3	100*
92	83	20		
88		<1	<1	<1
80	15	38	13	
76				<1
72	4			
68	30	14	48	19
64				2
62				
60	12	3		
56	17	12	21	25
50				
48	8	7	2	
44	22	39	100	27
36	4	9	18	9
32	2	8	37	13
24	<1	2	6	2
12	<1	1	4	<1

[a] Intensities are expressed in % of the base peak intensities. The recovery signals $C_nS_2^{+\bullet}$ are marked with an asterisk*. The NR mass spectrum of $C_2S_2^{+\bullet}$ is given in ref.[4].

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CAS Registry Numbers

1: 119449-10-4 / $C_nS_2^{+\bullet}$ (n = 2): 116952-95-5 / $C_nS_2^{+\bullet}$ (n = 3): 128329-04-4 / $C_nS_2^{+\bullet}$ (n = 4): 122293-59-8 / $C_nS_2^{+\bullet}$ (n = 5): 128329-05-5 / $C_nS_2^{+\bullet}$ (n = 6): 128329-06-6

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