Kurzmitteilungen / Short Communications

Generation of C_6S_6 and Its Radical Anion and Cation in the Gas Phase

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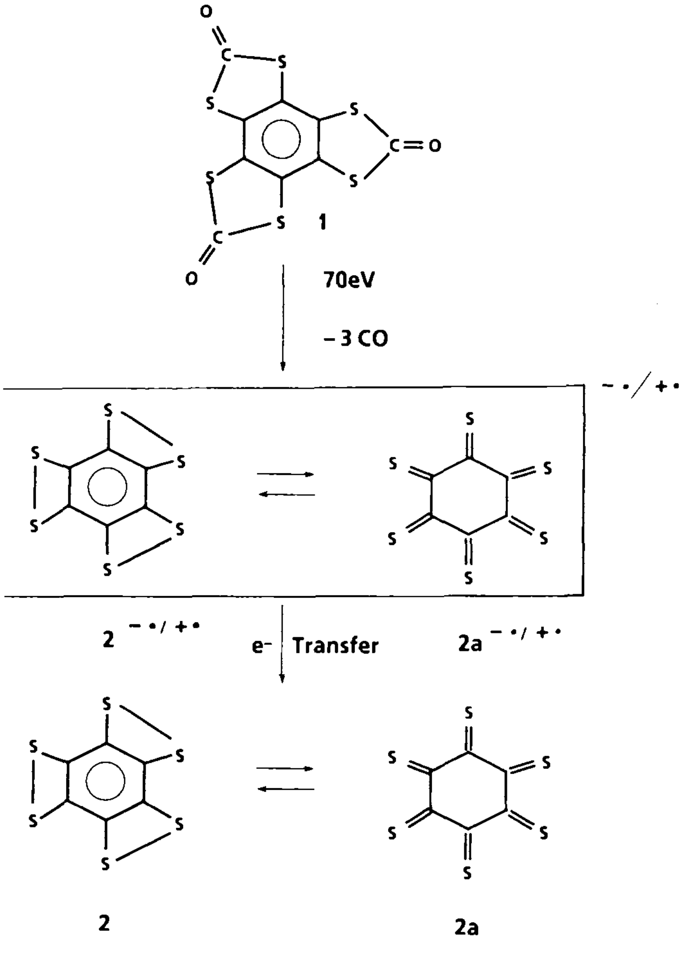
The as yet unknown benzo-tri(1,2-dithiet) 2 can be generated as a stable neutral molecule in beam experiments by subjecting $C_6S_6^{-\bullet}$ to neutralization reionization mass spectrometry.

Among the many conceivable C_xS_y molecules, the as yet unknown benzo[1,2-*c*:3,4-*c*′:5,6-*c*″]tri(1,2-dithiet) ("tri-dithiethylene") C_6S_6 (**2**) occupies a particular position from a theoretically as well as synthetic viewpoint as this species is expected to exhibit remarkable properties. Following a series of successful experiments[1] in which several elusive carbon sulfides where generated by gas-phase electron transfer processes, using the quite powerful technique of neutralization reionization mass spectrometry (NRMS)[2], it was recently suggested[3] that **2** may also be accessible in the gas phase by subjecting $C_6S_6^{-\bullet/+\bullet}$ to an NRMS experiment. The radical ions of C_6S_6 are indeed easily formed in high abundance by dissociative ionization of, for example, benzo[1,2-*d*:3,4-*d*′:5,6-*d*″]-tri(1,3-dithiol)-trione[3] (**1**).



Electron-impact ionization (70 eV)[4] of **1** in the negative ion mode (using NH_3 as an electron energy moderation gas) gives rise to an intense signal at *m/z* 264, which, according to its isotope pattern, corresponds to the elemental composition $C_6S_6^{-\bullet}$. The mass selection of $C_6S_6^{-\bullet}$ (*m/z* 264) using B/E in a tandem mass spectrometry experiment[5], followed by collisional activation[6] of the 8-keV translational energy beam with helium as collision gas (90% transmittance, T) affords the collisional activation (CA) mass spectrum shown in Figure 1. In view of the fact that rearrangement processes in *radical anions*, as compared with *radical cations*, are of minor importance[7], we presume that the consecutive loss of 3 CO from $\mathbf{1}^{-\bullet}$ gives rise to a $C_6S_6^{-\bullet}$ radical anion whose C_6 skeleton has remained intact. We are, of course, not in a positon to distinguish $\mathbf{2}^{-\bullet}$ from its valence isomer $\mathbf{2a}^{-\bullet}$. In addition, several other quinoide structures (not shown in Scheme 1) are conceivable. From the CA spectrum we note the preferred formation of $C_xS_2^{-\bullet}$ species ($x = 2-6$), which may structurally correspond to cumulene disulfides $S(C_x)S^{-\bullet}$. In addition, $C_6S_6^{-\bullet}$ (in contrast to $C_6S_6^{+\bullet}$, see below) has a strong propensity to undergo loss of S, CS, S_2, and CS_2 which give rise to the formation of $C_6S_5^{-\bullet}$, $C_5S_5^{-\bullet}$, $C_6S_4^{-\bullet}$, and $C_5S_4^{-\bullet}$, respectively. For these species, no structural assignments are possible for the time being.

Charge reversal (CR)[8] of mass-selected $C_6S_6^{-\bullet}$ in a two-electron transfer collison experiment with helium gives rise to the spectrum given in Figure 2. We note the following: (i) The "recovery signal"

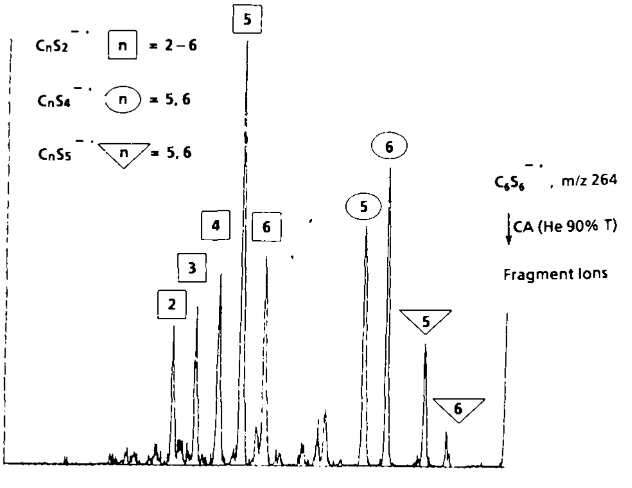


Figure 1. Collisional activation (CA) mass spectrum of $C_6S_6^{-\bullet}$ (*m/z* 264; collision gas: helium (90% transmittance, T)

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at m/z 264 proves that $C_6S_6^{+\bullet}$ is, as its radical anionic counterpart, a species which must residue in a potential well. In view of the vertical nature[5] of the oxidation step $C_6S_6^{-\bullet} \rightarrow C_6S_6^{+\bullet}$, it is very likely that the connectivity of the $C_6S_6^{-\bullet/+\bullet}$ species is preserved. (ii) In the CR experiment, $C_6S_6^{+\bullet}$ is formed with some excess energy which causes dissociation. The by far most prominent decomposition paths of $C_6S_6^{+\bullet}$ corresponds to the formation of species of the general composition $C_xS_2^{+\bullet}$ ($x = 2-6$). Again, it cannot be ruled out that loss of sulfur atoms from $C_6S_6^{+\bullet}$ is accompanied with structural reorganization to eventually generate cumulene-type species $S(C_x)S^{+\bullet}$. We recall that the cumulenes $S(C_2)S^{+\bullet}$ and $S(C_4)S^{+\bullet}$, respectively, were recently identified as stable species in the gas phase together with their neutral counterparts[1a,c]. As already mentioned, the formation of $C_6S_5^{+\bullet}$, $C_5S_5^{+\bullet}$, $C_6S_4^{+\bullet}$, or $C_5S_4^{+\bullet}$ (which are prominent in the CA spectrum of $C_6S_6^{-\bullet}$) is of negligible importance. The origin of this distinct fragmentation behaviour of $C_6S_6^{+\bullet}$ versus $C_6S_6^{-\bullet}$ remains to be established.

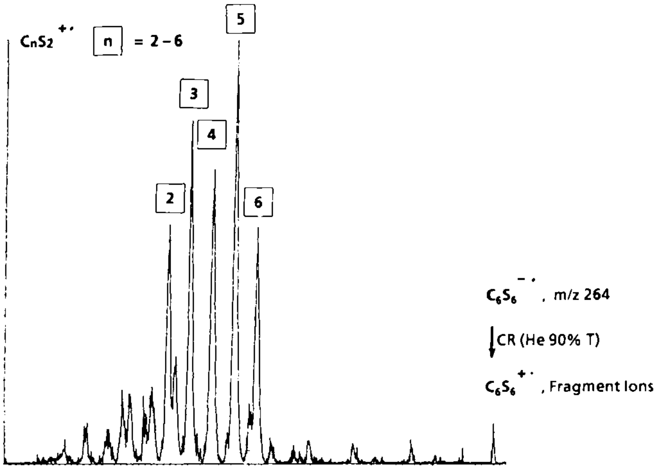

Figure 2. Charge reversal (CR) mass spectrum of $C_6S_6^{-\bullet}$ (m/z 264); collision gas: helium (90% T)

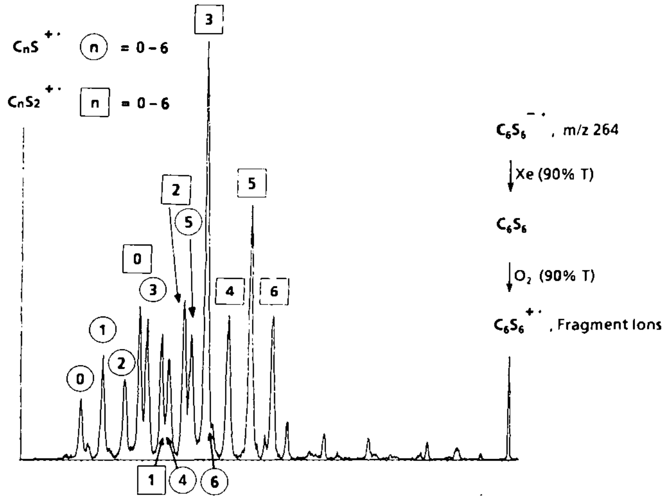

Figure 3. Neutralization reionization mass spectrum of $C_6S_6^{-\bullet}$ (m/z 264); (Xe 90% T/O_2 90% T)

Can $C_6S_6^{-\bullet}$ also be successfully oxidized to the as yet unknown neutral molecule C_6S_6? According to the NRMS experiment the answer is unequivocally yes. The NR mass spectrum (Figure 3) contains a quite intense "recovery" signal for a survivor species C_6S_6 having a lifetime $t > 2$ µs (determined by the time of flight form the first to the second collision chamber); in addition, we note the formation of two series of fragment ions corresponding to $C_xS_2^{+\bullet}$ ($x = 0-6$) and $C_xS^{+\bullet}$ ($x = 0-6$), which may possess cumulene-type structures. With regard to the structure of neutral C_6S_6 it is quite likely that, due to the vertical nature of the process $C_6S_6^{-\bullet} \rightarrow C_6S_6 + e^-$, the long-sought-after C_6S_6 molecule possesses an intact cyclic C_6 skeleton (**2** or **2a**).

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CAS Registry Numbers

1: 119449-10-4 / **2**: 123439-59-8 / $\mathbf{2}^{-\bullet}$: 123439-60-1

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