A Theoretical Study on the Relative Stability of β-Thiovinyl Cation and Thiirenium Ion

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Summary The results of a nonempirical SCF–MO calculation on the linear and cyclic structures of the ion $C_2H_3S^+$ indicate that the cyclic form is 65·9 kcal/mole more stable than the linear form.

Theoretical calculations carried out in several laboratories[1,2] indicate that the protonated acetylene ($C_2H_3^+$) and similar simple unsaturated cations are more stable in the linear form (I) than in the bridged form (II). These results agree well with studies on the unimolecular solvolysis of vinyl halides and sulphonates which suggest a linear geometry for the intermediate cation.[3,4]

On the other hand, extended chemical and kinetic studies[3–5] on the reactions of β-thiovinyl sulphonates lead to the conclusion that β-sulphur may participate in the reaction and that the intermediate cation may be better represented by the cyclic structure (II) rather than by the linear one (I). Furthermore, studies on the electrophilic addition to triple bonds indicate that light electrophiles, in particular the proton, give rise to linear cationic inter-

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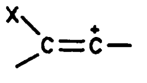
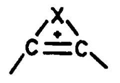
mediates whereas heavy electrophiles (sulphur of sulphenyl halides, bromine, iodine) show a definite trend of preferring bridged unsaturated cations (type II structures) as reactive intermediates.



(I)



(II)

For this reason it seemed necessary to investigate theoretically the importance of heteroatoms on the relative stability of bridged (II) as opposed to open (I) structures.

Nonempirical molecular-orbital (MO) calculations have been carried out within the self-consistent field (SCF) framework on the model species $[C_2H_3S]^+$ in the two limiting structures represented by (I) and (II) (X = SH). The SCF–MO were expanded in terms of contracted Gaussian type functions[6] and the calculations were carried out on an IBM 360/65 computer using the IBMOL-IV system.[7] The bond lengths and bond angles used are shown in the Table, and were taken from standard tables[8] and from previous theoretical optimization.[2] For the thiirenium ion (II) the position of the proton represents an important variable. In this work primary consideration was given to the planar geometry with a mercaptan-type S–H bond length.

Geometric parameters used for the linear (I) *and cyclic* (II) *structures of* $C_2H_3S^+$ *ion*

Parameter	(I) (linear)	(II) (cyclic)
C–C distance	1·38 Å	1·39 Å
C–S distance	1·817 Å	1·78 Å
S–H distance	1·329 Å	1·329 Å
C–H distance	1·078 Å	1·06 Å
$^+$C–H distance	1·065 Å	
H–S–C– angle	100°	157° 20′
S–C–C angle	121° 30′	67°

The computed energy values for the two limiting structures (I) and (II) (X = SH) for $[C_2H_3S]^+$ are graphically shown in the Figure together with those for the corresponding unsubstituted cation $[C_2H_3]^+$ (I) and (II) (X = H) recently published.[2]

In full agreement with the experimental results, the cyclic structure for the sulphur derivative is more stable than the corresponding open structure. This difference is far greater than, and in the opposite sense to, that associated with protonated acetylene (*cf.* Figure).

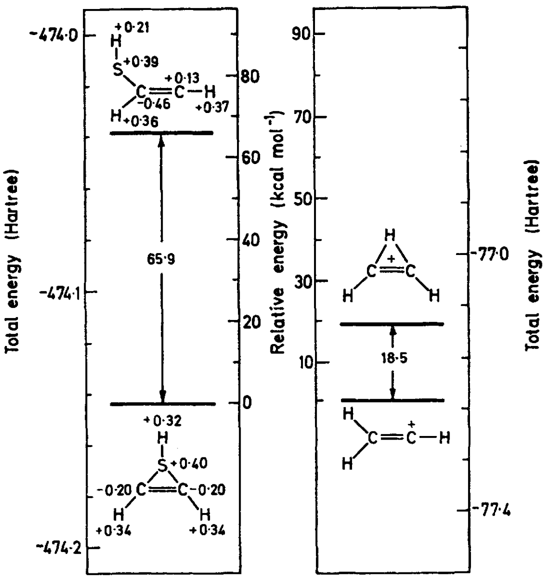


FIGURE. *Relative energies and charge distribution for the linear* (I) *and cyclic* (II) *structures of* $C_2H_3S^+$ *and of* $C_2H_3^+$.

Geometrical optimization may lower the energy levels evaluated. In particular the out-of-plane bending of the S–H bond is expected to decrease considerably the energy of the bridged structure, since this mode of motion may be associated with the pyramidal inversion of tri-co-ordinated sulphur which is known to be substantial.[9]

Consequently the conclusions of the present work may be enforced rather than invalidated by optimization of all the variables.

The computed net charges (Figure) indicate that much of the positive charge is dispersed on the hydrogen atoms in the thiirenium ion. Consequently, the stability of the bridged species would greatly depend on the electronegativity of the peripheral atoms or groups. This is, once again, in agreement with the increased stability of the thiirenium ion associated with the substitution of a hydrogen with a methyl as inferred from kinetic results.[5]

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