A Quantum Chemical Study on the Relative Thermodynamic Stabilities of the Two Isomeric Species † of $C_2H_3S^+$

By **Imre G. Csizmadia,*** Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada
A. Jonathan Duke, Centre for Computer Studies, University of Leeds, Leeds
Vittorio Lucchini and **Giorgio Modena,*** Centro di Studio Meccanismi di Reazioni Organiche del CNR, dell'Università, Padova, Padova, Italy

Non-empirical SCF-MO wave functions were computed for the two limiting structures of $C_2H_3S^+$ with full geometry optimization using three different atomic orbital bases. It was found that the bridged structure (thiirenium ion) was somewhat more stable (1–14 kcal mol^{-1} depending on the basis set) than the open structure (β-thiovinyl cation). The barrier of interconversion between these two valence tautomers was calculated to be 12·8 kcal mol^{-1} without geometry optimization. The pyramidal inversion at sulphur in the thiirenium ion was computed to be 72·9 kcal mol^{-1}.

THE experimental observations that the addition of sulphenyl chlorides to acetylenes is an anti-stereospecific reaction[1] and that the β-sulphur atom participates in the solvolysis of β-thiovinyl sulphonates[2-4] lead to the hypothesis that the cationic intermediates involved in these reactions could be in the bridged structure (2) or that a fast equilibrium between structures (1) and (2) was readily established. Studies on similar reactions in which RS is replaced by halogen, particularly by bromine and iodine, lead to similar conclusions.[2,3,5,6] On the other hand, it seems that the cyclic structure should not play any role whenever the bridging atom is hydrogen or saturated carbon.[2,3,6-10]

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† Table numbers in this paper refer to Supplementary Publication No. SUP 21130 (11 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

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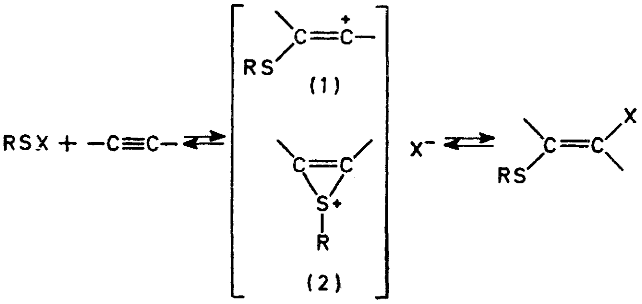
The great insight on the relative stabilities of open and bridged structures given by non-empirical MO calculations in the case of β-substituted carbonium ions, as well as neutral systems,[11-14] lead us to extend this approach [7,8] to the β-thiovinyl cation–thiirenium ion system. A brief account of the preliminary results has already been published.[15]



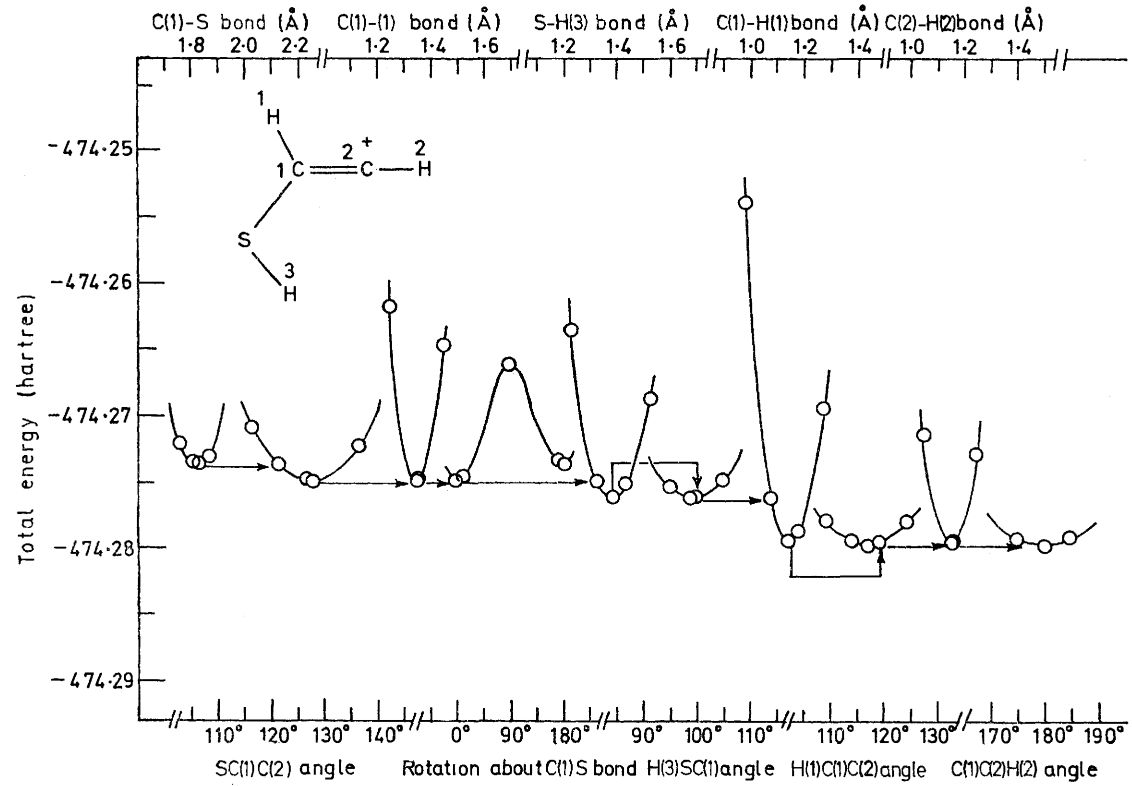


FIGURE 1 Geometry optimization of β-thiovinyl cation

METHOD

The non-empirical SCF-MO calculations were carried out on a CDC 6600 computer using a modified [16] POLYATOM II system.[17] The MO basis was obtained by linear transformation of an AO basis which in turn was generated from a set of primitive Gaussian type functions (GTF) by contraction.

Three basis sets, corresponding to 31*sp*, 53*sp*, and 77*spd*, were used throughout this project. The details of these bases are summarized in Table 1. For the first part of the work, where many points had to be computed for the geometry optimization, economy dictated the application of the smaller, 31*sp*, basis set. It should be pointed out that this basis was successfully employed [18] for a study of the episulphide molecule.

RESULTS

The geometry optimization started with the values reported earlier [15] for both the β-thiovinyl cation * and the thiirenium ion. Only one geometrical parameter (bond length, bond angle, torsional angle, angle of pyramidal inversion) was varied at a time while all the others were kept constant. The minimum of the energy as a function of the independent variable (the geometrical parameter under investigation) was found by fitting a quadratic equation to the computed points. The total energy value was recomputed by a new SCF-MO calculation for this optimum geometry. This recomputed value was the first point in the variation of the next internal mode of motion. The overall process is illustrated for both the β-thiovinyl cation and the thiirenium

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* It should be noted that in the previously reported calculation there was a numerical error in the co-ordinates used for the β-thiovinyl cation which has been eliminated in the present paper.

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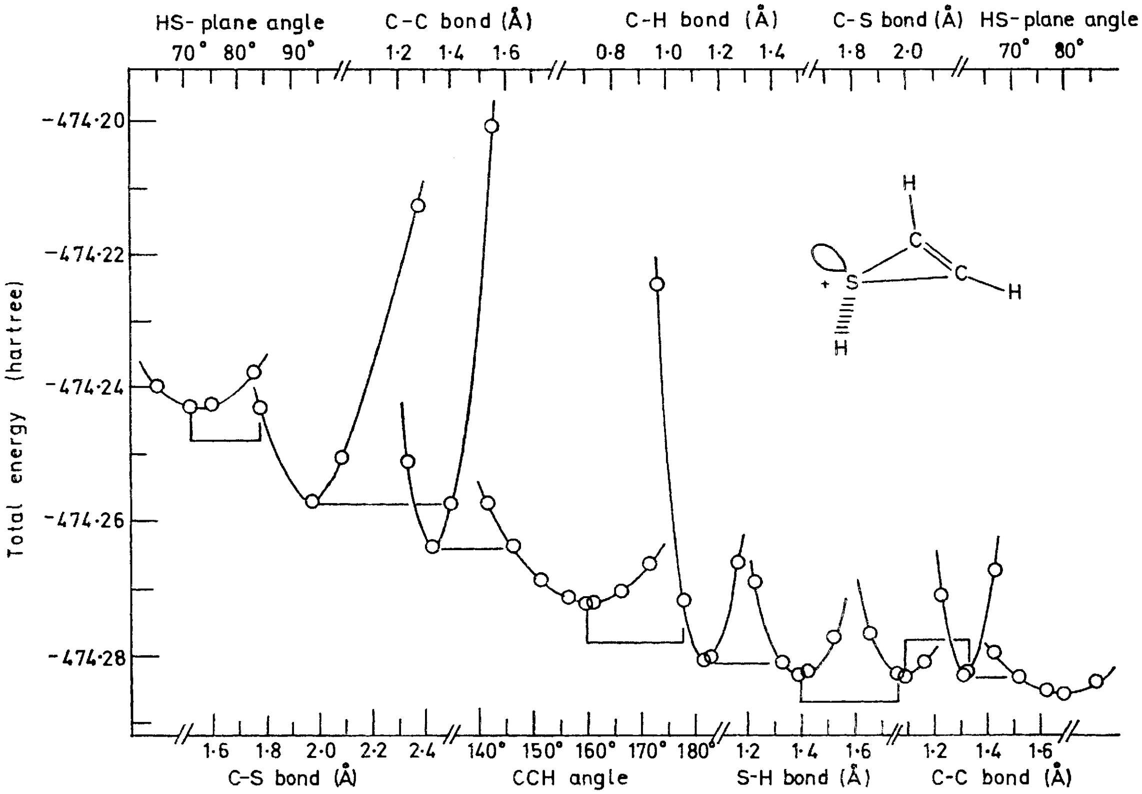


FIGURE 2 Geometry optimization of thiirenium ion

ion in Figures 1 and 2 respectively. The numerical values for these two species are summarized in Tables 2 and 3 and the optimized atomic co-ordinates are shown in Table 4.

The total energies in themselves are of no chemical interest but their relation to one another, *i.e.*, the energy difference, is a measure of the thermodynamic stability of one isomer with respect to the other. These total energy values (the last entries in Tables 2 and 3, also shown in Table 5) gave 3·88 kcal mol^{-1} as the energy of stabilization of the cyclic species over the open structure.

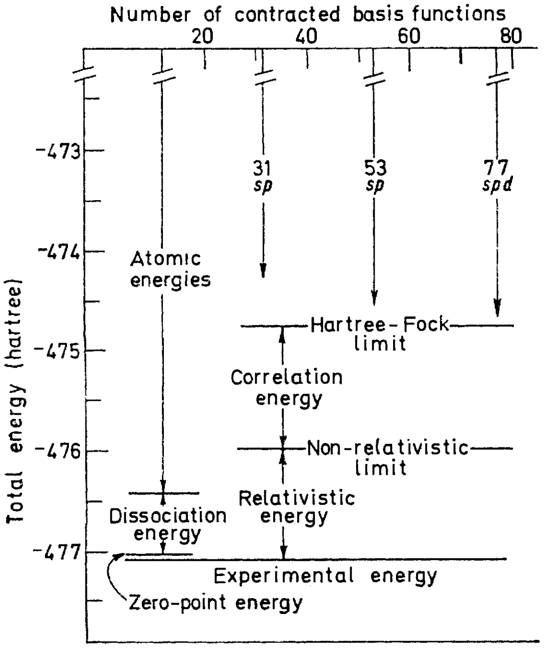


FIGURE 3 A breakdown of total energy to experimental and theoretical components for thiirenium ion

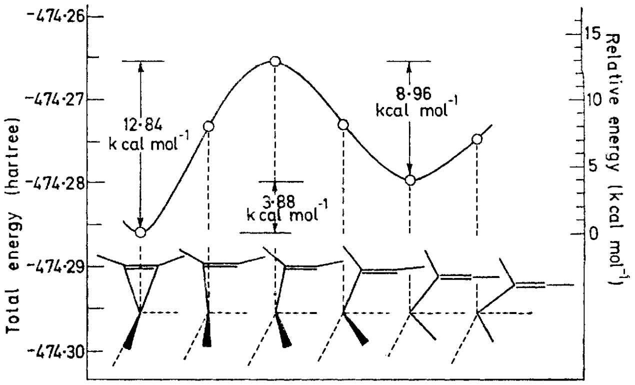


FIGURE 4 Reaction profile for thiirenium ion–β-thiovinyl cation interconversion

The total energy values of these species were recomputed using the two larger basis sets (53*sp* and 77*spd*) and these results are also included in Table 5. The estimated (Table 6) Hartree–Fock limit (HFL) seems to be gradually approached with the increase in the basis set size (Figure 3). It is expected that the computed energy difference (ΔE) also approaches, although not monotonically, the relative stability of the two limiting structures at the HFL.

The energy barrier separating structures (1) and (2) was estimated by computing the total energy values with the 31*sp* basis set at three intermediate structures corresponding to nominal 25, 50, and 75% conversion. The atomic co-ordinates were chosen with the assumption that the motions of all the atoms are occurring in a synchronized fashion. The computed reaction profile is shown in Figure 4 (*cf.* Table 7).

DISCUSSION

The first point that emerges from the results of the calculations reported above is that the cation has two energy minima, one corresponding to the open linear cation (1) and the other to the cyclic ion (2). Calculations along the assumed path connecting (1) and (2) indicate that the two minima are separated by a potential barrier. The true magnitude of this barrier is probably lower than that suggested by our computation (*ca.* 13 kcal mol^{-1}) because no optimization was carried out on the intermediate structures. However, the value found is in fair agreement with the chemical evidence [2-4] which suggests an easy interconversion. The two structures (1) and (2) of the simplest cation ($C_2H_3S^+$), appear to be of almost the same energy in agreement with the recent finding of Clark *et al.*[19] Large substituent effects, albeit different, could be anticipated for both structures. It follows therefore that the relative stability of cyclic and open ions should depend very much upon the location and the nature of substituents. This, however, does not affect the important conclusion reached here, namely that when sulphur is the bridging atom the cyclic structure is at an energy minimum and at a level similar to, if not lower than, the open structure.

One question that comes to mind in connection with the thermodynamic stabilities of (1) and (2) is the relative importance of the various factors that stabilize one structure rather than the other. Although traditionally *d* orbital participation was considered to be the major factor in the field of sulphur chemistry, the fact that the two *sp* basis sets gave the same order of thermodynamic stability as that computed by the *spd* basis set rules out the validity of this point of view, even if the magnitude of ΔE varies with the basis set size.

Another possible way to analyse the problem, at this stage, is to examine the components of the total energy in the two limiting structures. This method has been used successfully by Allen [20] and Wolfe *et al.*[21] Accordingly, one should compare the expected values of the kinetic (T), electron–electron repulsion (V_{ee}), and nuclear–electron attraction (V_{ne}) operators in addition to the nuclear–nuclear repulsion (V_{nn}) [equation (1)].

$$E = \underbrace{V_{nn} + T + V_{ee}}_{\text{repulsive}} + \underbrace{V_{ne}}_{\text{attractive}} \qquad (1)$$

The actual values for the optimized structures (1) and (2) as well as for the interconversion are summarized in Table 7.

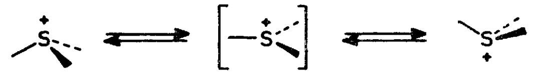
When the attractive and repulsive components are plotted against the assumed reaction co-ordinate and the curvature of these plots are compared to that of the reaction profile (Figure 4) then it becomes clear that the cyclic structure (the lower minimum in Figure 4) is dominated by attractive forces while the open structure (the higher minimum in Figure 4) is dominated by repulsive forces.

Another important point in connection with the structure of the thiirenium ion is the large deviation from coplanarity, *i.e.* the angle between the S–C(1)–C(2) plane and the hydrogen attached to sulphur is 79·6°. The corresponding barrier to inversion was found to be 72·9 kcal mol^{-1}.*

It should be noted that if the thiirenium ion were planar, the unshared electrons on sulphur would, formally, be in a *p* type orbital, parallel to the π orbital of the C(1)=C(2) double bond. Since four electrons in a cycle cannot be stabilized by resonance (they violate the $4n + 2$ Hückel rule) electron–electron repulsion between the two doubly occupied parallel orbitals could be anticipated. However, it is remarkable that the avoidance of coplanarity cause so large (72·9 kcal mol^{-1}) a stabilization.

For this reason we attempted to obtain more information on the nature of this barrier. First, we tried to estimate the contribution of unsaturation in related systems. The tabulated results (Table 8) indicate that unsaturation in a five-membered ring (where a 6π electron system is achieved in the planar structure) will lower the inversion barrier while unsaturation in a three-membered ring (where only a 4π electron system is achieved) will raise the inversion barrier.

Secondly, we tried to ' calibrate ' our 31*sp* basis set as well as the mode of motion studied in the present investigation. For this reason three series of studies were carried out on the inversion process of H_3S^+. In the first series [mode (2)] the symmetrical inversion mode was examined. In the second series (3) two of the three hydrogens were kept in their original position and only the third proton was moved to achieve coplanarity. In this mode the two fixed hydrogen atoms simulate the rigid three-membered ring but at a larger angle (92°) than that present in the thiirenium ion. In the third mode of motion (4) the bond angles of the hydrogen atoms were changed to the optimized bond angles about the sulphur atom in the thiirenium ring (38·78 and 99·77°). The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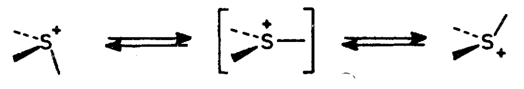
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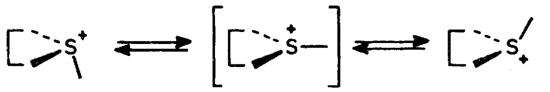
(4)

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* A similar value for the inversion barrier was reported by Clark.[19]

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three inversion potentials associated with modes (2)—(4) are shown in Table 9, together with the inversion barrier of the thiirenium ion. These barriers for modes (2)—(4) are 9·80, 23·32 and, 78·90 kcal mol^{-1} respectively which may be compared with 72·90 kcal mol^{-1} for the pyramidal inversion barrier of thiirenium ion. Table 9 also reports the energy components for the planar and pyramidal structures of SH_3^+ and $C_2H_3S^+$. When they are analysed for pyramidal inversion at sulphur it becomes clear that the barrier to inversion in all these cases is attractive dominant.

More interesting, however, is the fact that when the peculiar geometry, characteristic of the three-membered ring structure of $H_2C_2SH^+$ is enforced about the sulphur atom in H_3S^+ then the unusually large barrier height (ΔE *ca.* 70 kcal mol^{-1}) to inversion is practically reproduced. This would suggest that most if not all the height of the energy barrier is related to the strained geometrical situation about the inverting sulphur atom and that repulsion between the non-bonding and the π electron pairs makes at most a minor contribution to the inversion barrier. This particular problem is now under investigation.

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