Molecular Orbital Calculations on the $C_2H_4SH^+$ Cation †

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Systematic non-empirical SCF-MO calculations were carried out on the two limiting structures of $C_2H_4SH^+$. In both of these cases two different atomic orbital basis sets were used. The results indicate that the open structure (β-thioethyl cation) lacks thermodynamic stability and spontaneously interconverts into the bridged structure (thiiranium ion). The pyramidal inversion at sulphur in the thiiranium ion was computed to be 78.11 kcal mol^{-1}.

THE experimental observation that sulphenyl halides add to olefins in an anti-stereospecific manner has lead to the hypothesis that the bridged thiiranium ion is an important intermediate in this reaction.[1]

The possible dependence of the mode of addition upon the relative stabilities of the open (I) and bridged (II) cationic intermediates postulated in electrophilic additions to carbon–carbon multiple bonds has raised considerable theoretical interest in these reactions.

Very recently[2] non-empirical SCF-MO calculations have been carried out on the two limiting structures, open and bridged valence tautomers, of the $C_2H_4F^+$ [2a] and $C_2H_4Cl^+$ [2b] cations. The two geometries in each case were optimized by application of a split valence shell basis set. The total energy values of the optimized structures were then recomputed using a double zeta basis set. In the case of fluorine it appears that the β-fluoroethyl cation is more stable than the corresponding bridged fluoronium ion by 10.30 kcal mol^{-1}. However, the chloronium ion is more stable than the β-chloroethyl cation by 9.35 kcal mol^{-1}. It should however be emphasized that all four species had thermodynamic stability.

A theoretical study of the two limiting forms of the

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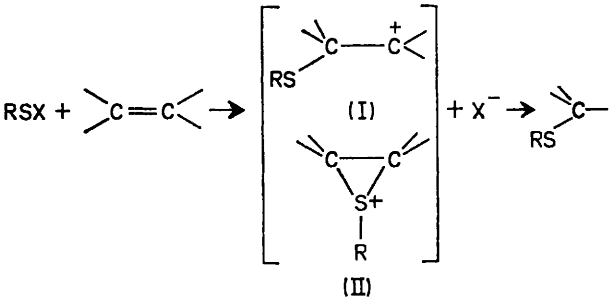
† Table numbers in this paper refer to Supplementary Publication No. SUP 21510 (10 pp.), 1 microfiche. For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[1] W. H. Mueller, *Angew. Chem. Internat. Edn.*, 1969, **8**, 482.

[2] (*a*) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*; (*b*) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, unpublished results.

unsaturated $C_2H_2SH^+$ cation using the non-empirical SCF-MO method has also been reported.[3] Geometry optimization of the bridged and open forms of $C_2H_2SH^+$ were carried out. It was found that the bridged thiirenium ion was more stable than the open β-thiovinyl cation by 3—5 kcal mol^{-1} and again both of these structures were stable in the thermodynamic sense. The barrier of interconversion between the two limiting structures was calculated to be 12.8 kcal mol^{-1}.



(1)

The present study was undertaken in order to extend the theoretical approach to a system representative of the simplest possible addition of a sulphenyl halide to an olefin as exemplified by equation (1).

In this paper we present the results of non-empirical SCF-MO calculations on the $C_2H_4SH^+$ cation with full geometry optimization of the bridged thiiranium ion and the open β-thioethyl cation.

METHOD

The non-empirical or Hartree–Fock type SCF-MO calculations were carried out on an IBM 370/165 computer using a GAUSSIAN 70 program.[4] The set of basis functions used were obtained by contraction from primitive Gaussian type functions. The molecular orbitals (MO) were constructed from the contracted basis by a linear combination according to Roothaan's self-consistent field (SCF) procedure.[5]

Two basis sets were used in the calculations, corresponding to minimal 24*sp* and split valence shell 41*sp* basis sets. Some of the details of these bases are summarized in Table 1. Both the 24*sp* and 41*sp* basis sets were applied to the calculation of the points for the geometry optimization.

The 24*sp* (STO-NG) basis set is a least squares representation of Slater-type orbitals (STO) by a linear combination of *N* Gaussian functions. Each orbital is represented by a weighted sum of *N* Gaussian functions.

The 41*sp* basis set is a split valence shell basis set in which each inner-shell orbital is represented by a sum of four Gaussian functions and the valence atomic orbitals are split into an inner and an outer part. These two parts are represented by three and one Gaussian function respectively. The splitting of the valence shell seems to allow for anisotropic atomic shape which occurs when atoms are combined to form molecules.

RESULTS AND DISCUSSION

Starting values for the geometry optimization of the bridged thiiranium ion and open β-thioethyl cation were chosen from the analogous studies carried out earlier on $C_2H_4F^+$ [2] and $C_2H_2SH^+$.[3]

One geometrical parameter (bond length, bond angle, dihedral angle) was varied at a time and the others were maintained constant. The total molecular energy was minimized with respect to the geometrical parameter under investigation by applying a quadratic fit to the computed points. A new total energy value was then calculated for this optimum geometry. This recomputed value was the first point in the variation of the next internal mode of motion.

Optimization of the $\widehat{SCC'}$ angle of the open β-thioethyl cation yielded a value of 72° (Figure 1) corresponding to a molecular structure more closely resembling the bridged thiiranium ion for which $\widehat{SCC'}$ is 66.70°. Therefore, it was decided to arbitrarily fix $\widehat{SCC'}$ at 110° until all other geometrical parameters were optimized.* The variation of total energy with $\widehat{SCC'}$ was then re-examined and is also shown in Figure 1. No value of this angle giving a molecular geometry corresponding to an open β-thioethyl cation was found. This seems to suggest that an open $C_2H_4SH^+$ species has only transient existence and immediately collapses to the stable bridged form of the $C_2H_4SH^+$ ion. Further investigation of this point of interest will appear later in the paper.†

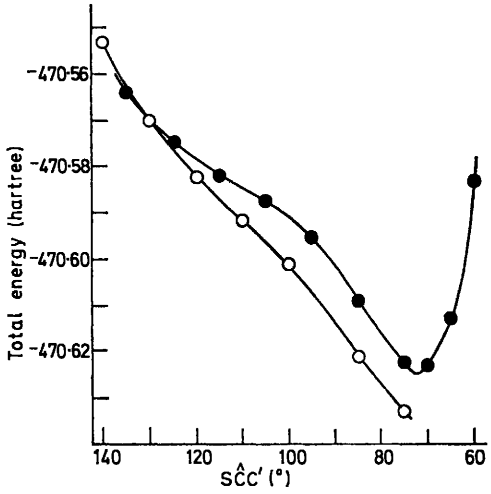
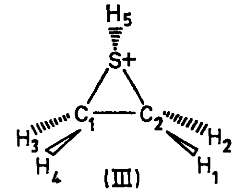
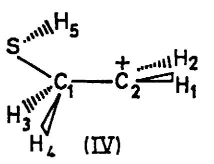


FIGURE 1 Variation of total energy with angle $\widehat{SCC'}$ in the β-thioethyl cation; ● and ○ denote respectively without and with prior optimization of all other geometrical parameters



(III)



(IV)

The atomic co-ordinates of the bridged (III) and open ion (IV) structures optimized using the 24*sp* basis set are

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* The equilibrium $\widehat{SCC'}$ is *ca.* 110° in ethanethiol.

† For the rest of this paper calculations on the β-thioethyl cation will refer to the structure optimized with $\widehat{SCC'}$ fixed at 110°.

[3] I. G. Csizmadia, J. A. Duke, V. Lucchini, and G. Modena, *J.C.S. Perkin II*, 1974, 1808.

[4] GAUSSIAN 70, Quantum Chemistry Program No. 236, Indiana University, Bloomington, Indiana.

[5] C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

shown in Table 2. Optimized values of all geometrical parameters for both structures are given in Table 3. At this point in the paper it should be noted that one geometrical parameter * of the bridged thiiranium ion was re-optimized using the 41*sp* basis set. This partially re-optimized structure was used in all subsequent calculations involving use of the 41*sp* basis set.

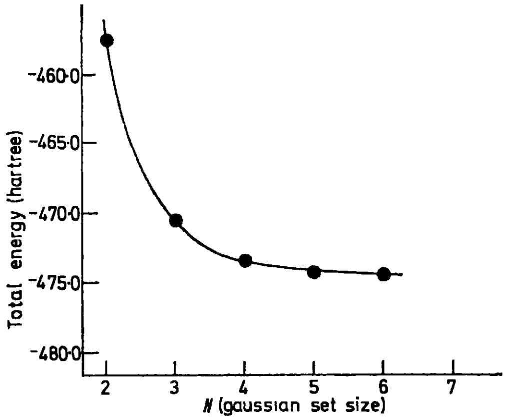

FIGURE 2 Variation of total energy of the $C_2H_4SH^+$ cation with gaussian set size within the 24*sp* basis set

The computed total energy values of the optimized bridged and open structures, as well as the corresponding energy differences (ΔE), rapidly converge to limiting values as N is increased (the number of Gaussians per STO). This is seen in Figures 2 and 3 respectively. The numerical values are summarized in Tables 3—5. The total energy value of the bridged $C_2H_4SH^+$ species can be seen to be approaching the estimated (Table 6) Hartree–Fock Limit (HFL). Increasing the size of the Gaussian set within the 24*sp* basis set gradually lowers the SCF energy. A further decrease in total energy is again observed upon application of the 41*sp* basis set. These ideas are conveniently illustrated in Figure 4.

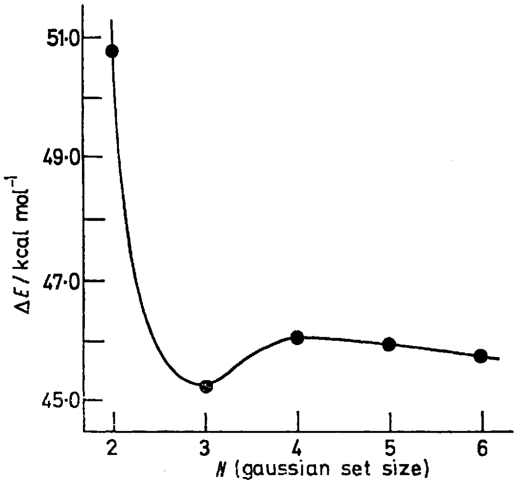

FIGURE 3 Difference in total energies, ΔE, of the optimized bridged and open ion structures plotted as a function of gaussian set size within the 24*sp* basis set

It was decided that the total energy profile, showing interconversion of the bridged and open structures, be calculated using both the 24*sp* and 41*sp* basis sets. Total energy values were calculated at three intermediate structures corresponding to 25, 50, and 75% conversion and also at a structure corresponding to 125% conversion. The choice of atomic co-ordinates was based on the assumption that the motions of all the atoms are occurring in a synchronous fashion. The numerical values are summarized in Table 7. The calculated total energy profiles using the 24*sp* and 41*sp* basis sets are shown in Figures 5 and 6 respectively.

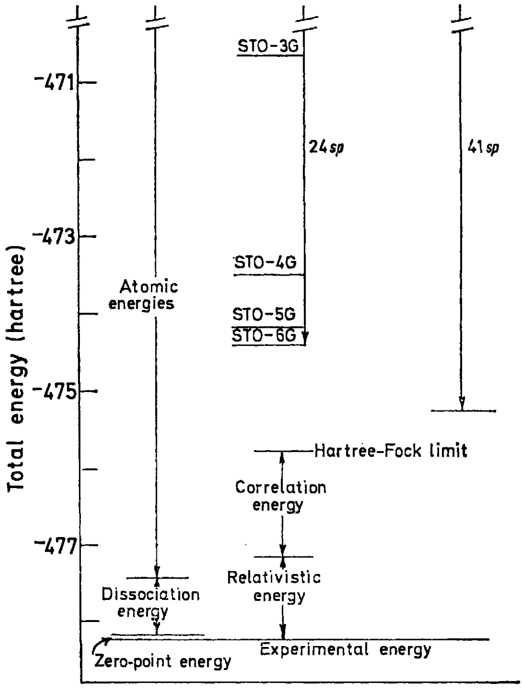

FIGURE 4 A comparison of various computed total energy values of the thiiranium ion with experimentally observed and theoretically computed fractions of the experimental total energy

The results obtained through use of both the 24*sp* and 41*sp* basis sets indicates that the $C_2H_4SH^+$ cation has only one energy minimum corresponding to the bridged structure. The crude total energy curve obtained with the 24*sp* basis set shows a slight inflection point at the position corresponding to the open ion structure indicative of perhaps transient stability associated with this species. However, the total energy profile could quite possibly assume a smooth parabolic shape, as found using the 41*sp* basis set, if complete optimization was carried out on all intermediate structures used in the calculation.

These results are in accord with the bulk of experimental evidence [1] which suggests that only the bridged thiiranium ion is involved in the addition of sulphenyl halides to olefins. The conclusions from this study

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* The distance of the SH to the C_2H_4 portion of $C_2H_4SH^+$ was re-optimized as it produced the greatest variation in total energy during optimization with the 24*sp* basis set.

apply only to the addition of the simplest sulphenyl halide (HSX) to ethylene (C_2H_4), as shown in the Scheme.

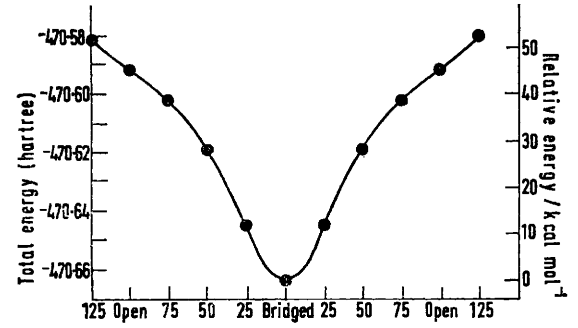


FIGURE 5 Total energy profile, showing interconversion of the bridged and open $C_2H_4SH^+$ structures, calculated with the 24*sp* basis set

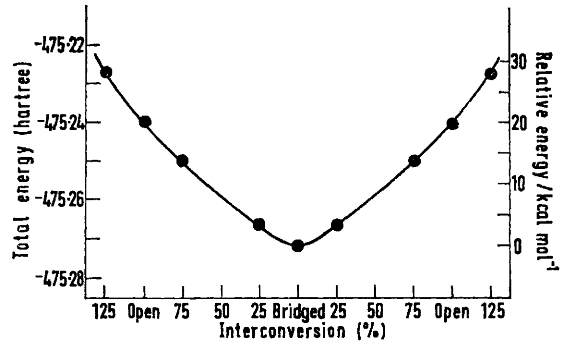
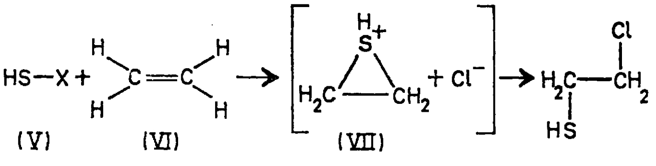


FIGURE 6 Total energy profile, showing interconversion of the bridged and open $C_2H_4SH^+$ structures, calculated with the 41*sp* basis set

Additional information concerning the addition reaction illustrated in the above scheme can be obtained from the calculation of the localized charge distributions of optimized forms * of (V)—(VII) by application of the mulliken population analysis using both the 24*sp* and 41*sp* basis sets. The results are conveniently shown in Figure 7. The calculated localized charges are qualitatively similar for the two basis sets. In both cases the thiiranium ion delocalizes the unit positive charge so as to produce an alteration of the sign of the charge, the C atoms negative in sign whereas the S and H atoms retain a positive sign.



SCHEME

The above discussion has only considered the existence of a bridged intermediate ion; however, under appropriate conditions, *i.e.* choice of solvent, temperature, olefin, and sulphenyl halide structure, the addition has been shown to occur in a non-stereospecific manner.[6] This has lead to the hypothesis that substituent and solvent effects can sufficiently stabilize the open relative to the bridged structure so that both forms are important either in the rate- or product-determining steps or both. Further experimental investigation of the factors affecting the thermodynamic stabilities of the bridged and open ion structures is presently in progress.[7]

Another possible theoretical approach to this problem is to examine the components of the total energy in the two limiting structures, a method employed extensively by Allen.[8,9] The total energy of a system is partitioned into the kinetic energy of the electrons T, the attraction of the electrons for the nuclei V_{ne}, the interelectronic repulsion term V_{ee}, and the internuclear repulsion term V_{nn} [equation (2)].

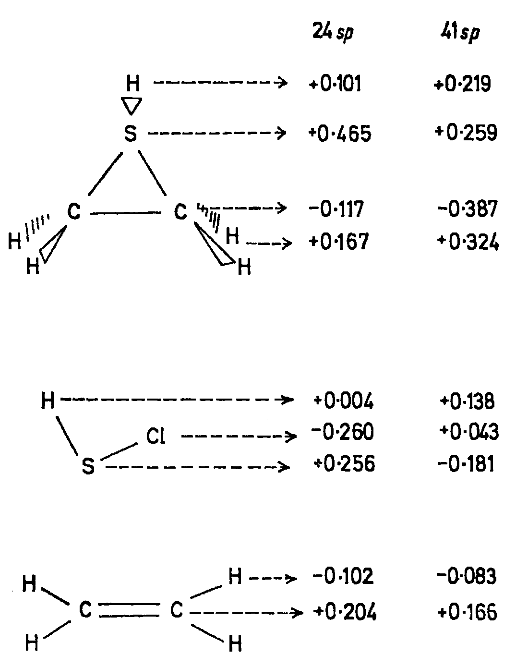


FIGURE 7 Localized charge distributions of the optimized structures of HSCl, C_2H_4, and the bridged $C_2H_4SH^+$ cation calculated with the 24*sp* and 41*sp* basis sets

$$E = \underbrace{V_{nn}}_{\text{nuclear}} + \underbrace{T + V_{ee} + V_{ne}}_{\text{electronic}} \qquad (2)$$

Numerical values for the nuclear and electronic energy components, as defined above, are given along with the corresponding total energy values, for both optimized structures and energy profile of interconversion in Table 7 for the 24*sp* and 41*sp* basis sets. The total, nuclear, and electronic energy components of $C_2H_4SH^+$ ion are plotted as a function of % interconversion in

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* Structure (V) was optimized through application of the minimal *sp* basis set and the optimized geometry of (VI) was taken from J. M. Schulman, J. W. Moskowitz, and C. Hollister, *J. Chem. Phys.*, 1967, **46**, 2759.

[6] G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, 1972, **37**, 3086.

[7] J. W. Gordon and G. H. Schmid, University of Toronto.

[8] L. C. Allen, *Chem. Phys. Letters*, 1968, **2**, 597.

[9] W. H. Fink and L. C. Allen, *J. Chem. Phys.*, 1967, **46**, 2261.

Figure 8. Examination of the curvature of these plots reveals that the entire total energy curve is dominated by electronic forces, not nuclear forces.

The barrier to pyramidal inversion at sulphur in the thiiranium ion was investigated using the 24*sp* basis set and is illustrated in Figure 9. The corresponding numerical values are given in Table 8. The angle between S–H and the plane defined by the S, C, and C′ atoms ($\widehat{HS}$plane) is 81.7°. The resulting barrier to inversion was found to be 78.11 kcal mol^{-1} and is dominated by electronic forces when analysed in terms of the energy components.

Similar studies[3] carried out on the unsaturated thiirenium ion $C_2H_2SH^+$ also give a large barrier to inversion at sulphur. The $\widehat{HS}$plane angle is 81.7 and 79.6° for the thiiranium and thiirenium ions respectively. The corresponding barriers to inversion are 78.11 and 72.90 kcal mol^{-1} respectively. The similarity between the two structures with respect to the above stated angles and barrier heights suggest that the repulsion between the non-bonding electrons on the S atom and the π-electron pair in the thiirenium ion makes at most a minor contribution to the inversion barrier.

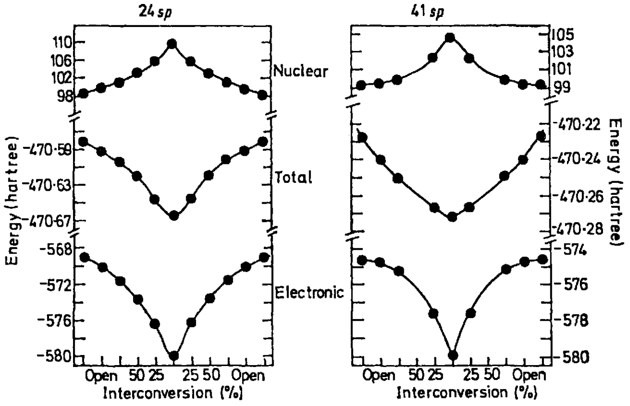

FIGURE 8 Total energy and the nuclear and electronic components of the total energy of $C_2H_4SH^+$ cation plotted as a function of % interconversion shown for both the 24*sp* and 41*sp* basis sets

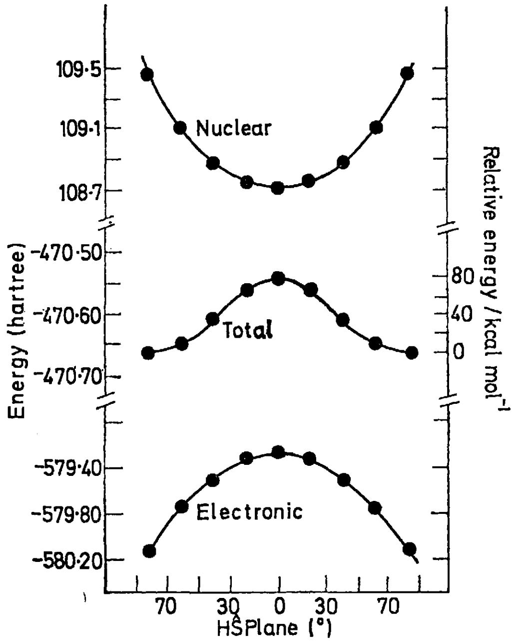

FIGURE 9 Pyramidal inversion at sulphur in the thiiranium ion calculated with the 24*sp* basis set

Studies of the corresponding inversion barrier in the H_2SH^+ cation[3] demonstrate that most if not all of the height of the inversion barrier in the thiiranium (as well as thiirenium) ion is related to the strained geometrical situation about the inverting sulphur atom.

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