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Mechanistic Study of the Electrocyclic Ring-Opening Reaction of Thiirane

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Abstract: The electrocyclic ring opening of the C–C bond in thiirane is investigated in detail within the context of ab initio molecular orbital theory. The conrotatory and disrotatory reaction pathways are studied with three different basis sets ranging from double-ζ plus polarization (DZP) through triple-ζ plus double polarization (TZ2P) in conjunction with self-consistent-field (SCF), two-configuration SCF (TCSCF), and configuration interaction with single and double excitations (CISD) levels of theory. The conrotatory and disrotatory stationary points were located on the potential energy surface and characterized via harmonic vibrational frequency analyses. At all levels of theory considered, the conrotatory stationary point is found to be a genuine transition state. The disrotatory stationary point, located with the two configuration methods, is found to have two imaginary vibrational frequencies. The conrotatory process is shown to be the favored mechanistic route for thiirane ring opening by 13.2 ± 4.0 kcal mol^{-1} with the zero point vibrational energy correction, relative to the disrotatory pathway at the highest level of theory employed (TZ2P TCSCF-CISD+Q). The potential energy hypersuurface for thiirane ring opening is compared with the corresponding surface for oxirane.

Introduction

The stereoselective nature of the electrocyclic ring-opening reaction of cyclopropyl anion leading to allyl anion via C–C cleavage can be rationalized in terms of orbital symmetry arguments and is a direct consequence of the reaction mechanism. Rotation of the terminal methylene groups in the same direction defines a conrotatory process and in the opposite direction a disrotatory process. For various cyclic systems, whether a ring opening reaction pathway is allowed or forbidden can be determined by applying the principle of conservation of orbital symmetry. Woodward and Hoffmann thus postulated that the conrotatory mechanism should be favored for the thermolysis and the disrotatory mechanism for the photolysis of the cyclopropyl anion.[1,2] Extensive experimental[3-12] and theoretical[13-31] investigations that have been undertaken confirm the validity of these predictions, in particular for heterocyclic systems isoelectronic with the cyclopropyl anion, such as aziridine and oxirane (H_2CXCH_2, X = NH, O). The C–C electrocyclic ring opening of these heterocycles, leading to azomethane and carbonyl ylides, respectively, was shown to occur in a concerted manner in accordance with the Woodward–Hoffmann (W–H) rules. Studies concerning azomethane and carbonyl ylides have formed an active area of chemical research since they have been used as intermediates in the synthesis of many organic compounds.[3-9]

Clearly, the relative activation barriers for the conrotatory (in C_2 symmetry) and disrotatory (in C_s symmetry) ring-opening pathways determine the preferred route. The barrier for conrotatory ring opening via C–C bond cleavage for unsubstituted oxirane was found to be 47.6 kcal/mol with use of multireference configuration interaction (MR CISD) techniques and the 4-31G basis set.[18] The barrier height for the disrotatory reaction pathway was predicted to be 10.9 kcal mol^{-1} above that of the conrotatory pathway; however, the corresponding disrotatory stationary point was shown to be an energy maximum with respect to two coordinates of reaction. Thus the disrotatory stationary point is not a genuine transition state at this level of theory.[18] A nonsynchronous pathway in C_1 symmetry was also proposed for oxirane[18] in which one methylene group is initially allowed to rotate, the other being kept orthogonal to the COC plane. Energetically the stationary point for the nonsynchronous pathway in C_1 symmetry was predicted to lie 8.3 kcal mol^{-1} above the conrotatory stationary point in C_2 symmetry. Also the open structure, carbonyl ylide, was found to be 34.1 kcal mol^{-1} above the ring form, oxirane. In comparison, theoretical studies for cyclopropane ring opening at the two-configuration self-consistent-field (TCSCF) level with the 3-21G basis set showed that the conrotatory stationary point in C_2 symmetry was below the disrotatory stationary point in C_s symmetry, although by less than 1 kcal mol^{-1}.[24]

Vibrational analysis of planar unsubstituted carbonyl ylide by Yamabe and co-workers[20] at the 4-31G TCSCF level of theory

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showed two imaginary frequencies, 455i (a_2) and 369i cm^{-1} (b_1). Following the a_2 mode, a nonplanar structure was located involving pyramidalization of the two methylene groups and was found to be stabilized by less than 1 kcal mol^{-1} relative to the planar isomer.[20] Following the b_1 mode yielded the ring isomer.[20] A number of other distinct structures for carbonyl ylide, involving rotation of the methylene groups, have been examined with molecular orbital theory.[16-27]

Much research in recent years has been concerned with the comparison of systems containing first-row atoms with the analogous isovalent systems containing second- (or third) row atoms. The similarities and differences in the structures and bonding of such systems have been analyzed closely.[32-37] The purpose of the current research is to investigate the effect of the second-row atom on the electrocyclic ring-opening reaction of H_2CSCH_2, the thiirane molecule. The electrocyclic ring opening of thiirane via C–C cleavage, leading to thione methylide, has been studied with semiempirical methods.[38] The conrotatory barrier was found to be lower in energy than the disrotatory barrier in accordance with the conservation of orbital symmetry (W-H rules). The quantitative results of this work, however, should be treated cautiously due to the nonrigorous nature of the CNDO procedure employed.

Contrary to the analogous oxygen case, thione methylides cannot be generated by the electrocyclic *ring opening* of thiiranes because of the relative weakness of C–S as compared to C–C bonds. However, experimental investigations[39,40] have been able to examine the related cyclization of thione methylides (which had to be generated from different precursors).

The geometrical parameters and harmonic vibrational frequencies of (cyclic) thiirane have previously been determined theoretically,[41] and the predicted values are in satisfactory agreement with the experimentally derived values.[41-43] To our knowledge there has been no high-level theoretical determination of the molecular properties of the open isomer (thione methylide) or the activation barriers for conrotatory and disrotatory motion. In this research a detailed ab initio theoretical analysis of the thiirane ring opening potential energy surface was performed involving location of stationary points corresponding to the above mentioned structures employing methods that include electron correlation effects. Harmonic vibrational frequency analyses were carried out to characterize each stationary point and to determine the zero-point vibrational energy (ZPVE). The relative energies of the ring and open isomers and the energetic competition between the conrotatory and disrotatory pathways will be discussed at various levels of theory and compared with the corresponding oxirane values.

The current research is concerned with the synchronous conrotatory (in C_2 symmetry) and disrotatory (in C_s symmetry) ring-opening mechanisms. We will also examine whether the W-H rules are applicable in a straightforward manner for thiirane, as they are for the first-row analogue oxirane. Ring opening of oxirane is also known to occur via C–O cleavage.[16] However, the criterion of potential reversibility of an oxirane opening via C–O cleavage is not appropriate for thiirane analysis. Not only is C–S more likely than is C–O cleavage, but the corresponding diradicals easily stabilize via loss of elemental S.

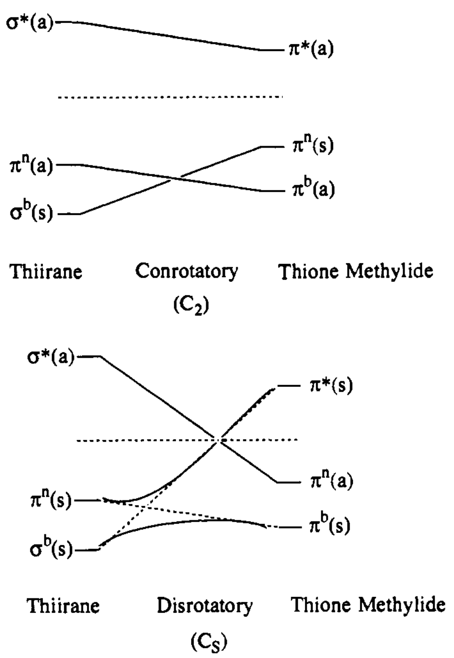

Figure 1. Schematic correlation diagrams for the conrotatory and disrotatory isomerization of thiirane to thione methylide.

Electronic Structure Considerations

For W-H allowed pathways of ring-opening reactions the single configuration level often represents a reasonable zeroth-order wave function for a qualitative description of the process. W-H forbidden pathways of ring-opening reactions, however, usually require MCSCF based methods for even a qualitative description. The selection of the configurational space for the MCSCF is not always obvious, and this aspect will be discussed for the ring opening of thiirane.

The stereoselectivity of the electrocyclic ring opening of thiirane may be understood in terms of a correlation diagram involving C–C σ^b, σ^*, and ring π^n orbitals of thiirane that transform smoothly into three C–S π orbitals of planar thione methylide, as shown schematically in Figure 1. This is analogous to the diagram for oxirane ring opening.[16] The methylene motion dictates the behavior of the molecular orbitals centered on the carbons, while molecular orbitals centered mainly on sulfur tend to correlate with their sulfur counterparts since they are not significantly affected by the motion. During the conrotatory process the symmetry of the molecule is constrained to C_2, while during the disrotatory process the symmetry is constrained to (C_s). The correlation diagram for the conrotatory process (Figure 1) shows a crossing between a pair of occupied orbitals and this is referred to as a symmetry-allowed mechanism.[1,2] Following the disrotatory pathway the C–C σ^b bonding orbital (a′ in C_s symmetry) of thiirane appears to correlate with the unoccupied C–S π^* antibonding orbital (a′) of thione methylide and the occupied nonbonding π^n orbital (a′) correlates with the occupied C–S π bonding orbital. The C–C σ^b and π^n orbitals are both of a′ symmetry and thus an avoided crossing results. The unoccupied C–C σ^* antibonding orbital (a″) of thiirane correlates with the occupied nonbonding π^n orbital (a″) of thione methylide and, therefore, the disrotatory process involves the actual crossing of an occupied and unoccupied pair of orbitals and corresponds to a symmetry-forbidden mechanism.

From the correlation diagram it can be argued that the conrotatory mechanism can be qualitatively described with a single configuration wave function. Conversely, description of the disrotatory process evidently requires at least a two-configuration wave function which spans the occupied–virtual orbital crossing. This may also be understood by consideration of the ground-state

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valence-electron configurations of the various species involved in the ring-opening reaction. For thiirane the ground-state configuration can be described by (in C_{2v} symmetry)

$$\ldots 2b_1{}^2 1a_2{}^2 8a_1{}^2 3b_1{}^2 5b_2{}^0 \tag{1}$$

and the ground-state configuration for the open structure may be expressed by (in C_{2v} symmetry)

$$\ldots 5b_2{}^2 8a_1{}^2 2b_1{}^2 1a_2{}^2 3b_1{}^0 \tag{2}$$

The symmetry is constrained to C_2 during the conrotatory process. In C_2 symmetry the above electronic structures correlate with the following configuration

$$\ldots 6b^2 8a^2 7b^2 9a^2 8b^0 \tag{3}$$

thus a single-configuration wave function correctly describes the conrotatory ring-opening pathway.

For the disrotatory mechanism C_s symmetry is maintained. With this constraint thiirane and thione methylide give rise to distinct configurations

$$\text{thiirane in } C_s \rightarrow \ldots 9a'^2 5a''^2 10a'^2 11a'^2 6a''^0 \tag{4}$$

$$\text{thione methylide in } C_s \rightarrow \ldots 5a''^2 9a'^2 10a'^2 6a''^2 11a'^0 \tag{5}$$

It is evident that a single configuration model is inadequate. Configuration 4, the electronic structure for thiirane in C_s symmetry, corresponds to the $(\pi^*)^2$ configuration of the open structure

$$\ldots 5b_2{}^2 8a_1{}^2 2b_1{}^2 3b_1{}^2 1a_2{}^0 \tag{6}$$

resulting from the $(\pi^{n})^2 \rightarrow (\pi^*)^2$ $[1a_2{}^2 \rightarrow 3b_1{}^2]$ double excitation, while configuration 5, the electronic structure for thione methylide in C_s symmetry, corresponds to the $(\sigma^*)^2$ configuration of cyclic thiirane

$$\ldots 2b_1{}^2 1a_2{}^2 3b_1{}^2 5b_2{}^2 8a_1{}^0 \tag{7}$$

resulting from the $(\sigma^{b})^2 \rightarrow (\sigma^*)^2$ $[8a_1{}^2 \rightarrow 5b_2{}^2]$ double excitation. This excitation was used rather than $(\pi^{n})^2 \rightarrow (\sigma^*)^2$ $[3b_1{}^2 \rightarrow 5b_2{}^2]$ since the C–C bond is broken during ring opening.

The two-configuration wave function (4 + 5) encompasses the occupied–virtual orbital crossing for the disrotatory process, as suggested by Figure 1, and smoothly correlates with both the ring and open structures in the C_s symmetry point group. For the conrotatory process a single configuration for each stationary point will, in principle, suffice on the basis of orbital symmetry; however, for a more unbiased comparison of the activation energies for the conrotatory and disrotatory mechanisms, a second configuration was incorporated in the wave function for the conrotatory process described by

$$\ldots 6b^2 8a^2 7b^2 8b^2 9a^0 \tag{8}$$

Configuration 8 correlates smoothly with doubly excited configurations (6) and (7) of thiirane and thione methylide, respectively. The two-configuration wave function (3) + (8) is also consistent with the two-configuration wave function for the disrotatory process (4) + (5).

Theoretical Procedures

Three basis sets, DZP, TZ2P/DZP, and TZ2P, were employed in this study. The DZP basis set is constructed from the standard Huzinaga–Dunning[44–46] double-ζ contraction of Gaussian functions augmented with a set of Cartesian d-like functions for C, S, and p-like functions for H. This complete double-ζ plus polarization (DZP) basis set is designated S(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p). The polarization function orbital exponents employed were $\alpha_d(\mathrm{S}) = 0.5$, $\alpha_d(\mathrm{C}) = 0.75$, $\alpha_p(\mathrm{H}) = 0.75$. The oxygen DZP basis set used for oxirane calculations (see below) is from the same source as for carbon, with the polarization function orbital exponent $\alpha_d(\mathrm{O}) = 0.85$. The more flexible basis set of triple-ζ plus double polarization function (TZ2P) quality was utilized since energy differences, particularly involving cyclic structures, are often sensitive to the quality of the basis set.[47,48] This TZ2P orbital set involves McLean and Chandler's[49] 6s5p contraction of Huzinaga's[44] 12s9p primitive set for sulfur and Dunning's[45] 5s3p and 3s contractions of Huzinaga's 10s6p and 4s sets for carbon and hydrogen, respectively, augmented with two sets of Cartesian d-like functions for C, S, and p-like functions for H. The polarization function orbital exponents employed were $\alpha_d(\mathrm{S}) = 1.0, 0.25$, $\alpha_d(\mathrm{C}) = 1.5, 0.375$, $\alpha_p(\mathrm{H}) = 1.5, 0.375$. This basis set is designated S(12s9p2d/6s5p2d), C(10s6p2d/5s3p2d), H(4s2p/3s2p). The TZ2P/DZP basis set consists of TZ2P on C and S and DZP on the H atoms. The hydrogen s functions have been scaled by the standard factor of 1.2 in all three basis sets.

The geometries of the various structures involved in thiirane ring opening have been fully optimized within the given symmetry constraints with use of the two-configuration self-consistent-field (TCSCF) analytic first derivative method.[50] The nature of the stationary points was determined via prediction of harmonic vibrational frequencies with analytic TCSCF second derivative techniques.[26,51] The geometries of the three species involved in the conrotatory process, thiirane, thione methylide, and the conrotatory stationary point, were also optimized using single configuration SCF[50] and single reference configuration interaction CISD[37,52] analytic gradient procedures. At the SCF level of theory harmonic vibrational frequencies were determined via analytical second-derivative techniques[53,54] and at the CISD level of theory via a finite difference of analytic gradients. For the sake of comparison, the geometries of the structures involved in oxirane ring opening were optimized at the TCSCF level with the DZP basis set. The three species involved in the oxirane conrotatory process were also subject to geometry optimizations at the DZP SCF level of theory.

The frozen core and frozen virtual approximation was applied at the CISD level of theory. Specifically, the seven lowest occupied molecular orbitals (S 1s, 2s, 2p; C 1s-like orbitals) were held doubly occupied (frozen cores) and the three highest lying virtual orbitals (S 1s*, C 1s*-like orbitals) were deleted (frozen virtuals) in all configurations. Otherwise all singly and doubly excited configurations with respect to the SCF (SCF-CISD or 1R CISD) and TCSCF (TCSCF-CISD or 2R CISD) references have been included. With the TZ2P basis set the TCSCF-CISD wave function involves 212 027 and 223 299 configurations for thiirane and thione methylide in C_{2v} symmetry and 419 662 and 419 483 configurations for the conrotatory and disrotatory stationary points in C_2 and C_s symmetries, respectively. These CISD wave functions were determined by using the shape driven graphical unitary group approach.[55] The effect of unlinked quadruple excitations on the CISD relative energies is estimated by incorporating the Davidson correction,[56] and the subsequent energy differences are labeled CISD+Q. Refined energetic predictions were obtained from TZ2P 1R CISD and DZP, TZ2P/DZP, TZ2P 2R CISD single-point energies at the appropriate SCF or TCSCF optimized geometries.

Results and Discussion

In Tables I–VI we report the optimized geometries, dipole moments, harmonic vibrational frequencies, and infrared intensities for the isomeric forms of C_2H_4S considered in this investigation at various levels of theory. Relative energies for the thiirane isomers are reported in Tables VII. Total and relative energies for the oxirane system are shown in Table VIII.

Thiirane. The symmetry of thiirane was constrained to the C_{2v} point group during the geometry optimizations and the resulting

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Table I. Theoretical Prediction of the Total Energy, Structure, and Dipole Moment[a] for Thiirane

level of theory	energy[b]	r_e(C–S)	r_e(C–C)	r_e(C–H)	θ_e(SCH)	θ_e(CCH)	θ_e(CSC)	μ
DZP SCF	−0.558 154	1.817	1.479	1.077	115.2	118.2	48.0	2.257
TZ2P SCF	−0.600 901	1.817	1.471	1.071	114.8	118.2	47.7	2.237
DZP CISD	−0.954 037[c]	1.820	1.487	1.084	115.5	118.0	48.2	1.979
DZP TCSCF	−0.573 584	1.815	1.504	1.077	115.4	118.0	49.0	2.214
TZ2P/DZP TCSCF	−0.614 332	1.816	1.495	1.074	115.1	118.1	48.6	2.210
TZ2P TCSCF	−0.616 448	1.815	1.495	1.072	115.0	118.1	48.6	
experiment[d]		1.820	1.492	1.078	114.9	117.8	48.4	

[a] Energy in hartree, bond lengths in Å, angles in deg, dipole moment (μ) in D. [b] Add −475 hartrees. [c] With inclusion of the Davidson correction, the DZP CISD+Q energy is −476.003 747. [d] The experimental structure parameters are r_0 and θ_0 values from refs 42 and 43.

Table II. Theoretical Harmonic Vibrational Frequencies and Infrared Intensities[a] for Thiirane

approx description	symmetry	DZP SCF	TZ2P SCF	DZP CISD	DZP TCSCF	TZ2P/DZP TCSCF	experiment[b]
C–H stretch	a_1	3308 (19.2)[c]	3297 (14.5)	3246	3304 (21.3)	3278 (16.8)	3014 (x[d,e])
CH_2 scissor	a_1	1629 (2.7)	1630 (3.3)	1572	1614 (4.2)	1613 (5.0)	1457 (7)
C–C stretch	a_1	1231 (4.3)	1216 (2.4)	1199	1182 (1.6)	1179 (1.1)	1110 (4)
CH_2 wag	a_1	1138 (0.1)	1140 (0.3)	1099	1104 (0.2)	1097 (0.2)	1024 (1)
C–S stretch	a_1	686 (46.9)	654 (46.3)	690	678 (45.2)	647 (45.1)	627 (75 − y[e])
C–H stretch	a_2	3393 (0.0)	3376 (0.0)	3336	3392 (0.0)	3361 (0.0)	
CH_2 twist	a_2	1294 (0.0)	1307 (0.0)	1241	1255 (0.0)	1268 (0.0)	
CH_2 rock	a_2	972 (0.0)	976 (0.0)	941	974 (0.0)	975 (0.0)	
C–H stretch	b_1	3407 (12.6)	3392 (2.8)	3348	3405 (14.3)	3376 (3.8)	3088 (18)
CH_2 rock	b_1	1041 (2.7)	1043 (3.0)	1004	1044 (2.6)	1044 (2.7)	945 (8)
CH_2 twist	b_1	893 (0.7)	897 (0.6))	872	867 (0.7)	871 (0.5)	824 (<1)
C–H stretch	b_2	3301 (22.4)	3291 (11.3)	3240	3298 (24.2)	3273 (15.2)	3013 (100 − x[e])
CH_2 scissor	b_2	1590 (0.5)	1594 (1.0)	1535	1583 (0.1)	1584 (0.2)	1436 (5)
CH_2 wag	b_2	1183 (43.6)	1198 (28.8)	1127	1171 (42.2)	1186 (28.0)	1051 (80)
C–S stretch	b_2	740 (0.7)	725 (0.4)	725	746 (0.5)	727 (0.2)	

[a] Harmonic frequencies in cm^{-1} and infrared intensities in km mol^{-1}. [b] Experimental frequencies from ref 41. [c] Infrared intensities in parentheses. [d] The experimental infrared intensity is a relative value. [e] Overlapping bands, x and y change value with change of isotopomer.

Table III. Theoretical Prediction of the Total Energy, Structure, and Dipole Moment[a] for Thione Methylide

level of theory	energy[b]	r_e(C–S)	r_e(C–C)	r_e(C–H_a)	r_e(C–H_b)	θ_e(SCH_a)	θ_e(HCH)	θ_e(CSC)	μ
DZP SCF	−0.470 102	1.619	2.749	1.074	1.073	123.3	121.1	116.3	0.020
TZ2P SCF	−0.519 965	1.605	2.731	1.069	1.068	123.5	121.2	116.6	0.232
DZP CISD	−0.873 131[c]	1.635	2.761	1.080	1.078	123.2	121.3	115.2	0.044
DZP TCSCF	−0.507 532	1.666	2.774	1.074	1.072	123.0	121.2	112.8	0.610
TZ2P/DZP TCSCF	−0.551 069	1.647	2.758	1.070	1.069	123.2	121.3	113.7	0.654
TZ2P TCSCF	−0.553 055	1.647	2.758	1.069	1.068	123.2	121.3	113.7	0.652

[a] Energy in hartree, bond lengths in Å, angles in deg, dipole moment (μ) in D. [b] Add −475 hartrees. [c] With inclusion of the Davidson correction, the DZP CISD+Q energy is −475.927 632.

Table IV. Theoretical Harmonic Vibrational Frequencies and Infrared Intensities[a] for Thione Methylide

approx description	symmetry	DZP SCF	TZ2P SCF	DZP CISD	DZP TCSCF	TZ2P/DZP TCSCF	TZ2P TCSCF
C–H stretch	a_1	3474 (0.0)[b]	3452 (1.0)	3422	3472 (0.8)	3441 (0.1)	3453 (0.2)
C–H stretch	a_1	3346 (1.0)	3333 (0.4)	3290	3341 (5.2)	3316 (2.7)	3328 (2.3)
CH_2 scissor	a_1	1565 (2.7)	1569 (2.4)	1504	1552 (0.0)	1554 (0.2)	1556 (0.2)
CH_2 rock	a_1	1136 (5.2)	1133 (6.1)	1081	1095 (1.2)	1094 (1.3)	1096 (1.8)
C–S stretch	a_1	1009 (0.6)	1003 (0.1)	962	847 (15.0)	849 (8.0)	850 (7.9)
CSC bend	a_1	371 (4.0)	378 (3.5)	350	347 (0.3)	355 (0.6)	355 (0.6)
CH_2 twist[c]	a_2	414 (0.0)	424 (0.0)	297	474 (0.0)	510 (0.0)	510 (0.0)
CH_2 wag[c]	a_2	681 (0.0)	702 (0.0)	584	157i (-)	18i (-)	60 (0.0)
CH_2 twist	b_1	610 (93.8)	639 (41.2)	654	595 (29.1)	611 (27.4)	612 (27.4)
CH_2 wag	b_1	729 (221.6)	730 (201.8)	528	325 (183.6)	390 (148.4)	395 (146.0)
C–H stretch	b_2	3474 (0.0)	3453 (0.5)	3423	3472 (0.0)	3441 (0.5)	3452 (0.5)
C–H stretch	b_2	3345 (12.4)	3331 (14.5)	3289	3342 (0.8)	3317 (0.2)	3330 (0.2)
CH_2 scissor	b_2	1531 (72.8)	1536 (56.7)	1476	1524 (2.7)	1526 (4.5)	1527 (4.5)
C–S stretch	b_2	1171 (247.9)	1162 (234.9)	1139	1081 (2.8)	1074 (9.9)	1075 (9.6)
CH_2 rock	b_2	962 (5.1)	957 (4.5)	920	948 (0.8)	944 (1.1)	945 (0.9)

[a] Harmonic frequencies in cm^{-1} and infrared intensities in km mol^{-1}. [b] Infrared intensities in parentheses. [c] The a_2 symmetry CH_2 wagging and twisting modes are heavily coupled.

structures are shown in Table I. The valence electron configuration of cyclic thiirane is described by eq 1. Multiple bonding is not significantly involved in the CSC ring since the out-of-ring plane $1a_2$ and $2b_1$ molecular orbitals correspond to C–H bonding orbitals, and $3b_1$ is localized predominantly on sulfur. This is exemplified by the C–C and C–S bond lengths: 1.487 and 1.820 Å respectively at the DZP SCF-CISD level, which are within the range of typical single bond distances for cyclic compounds.

Table V. Theoretical Prediction of the Total Energy, Structure, and Dipole Moment[a] for the Conrotatory Transition State

level of theory	energy[b]	r_e(C–S)	r_e(C–C)	r_e(C–H_a)	r_e(C–H_b)	θ_e(SCH_a)	θ_e(HCH)	θ_e(CSC)	δ_e(H_aCSC)	δ_e(H_bCSC)	μ
DZP SCF	−0.433 630	1.687	2.377	1.072	1.078	118.1	119.4	89.6	51.0	−118.7	0.790
TZ2P SCF	−0.480 030	1.677	2.355	1.067	1.073	118.0	119.6	89.2	52.4	−119.0	0.891
DZP CISD	−0.843 533[c]	1.701	2.370	1.079	1.084	117.7	119.6	88.4	50.6	−117.8	0.735
DZP TCSCF	−0.493 867	1.743	2.520	1.076	1.079	117.4	118.2	92.6	48.7	−107.6	1.521
TZ2P/DZP TCSCF	−0.534 776	1.733	2.503	1.073	1.075	117.3	118.5	92.5	49.5	−107.7	1.642
TZ2P TCSCF	−0.536 588	1.733	2.501	1.071	1.073	117.3	118.6	92.4	49.5	−107.9	

[a] Energy in hartree, bond lengths in Å, angles in deg, dipole moment (μ) in D. [b] Add −475 hartrees. [c] With inclusion of the Davidson correction, the DZP CISD+Q energy is −475.902 178.

Table VI. Theoretical Prediction of the Total Energy, Structure, and Dipole Moment[a] for the Disrotatory Stationary Point

level of theory	energy[b]	r_e(C–S)	r_e(C–C)	r_e(C–H_a)	r_e(C–H_b)	θ_e(SCH_a)	θ_e(HCH)	θ_e(CSC)	δ_e(H_aCSC)	δ_e(H_bCSC)	μ
DZP TCSCF	−0.475 202	1.771	2.727	1.075	1.075	119.5	119.8	100.7	43.1	−122.7	1.735
TZ2P/DZP TCSCF	−0.515 227	1.764	2.723	1.072	1.071	119.4	120.1	101.0	43.4	−122.7	1.743
TZ2P TCSCF	−0.517 069	1.764	2.721	1.070	1.069	119.4	120.1	101.0	43.9	−122.9	

[a] Energy in hartree, bond lengths in Å, angles in deg, dipole moment (μ) in D. [b] Add −475 hartrees.

Table VII. Relative Energies (kcal mol^{-1}) for the Thiirane System[a]

level of theory	thiirane	thione methylide	conrotatory	disrotatory	conrotatory − disrotatory energy difference	conrotatory ring-closure barrier	disrotatory ring-closure barrier
DZP SCF	0.0	55.3 (52.4)	78.1 (75.1)			22.8 (22.7)	
TZ2P SCF	0.0	50.8 (48.0)	75.8 (72.8)			25.0 (24.8)	
DZP 1R CISD	0.0	50.8 (47.5)	69.3 (66.2)			18.5 (18.7)	
DZP 1R CISD+Q	0.0	47.8 (44.5)	63.7 (60.6)			15.9 (16.1)	
TZ2P 1R CISD	0.0	46.5 (43.7)	67.5 (64.5)			21.0 (20.8)	
TZ2P 1R CISD+Q	0.0	44.1 (41.3)	62.5 (59.5)			18.4 (18.2)	
DZP TCSCF	0.0	41.4 (36.9)	50.0 (45.9)	61.7 (55.3)	11.7 (9.4)	8.6 (9.0)	20.3 (18.4)
TZ2P/DZP TCSCF	0.0	39.7 (35.3)	49.9 (45.8)	62.2 (55.7)	12.3 (9.9)	10.2 (10.5)	22.5 (20.4)
TZ2P TCSCF	0.0	39.8 (35.4)	50.1 (46.0)	62.4 (55.9)	12.3 (9.9)	10.3 (10.6)	22.6 (20.5)
DZP 2R CISD	0.0	42.6 (38.1)	55.7 (51.6)	70.1 (63.7)	14.4 (12.1)	13.1 (13.5)	27.5 (25.6)
DZP 2R CISD+Q	0.0	42.5 (38.0))	56.2 (52.1)	71.0 (64.6)	14.8 (12.5)	13.7 (14.1)	28.5 (26.6)
TZ2P/DZP 2R CISD	0.0	39.1 (34.7)	54.8 (50.7)	69.9 (63.4)	15.1 (12.7)	15.7 (16.0)	30.8 (28.7)
TZ2P/DZP 2R CISD+Q	0.0	38.9 (34.5)	55.1 (51.0)	70.7 (64.2)	15.6 (13.2)	16.2 (16.5)	31.8 (29.7)
TZ2P 2R CISD	0.0	39.4 (35.0)	55.0 (50.9)	70.2 (63.7)	15.2 (12.8)	15.6 (15.9)	30.8 (28.7)
TZ2P 2R CISD+Q	0.0	39.1 (34.7)	55.4 (51.3)	71.0 (64.5)	15.6 (13.2)	16.3 (16.6)	31.9 (29.8)

[a] Energy differences based on the total energies in Tables I, III, V, and VI. The values in parentheses are those with the ZPVE correction. For those levels of theory where vibrational frequencies are not determined, the corresponding TZ2P SCF, DZP TCSCF, or TZ2P/DZP TCSCF ZPVE corrections were used. [b] The energy difference between the conrotatory and disrotatory stationary points.

Table VIII. Total and Relative Energies for the Oxirane System[a]

level of theory	oxirane	carbonyl ylide	conrotatory	conrotatory ring-closure barrier
		Total Energies		
DZP SCF	−152.903 845	−152.796 645	−152.766 906	
DZP 1R CISD	−153.331 870	−153.238 962	−153.213 640	
DZP 1R CISD+Q	−153.380 457	−153.295 038	−153.273 054	
DZP TCSCF	−152.921 590	−152.853 086	−152.841 361	
DZP 2R CISD	−153.336 655	−153.265 795	−153.247 463	
DZP 2R CISD+Q	−153.382 567	−153.312 006	−153.292 692	
		Relative Energies		
DZP SCF	0.0	67.3 (64.5)	85.9 (82.4)	18.6 (17.9)
DZP 1R CISD	0.0	58.3 (55.5)	74.2 (70.7)	15.9 (15.2)
DZP 1R CISD+Q	0.0	53.6 (50.8)	67.4 (63.9)	13.8 (13.1)
DZP TCSCF	0.0	43.0 (38.3)	50.3 (46.5)	7.3 (8.2)
DZP 2R CISD	0.0	44.5 (39.8)	56.0 (52.2)	11.5 (12.4)
DZP 2R CISD+Q	0.0	44.3 (39.6)	56.4 (52.6)	12.1 (13.0)

[a] Total energies in hartree, relative energies in kcal mol^{-1}. The DZP 1R and 2R CISD energies were obtained at the corresponding DZP SCF or TCSCF optimized geometries. The values in parentheses are those with the ZPVE correction. For those levels of theory where vibrational frequencies were not determined, the corresponding DZP SCF or TCSCF ZPVE corrections were used.

The DZP SCF geometrical parameters are very similar to the SCF values with a 6-31G* basis reported previously[41] and are in reasonable agreement with the experimentally derived values.[42,43] It should be noted that the theoretical predictions are for r_e equilibrium structures, while the experiments refer to r_0 vibrationally averaged structures. An increase in the basis set from DZP to TZ2P at the SCF level leads to a reduction in the C–C and C–H bond lengths, with the C–S distance remaining constant. The bond distances are all shorter than the experimental values at the TZ2P SCF level, with the major discrepancy being for the C–C bond length. At the TCSCF level with a TZ2P basis set, the C–C bond length is increased by 0.024 Å relative to TZ2P SCF, since the second configuration, eq 7 ($(\sigma^b)^2 \rightarrow (\sigma^*)^2$), introduces C–C antibonding character. The C–S and C–H bond lengths are not affected as much as the C–C distance by the inclusion of the second configuration in the wave function. The

CI coefficients for the TCSCF wave function are the following: $C_1 = 0.995$, $C_2 = -0.098$ with DZP and $C_1 = 0.995$, $C_2 = -0.096$ with the TZ2P basis set. Reoptimization at the DZP SCF-CISD level has the effect of increasing all the bond lengths relative to the values predicted by the DZP SCF method. The SCF-CISD wave function has CI coefficients $C_1 = 0.935$, $C_2 = -0.046$ ($4b_2^2 \rightarrow 5b_2^2$), suggesting the electronic structure of thiirane can be qualitatively described by a single configuration. The predicted bond angles are very consistent at all levels of theory considered and are close to the experimental values. The CSC bond angle is about 48° for the ring structure.

The ring form is characterized as a minimum on the potential energy surface since there are $3N - 6$ (N being the number of atoms) real vibrational frequencies as reported in Table II. The harmonic frequencies are overestimated by SCF, TCSCF, and CISD levels of theory, and average percent errors relative to the experimental values[41] are approximately 10% at SCF, 9% at TCSCF, and 7% at the CISD levels of theory. However, experimental fundamental frequencies, which are usually lower than harmonics, are being compared with theoretical harmonic frequencies which may account for about 2% of the error. For this system CISD bond lengths are longer than the equivalent SCF bond lengths resulting in lower predicted harmonic vibrational frequencies. Relative infrared intensities in the theoretical SCF and TCSCF spectra and in the experimental spectra are in reasonable general agreement. The geometrical parameters and physical properties at the DZP SCF-CISD level reproduce the experimental values[41] reasonably well for thiirane, confirming the qualitative adequacy of single reference procedures for this system. Vibrational analysis of oxirane at the DZP SCF and TCSCF levels of theory characterizes the ring from as a local minimum on the potential energy surface in agreement with thiirane. The TCSCF CI coefficients for oxirane are $C_1 = 0.994$, $C_2 = -0.113$ with the DZP bases set.

Thione Methylide. During the geometry optimizations the symmetry of thione methylide was constrained to the C_{2v} point group, planarity being maintained, and the optimized structures are reported in Table III. The valence electronic configuration of the open structure is described by eq 2. The open structure has a longer C–C distance and larger CSC angle relative to the ring isomer, since the $3b_1$ molecular orbital which is C–C π bonding is unoccupied, and the $5b_2$ orbital which involves C–C σ antibonding in character is occupied. The CSC angle is about 114° for this open structure. The doubly occupied out-of-plane $2b_1$ molecular orbital is delocalized over the CSC atoms and is C-S π bonding in character, hence the C–S bonds display some degree of multiple bond character. The C–S distance at the TZ2P TCSCF level, 1.647 Å, is significantly shorter than the single bond length in thiirane, 1.815 Å, and is closer to typical C–S double bond distances.

To our knowledge, the synthesis of unsubstituted thione methylide has not been reported in the literature, thus there are no experimental structures or molecular properties to compare with the theoretical predictions. At the theoretical levels employed predicted bond lengths are decreased as the basis set size is increased. In particular, the TCSCF C–S double bond distance is decreased by 0.019 Å from DZP to TZ2P. This is a typical basis set dependency for multiply bonded systems.[57] The inclusion of the dynamical electron correlation at the SCF-CISD level leads to the usual increase in all bond distances compared to SCF. The effect of the nondynamical electron correlation at the TCSCF level is to increase the C-S bond length relative to SCF, for example by 0.042 Å with the TZ2P basis set. The variation in CSC angle with the theoretical level reflects the changes in C–S bond lengths; longer C–S distances allow a smaller angle.

The CI coefficients for the TCSCF wave function are the following: $C_1 = 0.936$, $C_2 = -0.353$ with DZP and $C_1 = 0.945$, $C_2 = -0.326$ with the TZ2P basis set. The coefficient C_2 is significantly greater in magnitude than that for the second configuration of thiirane ($C_2 = -0.096$ at the TZ2P TCSCF level) and is the reason for the considerable diradical character of this ylide molecule.[14-26] The second configuration, eq 6 ($(\pi^n)^2 \rightarrow (\pi^*)^2$), introducing C–S antibonding character to the wave function, explains the substantial increase in the C–S bond length in the TCSCF structure compared to SCF and SCF-CISD.

At the SCF and SCF-CISD levels of theory, the open form is vibrationally characterized as a local minimum on the potential energy surface. However, with the DZP TCSCF method there is a single imaginary frequency 157i cm^{-1} of a_2 symmetry, suggesting the planar open structure is a transition state at this theoretical level. The imaginary frequency corresponds to puckering of the planar structure. Following this vibrational mode yields a C_2 symmetry structure lying only 0.03 kcal mol^{-1} lower in energy than the planar form. With the TZ2P/DZP basis set, the imaginary frequency is decreased to 18i cm^{-1}. When the largest basis set employed in this study, TZ2P, is used, the frequency becomes real with small magnitude, 60 cm^{-1}. The planar structure thus corresponds to a minimum on the potential energy surface at the TZ2P TCSCF level of theory. This suggests the antibonding π character, introduced by the second configuration, may be considerably overestimated with the DZP basis set. With the TZ2P basis set the antibonding π character in the TCSCF wave function is reduced due to the smaller weight of the second configuration and a planar structure is predicted. The surface is very shallow with respect to the a_2 symmetry conrotatory motion. Such low-frequency vibrations are known to be particularly sensitive to the level of theory and basis set employed.[57] With larger basis sets including higher angular momentum functions this frequency may become even larger in magnitude, while remaining real.

Planar carbonyl ylide is vibrationally characterized as a local minimum with the DZP SCF method; however, with DZP TCSCF this isomer shows two imaginary frequencies, 589i (a_2) and 505i cm^{-1} (b_1), corresponding to out-of-phase and in-phase CH_2 wagging motions, respectively (in agreement with the work of Yamabe and co-workers[20] at the 4-31G TCSCF level). The CI coefficients in the DZP TCSCF wave function are the following: $C_1 = 0.908$, $C_2 = -0.419$. The relatively large value of C_2 compared to that for thione methylide ($C_2 = -0.353$ at the DZP TCSCF level) suggests the TCSCF wave function involves significant antibonding π character leading to the preference for nonplanar carbonyl ylide structures.

The symmetric and asymmetric C–S stretching frequencies predicted for thione methylide with the TZ2P TCSCF method are 153 (15%) and 87 cm^{-1} (7%) smaller than TZ2P SCF, reflecting the longer C–S distance with the two-configuration method. The frequencies of the other in-plane modes are not changed considerably at the TCSCF level relative to SCF. Progressing from SCF to SCF-CISD, the in-plane modes decrease by about 2–3% for stretches and 5% for bends. The low-frequency out-of-plane modes (a_2, b_1) show significant variations at correlated levels compared to SCF, particularly the a_2 modes for which the methylene twisting and wagging motions are heavily coupled.

The geometrical parameters and harmonic vibrational frequencies for thione methylide yielded by the TZ2P TCSCF method are probably better estimates of the "true" values than the DZP SCF-CISD predictions due to the diradical character of this species. However, for more quantitative accuracy, particularly for the C-S bond length and the out-of-plane bending frequencies, higher levels of theory may be required involving larger basis sets and higher order electronic excitations.

Conrotatory Transition State. The only constraint adopted in the optimization of the transition state for the conrotatory mechanism was retention of C_2 point group symmetry. The C_2 axis in Figure 2 is in the plane of the paper, bisecting the C–C axis. The valence electron configuration of the conrotatory transition state is described by 3. The C–S bond in the structure retains some degree of multiple bond character as shown by the C–S distance, 1.733 Å at the TZ2P TCSCF level, which is between the values in thiirane, 1.815 Å, and thione methylide, 1.647 Å. The C–C distance is rather similar to the value in the open

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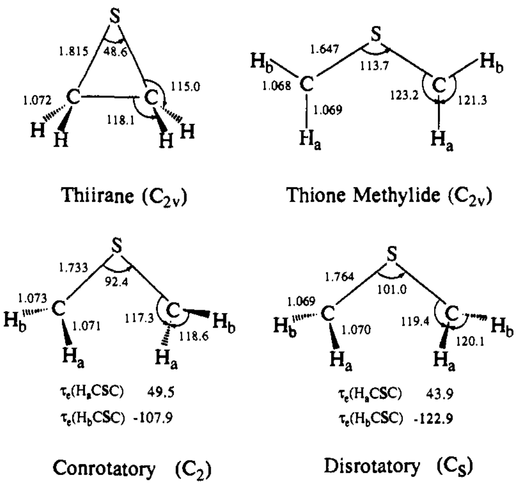
(57) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3187.



Thiirane (C_{2v}) Thione Methylide (C_{2v})

Conrotatory (C_2) Disrotatory (C_S)

Figure 2. Optimized geometries for thiirane, thione methylide, and the conrotatory and disrotatory stationary points at the TZ2P TCSCF level of theory.

isomer and is considerably longer than that in the ring structure since the occupied 7b orbital involves C–C σ antibonding character. This is also reflected by the CSC bond angle for the conrotatory stationary point, 92.4° at TZ2P TCSCF, which more closely resembles the bond angle in thione methylide, 113.7°, than that in thiirane, 48.6°. It is evident that the transition state for conrotatory motion is geometrically closer to the open isomer than the ring isomer. The Hammond postulate,[58] suggesting that a reaction is likely to be an endothermic process if the transition state structure for the reaction is closer to that of a product than a reactant, appears to hold for the conrotatory ring opening of thiirane.

The C–S distance predicted at the DZP TCSCF level of theory is longer by 0.056 and 0.042 Å relative to the DZP SCF and SCF-CISD C–S distances, respectively. The C-C bond length and CSC bond angle are also greater with the TCSCF method. This is due to the intrinsic nature of the TCSCF wave function including a large contribution from the second configuration, eq 8, which involves both C–S π and C–C σ antibonding character. The CI coefficients for the TCSCF wave function are the following: $C_1 = 0.898$, $C_2 = -0.441$ with the DZP basis set and $C_1 = 0.903$, $C_2 = -0.429$ with the TZ2P basis set. These CI coefficients strongly support the choice of a zeroth order wave function involving two configurations.

Vibrational analysis of the conrotatory stationary point yields a single imaginary frequency (a) at each level of theory and $3N - 7$ real frequencies. The imaginary frequency has magnitude 584i, 609i cm^{-1} at DZP, TZ2P SCF; 520i cm^{-1} at DZP SCF-CISD; and 333i, 349i cm^{-1} at DZP, TZ2P/DZP TCSCF levels of theory. The longer C–S bond length and C–C separation at the TCSCF level is reflected by the lower magnitude imaginary frequency. The normal mode for this imaginary frequency corresponds to conrotation of the methylene groups (90%) combined with stretching of the C–C bond (10%). This is the expected reaction coordinate for the conrotatory electrocyclic ring opening of thiirane via C–C cleavage. The stationary point is, therefore, the genuine transition state for the conrotatory process. The CH_2 wagging and other twisting frequencies and the C–S stretching frequencies also display the lowest magnitude with the two-configuration method. Harmonic frequencies predicted for the transition state are much closer to those of the open isomer than the ring form reflecting the geometrical similarities. The conrotatory transition state for oxirane ring opening shows a single imaginary frequency (a), 670i cm^{-1} at DZP SCF and 371i cm^{-1} at the DZP TCSCF level, which is rather similar in magnitude to the corresponding value for the thiirane conrotatory transition state. The CI coefficients in the DZP TCSCF wave function for the oxirane conrotatory transition state are the following: $C_1 = 0.872$, $C_2 = -0.489$. The value of C_2 is largerthan the corresponding thirrane value (−0.441 at DZP TCSCF).

Disrotatory Stationary Point. The C_s plane of symmetry was maintained in the geometrical search for the stationary point of the disrotatory pathway. This is the plane perpendicular to the plane of the paper in Figure 2, bisecting the C–C axis. The optimized structures are shown in Table VI. A TCSCF wave function corresponding to configurations (4) + (5) was necessary to locate the disrotatory stationary point between thiirane and thione methylide. The CI coefficients generated by the TCSCF method conform to this: $C_1 = 0.731$, $C_2 = -0.682$ with the DZP basis set and $C_1 = 0.732$, $C_2 = -0.681$ with the TZ2P basis set. The two configurations contribute almost equally to the wave function. The C–S distance is longer in the disrotatory stationary point than the conrotatory transition state due to the greater magnitude of C_2 and bears a closer resemblance to the C–S bond length in thiirane than thione methylide at the TCSCF level. Nevertheless, the C–C separation, 2.721 Å, and the CSC bond angle, 101.0° at the TZ2P TCSCF level, suggest that overall the structure of the disrotatory stationary point is closer to that of the open structure than the ring isomer.

Vibrational analysis of the disrotatory stationary point with the TCSCF method shows two imaginary frequencies: 592i (a′), 170i cm^{-1} (a″) with DZP and 613i (a′), 171i cm^{-1} (a″) with the TZ2P/DZP basis set. The imaginary frequencies do not change in magnitude with the larger basis set. The a′ mode corresponds to the expected disrotatory CH_2 twisting motion and the a″ mode corresponds to the conrotatory CH_2 twisting motion. The normal mode for the a″ imaginary frequency should lead to a lower order stationary point. This may correspond to the conrotatory transition state in C_2 symmetry or to a stationary point for the nonsynchronous pathway in C_1 symmetry. Volatron, Ahn, and Jean found the stationary point for the oxirane disrotatory pathway in C_s symmetry to be an energy maximum with respect to two coordinates (corresponding to conrotatory and disrotatory motion) at the 4-31G TCSCF level of theory.[18] Thus, for thiirane and oxirane a genuine transition state for disrotatory motion was not located within the constraint of the C_s symmetry point group at the theoretical levels employed.

Relative Energies

The energetics involved in the electrocyclic ring opening of thiirane and oxirane via C–C cleavage are shown in Tables VII and VIII, respectively. The values in parentheses are those corrected with the corresponding zero-point vibrational energies (ZPVE). At the single-configuration SCF and single-reference CISD levels, only the energy differences between three structures, thiirane, thione methylide, and the conrotatory transition state (or the corresponding oxirane structures), can be compared.

Ring-Open Thiirane Isomerization Energy. The third column in Table VII shows the energy difference between thiirane and thione methylide. The ring form thiirane is the most stable structure on the potential energy hypersurface at all levels of theory employed, in agreement with the most stable form of the isovalent system oxirane.[18] At the DZP SCF level, the open isomer thione methylide is 55.3 kcal mol^{-1} above the ring isomer, and with the TZ2P basis set this endothermicity for the ring-opening reaction is reduced to 50.8 kcal mol^{-1}. The effect of electron correlation at the single-reference CISD level is to decrease the value by 4.0–4.5 kcal mol^{-1} from the equivalent SCF value, and addition of the correction for unlinked quadruple excitations causes a further reduction of 2.5–3.0 kcal mol^{-1}. The highest single-reference method used in this study, TZ2P SCF-CISD+Q, yields a value of 44.1 kcal mol^{-1}. The SCF-CISD method thus stabilizes the yet-to-be-observed open form relative to the ring isomer.

The electronic configuration of thiirane can essentially by described by a single configuration; however, two configurations are required to describe the diradical character of thione methylide. Thus two-configuration methods significantly reduce the ring-open energy difference. With the TCSCF method the endothermicity for ring opening is decreased to 41.4 kcal mol^{-1} with DZP and

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to 39.8 kcal mol^{-1} with the TZ2P basis set. The value at the TCSCF-CISD level shows a decrease of only 0.4 kcal mol^{-1} relative to TCSCF with the TZ2P basis set. Inclusion of the correction for unlinked quadruple excitations has only a small effect on the TCSCF-CISD relative energies since a significant contribution from quadrupole excitations is accounted for via the TCSCF reference. At the highest theoretical level employed, TZ2P TCSCF-CISD+Q, the ring-open energy difference is 39.1 kcal mol^{-1} (34.7 kcal mol^{-1} with the ZPVE correction).

The corresponding energy difference between oxirane and carbonyl ylide is predicted to be 67.3 kcal mol^{-1} at SCF and 43.0 kcal mol^{-1} at TCSCF levels of theory with the DZP basis set. The oxirane energy difference is greater than that for thiirane with SCF and SCF-CISD methods. This is because replacing sulfur with oxygen leads to a lowering of the orbital energies involving these atoms and the ring isomer is stabilized more than the open structure. The orbital energies of the oxirane ring are lowered more than those of the open isomer, since the ring involves two oxygen lone pair orbitals, while the open structure involves just one such orbital. At the TCSCF level the oxirane ring-open energy difference is reduced more, compared to SCF, than the thiirane energy difference due to the greater diradical character, and thus stability of the carbonyl ylide compared to that of thione methylide. Therefore, the oxirane and thiirane ring-opening isomerization energies are similar in magnitude with the TCSCF method and, for the same reason, with the TCSCF-CISD method.

Conrotatory and Disrotatory Barriers for Thiirane Ring Opening. The activation energy for the conrotatory ring-opening process, reported in column 4 of Table VII, has been determined with both single-reference and two-reference methods; however, the disrotatory potential barrier, reported in column 5, has been predicted with the two-reference methods only. The variation in the conrotatory barrier height is similar to that for the thiirane–thione methylide relative energy at the different levels of sophistication. The DZP SCF classical conrotatory barrier height, 78.1 kcal mol^{-1}, is reduced with an increase of basis set size and inclusion of electron correlation. The TZ2P SCF-CISD value 67.5 kcal mol^{-1} is lowered to 62.5 kcal mol^{-1} with addition of the Davidson correction, since higher order excitations are more important at the transition-state geometry.

The two-configuration methods significantly stabilize the conrotatory transition state relative to thiirane and thione methylide. At the TZ2P TCSCF level, the conrotatory barrier for ring opening is 50.1 kcal mol^{-1}. This is probably an underestimate due to the large weight of the second configuration in the TCSCF wave function for the conrotatory stationary point. The barrier to conrotation is increased to 55.0 kcal mol^{-1} on inclusion of the dynamical correlation at the TZ2P TCSCF-CISD level, and addition of the correction for unlinked quadruple excitations yields a value of 55.4 kcal mol^{-1} (51.3 kcal mol^{-1} with the ZPVE correction).

The variation of the disrotatory barrier height with theoretical level with use of the two-configuration methods follows similar trends as for the conrotatory barrier height. The TZ2P TCSCF method yields a classical disrotatory barrier height of 62.4 kcal mol^{-1} which is increased to 70.2 kcal mol^{-1} on inclusion of the dynamical correlations at the TCSCF-CISD level. Addition of the Davidson correction yields a value of 71.0 kcal mol^{-1} (64.5 kcal mol^{-1} with the ZPVE correction).

The classical conrotatory barrier height for oxirane ring opening is predicted to be 85.9 kcal mol^{-1} at DZP SCF and 50.3 kcal mol^{-1} at DZP TCSCF levels of theory. Compared to the corresponding thiirane barrier height, this energy difference follows similar trends as for the ring-open energy difference discussed above. The oxirane conrotatory barrier height is above that for thiirane with SCF and SCF-CISD methods; however, the TCSCF and TCSCF-CISD conrotatory barrier heights for oxirane and thiirane are close in magnitude.

As expected, the disrotatory potential barrier is above the conrotatory barrier as reported in column 6 of Table VII. The energy difference between the two pathways is 11.7 kcal mol^{-1} at the DZP TCSCF level which is increased to 14.8 kcal mol^{-1} with the DZP TCSCF-CISD+Q method. With the TZ2P basis set the TCSCF energy difference is 12.3 kcal mol^{-1} and at the highest theoretical level employed in this work, TZ2P TCSCF-CISD+Q, the value is increased to 15.6 kcal mol^{-1} (13.2 kcal mol^{-1} with the ZPVE correction). This is in accordance with the "forbidden" nature of the disrotatory process.

Conrotatory and Disrotatory Barriers for Thiirane Ring Closure. The variation of the conrotatory and disrotatory barrier heights for thiirane ring closure shown in columns 7 and 8 of Table VII can be explained by the weight of the second configuration in the wave function for the particular level of sophistication applied. The SCF barrier for conrotation, 25.0 kcal mol^{-1} with the TZ2P basis set, is decreased to 21.0 kcal mol^{-1} upon inclusion of electron correlation at the SCF-CISD level due to the greater weight of the second configuration in the transition-state CI wave function relative to the thione methylide CI wave function. For the same reason, the TZ2P SCF-CISD value is lowered to 18.4 kcal mol^{-1} on addition of the Davidson correction for unlinked quadruple excitations. The DZP TCSCF barrier for conrotatory ring closure is rather low, 8.6 kcal mol^{-1} with DZP and 10.3 kcal mol^{-1} with the TZ2P basis set. These low TCSCF values are compensated for by including the dynamical correlation. The conrotatory barrier at the TCSCF-CISD level is 13.1 kcal mol^{-1} with DZP and 15.6 kcal mol^{-1} with the TZ2P basis set, which are increased to 13.7 kcal mol^{-1} (14.1 kcal mol^{-1} with the ZPVE correction) and 16.3 kcal mol^{-1} (16.6), respectively, on inclusion of the correction for quadruple excitations. The disrotatory barrier for ring closure varies in a similar manner in conjunction with the two-reference methods. The value is increased with increase of the basis set size and upon inclusion of the dynamical correlation, remaining about 14.0–16.0 kcal mol^{-1} above the conrotatory barrier. The conrotatory barrier height for oxirane ring closure follows similar trends as for the corresponding thiirane value.

Discussion

We predict the best values for energy differences in this study to be given by the full TZ2P TCSCF-CISD+Q method since this includes the major dynamical and nondynamical electron correlation effects. However, the energetic predictions may not have converged with respect to basis set of theoretical level. Concentrating on the predictions with the two configuration methods, augmenting the TZ2P basis set with f functions, may change the TCSCF-CISD energy differences by about 1.5 kcal mol^{-1} and inclusion of higher order excitations from the TCSCF reference, TCSCF-CISDTQ, may alter the energy differences by a further 1.5 kcal mol^{-1}. The ZPVE may also introduce errors of about 1.0 kcal mol^{-1}. Thus the error bar in our predictions is about 4.0 kcal mol^{-1}. Unfortunately, at present it is not feasible to determine the CISDTQ wave function for a large CI space with a large basis set (TZ2P or better) for the molecular species involved in this study. Nevertheless, we would not expect the qualitative correctness of our theoretical predictions to be altered.

In general, the predicted harmonic vibrational frequencies of thione methylide and those of the conrotatory and disrotatory stationary points display a reasonably close correspondence. The a_2 symmetry CH_2 twisting mode of thione methylide becomes the reaction coordinate for the conrotatory transition state (349i cm^{-1} at TZ2P/DZP TCSCF), while the b_1 symmetry CH_2 twisting mode corresponds to disrotation for the disrotatory stationary point (613i cm^{-1} at TZ2P/DZP TCSCF).

The C–S stretching frequencies for the various structures show the transition from single to double C-S bonding along the ring-opening reaction coordinate. At the TZ2P/DZP TCSCF level of theory the symmetric and asymmetric C–S stretching frequencies are predicted as 647, 727 cm^{-1} for thiirane, 799, 819 cm^{-1} for disrotatory, 884, 916 cm^{-1} for conrotatory, and 849, 1074 cm^{-1} for thione methylide. This correlates with the decrease in C–S bond distance along the reaction coordinate. The CSC bending vibrational frequency is intuitively expected to decrease along the ring-opening coordinate as the C-C bond is broken. This is indeed observed, although the bending mode is heavily coupled to other modes in the various structures. At the TZ2P/DZP

TCSCF level, the CSC bending frequency is predicted to be 1179 cm^{-1} for thiirane (C–C stretch coupled to CH_2 wag), 356 cm^{-1} for disrotatory (coupled to CH_2 wag), 479 cm^{-1} for conrotatory (coupled to CH_2 wag), and 355 cm^{-1} for thione methylide. The CH_2 wagging vibrational frequencies also span a large range, from 1186, 1097 cm^{-1} for thiirane, 268, 257 cm^{-1} for disrotatory, 677, 615 cm^{-1} for conrotatory, and 390 cm^{-1} (the other wagging mode is not easily assigned due to heavy coupling between a_2 symmetry CH_2 twisting and wagging motions) for thione methylide at the TZ2P/DZP TCSCF level. The latter values for the disrotatory stationary point are rather low, reflecting the longer C–S bond length and larger CSC bond angle compared with the conrotatory stationary point. Again, the conrotatory and disrotatory stationary points resemble the open structure more than the tightly held ring structure.

The dipole moment predicted for the various structures lies along the C_2 axis or the C_s mirror plane, bisecting the C–C axis. In general, the dipole moment is expected to decrease as the CSC and HCS bond angles are increased, since the projection of the C–S and C–H bond moments onto the axis of the dipole moment is reduced with an increase of the bond angles. The CSC bond angle shows considerably more variation between the different structures than the HCS angle, and thus affects the magnitude of the dipole moment to a greater extent. The dipole moment predicted for the open isomer is significantly smaller in magnitude than that for the ring isomer due to an increased CSC bond angle. The dipole moments for the conrotatory and disrotatory stationary points are intermediate between those of the ring and open forms as a result of intermediate CSC bond angles.

The geometrical structures, physical properties, and relative energies of the four species predicted with the TZ2P/DZP basis set are very similar to those with the TZ2P basis set. The exception is the imaginary frequency for the open structure with the TZ2P/DZP TCSCF method which becomes real at the TZ2P TCSCF level, although the absolute frequency change is rather small (18i → 60 cm^{-1}).

Conclusions

The ring opening of thiirane is predicted to follow a conrotatory mechanism with an activation barrier of 51.3 ± 4.0 kcal mol^{-1} with the ZPVE correction, the top of the barrier corresponding to a genuine transition state. The stationary point for disrotatory motion is found to be higher in energy than the conrotatory transition state by 13.2 ± 4.0 kcal mol^{-1} with the ZPVE correction and is characterized as a stationary point with Hessian index 2. The most stable structure on the thiirane potential energy surface is the ring isomer which is predicted to lie below the open structure by 34.7 ± 4.0 kcal mol^{-1} with the ZPVE correction.

The quantitative predictions for the ring opening mechanisms of thiirane are related to the corresponding results for oxirane. Replacing the second row atom sulfur with oxygen with use of the single-configuration methods (SCF, SCF-CISD) appears to have the effect of stabilizing the ring structure relative to the open isomer and the conrotatory transition state, thus increasing the corresponding energy differences. With the two-configuration methods (TCSCF, TCSCF-CISD), however, the thiirane and oxirane energy differences are very similar.

The ring opening of unsubstituted thiirane, involving the second row atom sulfur, is predicted to follow the W–H rules in agreement with the first row system oxirane. This implies high stereoselectivity for the ring-opening reaction of thiirane. For the case of substituted thiiranes, steric interactions may significantly affect the stereochemistry. The current research, however, provides a detailed picture of the potential energy surface associated with unsubstituted thiirane.

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Solvent Effects. 1. The Mediation of Electrostatic Effects by Solvents

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Abstract: Solvent effects on conformational equilibria, rotational barriers, charge distributions, and molecular properties of ionic and neutral dipolar molecules have been investigated by high-level ab initio reaction field theory. The calculated solvent effects on the conformational equilibrium of 1,2-dichloroethane and furfural are in good agreement with experiments. The rotational barriers for the interconversion of the *Z* and *E* isomers of (2-nitrovinyl)amine in solution are also reasonably reproduced by reaction field theory. In the presence of a solvent reaction field, the geometry, energy, and charge distribution of methoxide anion are found to alter significantly. For the application of reaction field theory to neutral dipolar species, we have examined the solvent effect of two simple 1,3-dipoles, diazomethane and acetonitrile oxide. Dielectric medium appears to have significant different effects on the calculated electronic structure of these two compounds. In this paper, we also have formulated a correlated version of the Onsager reaction field method for studying solvent effects. In some cases, the use of correlated wave functions is found to produce more reliable results.

Introduction

Electrostatic effects are often important in the gas phase. Conformations with no dipole moment are usually preferred over those leading to dipoles; ions in which the charge is distributed over a large volume element are preferred over those in which the charge is more localized. If these species were placed in a solvent with a high dielectric constant, the electrostatic energies would be reduced and other factors may become more important.

There are some experimental data supporting such a hypothesis. The gauche form of 1,2-dichloroethane has a 1 kcal mol^{-1} higher energy than the trans form in the gas phase, but in solvents of high dielectric constant, the energies of the two rotamers become almost equal.[2] The C=C rotational barriers in "push-pull"

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