An ab Initio MO–SCF Study of Ethylene Episulfide, Episulfoxide, and Episulfone

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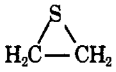
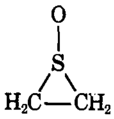
Abstract: A series of ab initio MO–SCF calculations have been performed on the three-membered ring compounds C_2H_4X, with X = S, SO, and SO_2. Optimal CC, CS, and SO distances have been determined. Calculated equilibrium geometries in all three molecules are in good agreement with available microwave data. The binding mechanism is discussed in terms of a donor–acceptor complex between ethylene and the fragment X. Orbital energies for X, in an appropriate valence-state configuration, have been calculated and correlated to the strength of the CC bond. The variations of these valence-state orbital energies, together with the corresponding variations of the CC overlap populations, can be used to understand the discontinuous variations of the CC and CS bond lengths in the series of molecules. This correlation was further illustrated by a calculation of acceptor and donor orbital energies for a number of other fragments X (CH_2, NH, O, SiH_2, PH, and CO).

1. Introduction

The series of three-membered heterocyclic ring systems: ethylene episulfide (I), ethylene episulfoxide (II), and ethylene episulfone (III), show some peculiar structural trends which make them interesting candidates for a theoretical investigation. Thus, while the bond distances in I and II are normal (cf. Table I), the episulfone III deviates from this trend by having a considerably shorter CS distance and a very long CC distance (Figure 1). In fact, the CC distance in III (1.59 Å) has been quoted to be the longest known.[3]


I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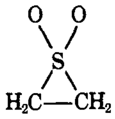
III

Recently Hoffmann et al.[4] have made an analysis of the irregularities in the structure of these molecules. Their analysis was based on extended Hückel calculations, and they concluded that the long CC bond in III is due to two main factors. First, the π^* level of the ethylene fragment is effectively populated through a low-lying orbital ($3b_2$, of π symmetry) in SO_2. Second, the 3d orbitals in SO_2 act as effective acceptors, thus depopulating the π orbital of C_2H_4. The combination of these two effects leads to a CS bond with considerable double-bond character and to a corresponding weakening of the CC bond.

However, the extended Hückel data were not able to explain the discontinuity in the structural changes in the series I and III. The CS bond is actually slightly *longer* in the episulfone (II) than in the episulfide (I), and the CC bond distance is only slightly longer in II than in I. Contrary to this result, the overlap populations obtained by Hoffmann et al. showed continuous changes along the series, the CS population increasing and the CC population decreasing.

In order to obtain a more detailed understanding of the electronic structure of these compounds, ab initio MO–SCF–LCAO calculations using fairly extended Gaussian basis sets have been performed.

Earlier theoretical studies of a series of sulfur compounds[5-7] have shown an almost linear relationship between sulfur 3d populations and the gross atomic charge on the sulfur atom. These calculations were made with the same basis set as has been used in the present work. We therefore have the possibility of comparing the influence of 3d orbitals in the strained three-membered ring systems with the situation in normal sulfur bonds. If, as has sometimes been suggested, 3d orbitals are more important in strained bonds, a deviation occurs from the linear relationship between the 3d populations and the atomic charge on sulfur.

A number of earlier theoretical studies have been made on I,[8-11] but to our knowledge no ab initio calculations have been reported for the molecules II and III.

2. Details of the Calculations

The calculations were performed with a medium-size contracted Gaussian basis set. The primitive set (S/10, 6, 1), (C, O/7, 3), and (H/4) was contracted to [S/6, 4, 1], [C, O/4, 2], and [H/2], with the obvious notation (X/N_s, N_p, N_d) for N_s s type, N_p p type, and N_d d type functions centered on atom X. Calculations were also made with the sulfur 3d functions deleted. The basis set employed was the same as had been used in earlier studies of a number of sulfur compounds ranging from H_2S to SF_6 and C_4H_4S.[12]

On each molecule several calculations were made with different CC, CS, and SO bond distances so as to minimize the energy with respect to the most important geometrical parameters. The CH bond distances, the HCH angles, the CSO angle (in II), and the OSO angle (in III) have been fixed at their experimental values in all calculations.

The calculations were performed with the program system MOLECULE.[13] The timing data for the generation of the super matrix elements for the three systems are as follows (central processing time on UNIVAC 1108): 11, 25, and 28 min, respectively, including 3d S functions; and 7, 15, and 16 min, respectively, without 3d S functions. The small difference in timing between II and III is due to the higher symmetry of the molecule III.

3. Results

Total energies are presented in Table II. For comparison the energies for C_2H_4 and SO_2, calculated with the same basis set,[6,14] are also given. Using these numbers, $C_2H_4SO_2$ is found to be 36 kcal/mol less stable than $C_2H_4 + SO_2$.

The total energy for C_2H_4S compares favorably to those reported in earlier studies of this molecule. Bonaccorsi et al.[10] reported a total energy of −474.5159 au, which was obtained using a minimal basis set of Slater type orbitals, including sulfur 3d functions. Clark[9] used a minimal uncontracted Gaussian basis set and obtained an energy of −456.0016 au, while Absar et al.,[11] with a slightly larger basis set, reported an energy of −474.8717 au. The lowest total energy obtained so far for this molecule has been reported by Strausz et al.[8] They used a somewhat larger set of

Table I. Experimental Geometries

Molecule	Distances, Å				Angle
	S–O	C–S	C–C	C–H	
$C_2H_4S^a$		1.819	1.492	1.078	∠ HCH = 116° 0' ∠ CSC = 65° 48' ∠ H_2CC = 151° 43'
$C_2H_4SO^b$	1.483	1.822	1.504	1.078	∠ OSC = 110° 1' ∠ CSC = 48° 46' ∠ HCH = 116° 0' ∠ H_2CC = 151° 43'
$C_2H_4SO_2{}^c$	1.439	1.731	1.590	1.078	∠ OSO = 121° 26' ∠ CSC = 54° 40' ∠ HCH = 116° 0' ∠ H_2CC = 151° 43'

[a] Reference 2a. [b] Reference 2b. [c] Reference 3.

Table II. Calculated Total Energies (au)

	C_2H_4S	C_2H_4SO	$C_2H_4SO_2$	$C_2H_4{}^a$	$SO_2{}^b$
Exptl geom no 3d S	−475.276	−549.871	−624.451	−77.946	−546.628
Exptl geom with 3d S	−475.319	−549.993	−624.677		−546.791
Opt geom no 3d S	−475.284	−549.898	−624.493		
Opt geom with 3d S	−475.319	−549.994	−624.678		

[a] Reference 14. [b] Reference 16.

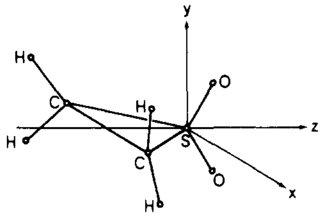

Figure 1. The structure and coordinate axes for $C_2H_4SO_2$. The direction of the axes is the same in all three molecules.

primitive Gaussian functions than has been used in the present work, but on the other hand a slightly smaller number of contracted functions. They reported a value of −475.4597 and −475.4206 au with and without 3d S functions, respectively. The greater accuracy compared to the present results is mainly due to a better description of the inner electron shells. The energy lowering due to the inclusion of 3d S functions in the basis set is the same in both calculations.

Calculated bond distances are presented in Table III. First we note the almost complete agreement between calculated (including 3d S functions) and observed bond distances. Such a close agreement is of course somewhat fortuitous, and should not be taken too seriously. However, experience with the present basis set has shown that values for bond distances within 0.00–0.02 Å from the experimental values are almost always obtained.

Second, we note that the variation of the distances is qualitatively the same whether 3d S functions are included or not. The effect of these functions on the CC bond is to lengthen it with 0.04 Å in all the three molecules, but with or without 3d S functions, the CC distance is almost the same in C_2H_4S and C_2H_4SO but is much longer in $C_2H_4SO_2$. Also for the CS bond, the qualitative behavior is independent of the 3d S functions. The distance is longer in C_2H_4SO than in C_2H_4S, but considerably shortened in $C_2H_4SO_2$. Here, one should, however, notice that the CS bond is considerably more weakened in II with respect to I if the 3d S functions are deleted from the basis set. The largest deviation from experiment occurs for the SO bond distance, the difference between measured and calculated (with 3d S functions) values being 0.02 and 0.01 Å for II and III, respectively.

Table III. Comparison between Calculated and Experimental Bond Distances (Å)

	C–C	C–S	S–O
	C_2H_4S		
No 3d S	1.454	1.951	
With 3d S	1.492	1.819	
Exptl	1.492	1.819	
	C_2H_4SO		
No 3d S	1.463	1.994	1.643
With 3d S	1.505	1.822	1.504
Exptl	1.504	1.822	1.483
	$C_2H_4SO_2$		
No 3d S	1.548	1.874	1.553
With 3d S	1.590	1.755	1.452
Exptl	1.590	1.731	1.439

The variation of the bond strengths is strongly connected with the variation of the overlap populations, as can be seen in Table IV. Overlap populations have been given for two geometries: the calculated minimum energy geometry and also with the CC and CS distances as in C_2H_4S for all three molecules. The variation of the overlap populations does not exactly mimic the distance variations. The CS bond population, as expected, first decreases (from I to II) and then increases (from II to III), but the CC bond population shows an almost linear decrease through the series. This anomaly partly explains why the analysis of Hoffmann et al., which was based on extended Hückel bond populations, could not fully explain the discontinuity in the structural charges. It should, however, be noticed that the extended Hückel bond populations for the CS bond also changes continuously from I to III, in contrast to the ab initio results. The CC overlap population becomes negative for the episulfone. This should not be taken too seriously, however. The negative populations from the antibonding orbitals are often larger in magnitude than the contributions from the corresponding bonding orbitals. In a weak bond composed of both bonding and antibonding orbitals, the overlap populations of the latter therefore often dominate.

The population analysis also shows a continuous decrease in the CH overlap populations and a corresponding increase in the positive charge on the hydrogen atoms (cf. Table V). It is also known experimentally that the introduction of a sulfone group into the ring highly activates the hydrogen atoms.[15]

Table IV. Overlap Populations at Minimum-Energy Geometries

	C–C	C–S	S–O	C–H
		C_2H_4S		
No 3d S	−0.001	0.306		0.724
With 3d S	0.278	0.353		0.756
		C_2H_4SO		
No 3d S	−0.115	0.069	0.313	0.688 0.686
With 3d S	0.111	0.203	0.721	0.707 0.702
a	0.073	0.204	0.775	0.707 0.703
		$C_2H_4SO_2$		
No 3d S	−0.766	−0.148	0.441	0.597
With 3d S	−0.039	0.232	0.969	0.673
a	−0.218	0.304	0.926	0.670

[a] Calculated with the same CC and CS distances as in C_2H_4S (with 3d S).

Table V. Total Populations and Atomic Charges (at Minimum-Energy Geometries)

	C_2H_4S		C_2H_4SO		$C_2H_4SO_2$	
	No 3d S	With 3d S	No 3d S	With 3d S	No 3d S	With 3d S
q(2s C)	1.425	1.353	1.437	1.373	1.475	1.383
q(2p C)	3.099	3.042	3.126	3.109	3.178	3.130
q(1s H)	0.744	0.763	0.718 0.734	0.734 0.760	0.700	0.730
q(3s S)	1.934	1.878	1.818	1.699	1.476	1.267
q(3p S)	4.043	4.139	3.486	3.322	3.043	2.907
q(3d S)		0.140		0.437		0.888
Q(C)	6.524	6.395	6.564	6.482	6.653	6.513
Q(H)	0.744	0.763	0.718 0.734	0.734 0.760	0.700	0.730
Q(S)	15.977	16.157	15.304	15.458	14.519	15.062
Q(O)			8.664	8.590	8.688	8.496

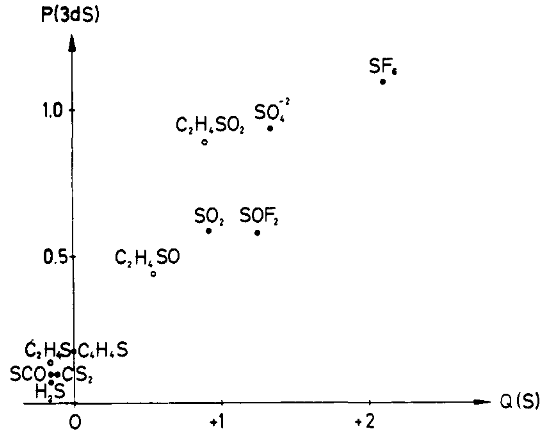

Figure 2. Sulfur 3d populations, *P*(3d S), versus the sulfur gross atomic charge, *Q*(S) for a number of sulfur-containing molecules. Data have been taken from the present work and also from ref 5, 6, and 7.

The effect of the 3d S orbitals is to increase both the CS and the CC overlap populations. Thus the danger in drawing definite conclusions about bond strengths from variations of the overlap populations is illustrated since the calculations have shown that the CC bond lengths increase when 3d S orbitals are included in the basis set. A detailed analysis of the effect of the 3d S orbitals on the electron density (using electron density difference maps not presented here) also shows that the electron density increases in the CS bond region while it decreases in the CC bond region.

The carbon atoms in ethylene have a gross atomic charge of −0.37 (calculated with the same basis set as used here).[14] This charge increases continuously in magnitude to −0.51 electron for the episulfone. The main cause of this increase is the increasing polarization of the CH bonds in the presence of the positively charged sulfur atom. Actually, there is very little charge migration from the ethylene part of the systems, indicating the covalent nature of the CS bonds. This effect can also be seen from the sulfur gross atomic charges. In C_2H_4S the sulfur atom has a slightly negative charge of −0.16 (exactly the same charge is found on the sulfur atom in H_2S).[6] The gross atomic charge on the sulfur atom in $C_2H_4SO_2$ is +0.94 electron, the same as in the SO_2 molecule (+0.92 with the same basis set).[6]

Figure 2 shows the relation between the sulfur 3d population, *P*(3d S), and the total sulfur population, *Q*(S), for a number of sulfur compounds. A larger positive charge on the sulfur atom results in more contracted 3d orbitals with lower energy, which more effectively can contribute to the bonding. It is interesting to see how the three molecules studied here fit into this picture. The sulfur atom has a slightly negative charge in C_2H_4S, which results in a small 3d population of the same magnitude as in H_2S and C_4H_4S. There is thus no indication that the strained bonds in C_2H_4S should lead to an increased 3d participation in the bonding mechanism.

The 3d S population in $C_2H_4SO_2$ is almost as large as in the sulfate ion, which can be understood if we view these compounds as formed from SO_2 plus C_2H_4 and $O_2{}^{2-}$, respectively. The electronegative oxygen atoms in SO_2 stabilize the 3d orbitals so that they effectively mix into the valence orbitals. The two orbitals $8a_1$ (the in-plane lone-pair orbital on sulfur) and $3b_2$ (the first virtual π orbital) in SO_2, which are used to form the additional bonds, therefore have an appreciable 3d population. Thus the total 3d population will increase when the two SC (or SO in $SO_4{}^{2-}$) bonds are formed.

Orbital energies are presented in Tables VI and VII. The values given correspond to the calculated minimum-energy geometries. A photoelectron spectrum has been reported for C_2H_4S.[20] The difference between calculated orbital energies and measured ionization energies is small for the outermost orbital and increases, as expected, with increasing ionization energy. The assignments made in ref 20 for the six lowest ionization energies are in complete agreement with the results of the present calculation.

4. Discussion

In order to get a deeper understanding of the CC bond-strength variations in the three-membered ring systems C_2H_4X, we construct the following model. Consider the interaction as taking place between the ethylene molecule in its ground state and the fragment X in an appropriately chosen valence state. We consider only one plane of symmetry, perpendicular to the CC bond and going through the third atom in the ring. The fragment X is supposed to be in a valence state with an empty orbital of a symmetry (symmetric with respect to the symmetry plane) and a doubly occupied orbital of b symmetry (antisymmetric with respect to the plane). The a orbital interacts with the doubly occupied π orbital of the ethylene fragment while the b orbital interacts with the empty π^* orbital (cf. Figure 3). For the sulfur atom the valence state configuration can be written as $(3p_x)^2(3p_z)^0$ with the coordinate system chosen as depicted in Figure 1 (only the occupation for the two orbitals of interest in the discussion is given). For simplicity we place the SO fragment perpendicular to the CCS plane (along the *y* axis) and obtain the valence configuration $(3\pi_x)^2(3\pi_z)^0$. The appropriate state for SO_2 corresponds to the doubly excited configuration $(8a_1)^0(3b_2)^2$. Notice that we consider the fragments S, SO, and SO_2 to be situated in an external field of C_s symmetry. The valence states there-

Table VI. Orbital Energies and Ionization Energies for C_2H_4S and C_2H_4 (eV)

Orbital	$-\epsilon$ No 3d S	$-\epsilon$ With 3d S	C_2H_4[b]	Exptl (C_2H_4S)[a]
$1a_1$ (1s S)	2502.57	2502.29		
$2a_1$ (1s C)	307.42	307.28	(1s C) 306.06	
$1b_2$ (1s C)	307.41	307.26	(1s C) 306.01	
$3a_1$ (2s S)	243.00	242.77		
$4a_1$ ($2p_z$ S)	180.43	180.24		
$2b_2$ ($2p_x$ S)	180.34	180.16		
$1b_1$ ($2p_y$ S)	180.28	180.10		
$5a_1$ (C–C, C–S)	31.85	31.37	σ(C–C) 28.24	
$3b_2$ (C–H)	23.33	23.16	(C–H) 21.48	
$6a_1$ (C–C, C–S)	22.82	22.64		
$2b_1$ (C–H)	18.64	18.39	(C–H) 17.45	16.69
$7a_1$ (C–C, C–S, C–H)	16.48	16.41	(C–H) 15.81	15.33
$1a_2$ (C–H)	15.00	14.83	(C–H) 13.60	13.59
$8a_1$ (π(C–C), C–S)	11.81	11.89	π(C–C) 10.14	11.72
$4b_2$ (π*(C–C), C–S)	11.66	11.54		11.32
$3b_1$ ($3p_y$ S)	9.53	9.31		9.05

[a] Vertical ionization energies obtained from a HeI photoelectron spectrum.[20] [b] From ref 14.

Table VII. Orbital Energies for C_2H_4SO and $C_2H_4SO_2$ (eV)

	C_2H_4SO			$C_2H_4SO_2$	
Orbital	No 3d S	With 3d S	Orbital	No 3d S	With 3d S
1a'	2505.39	2505.88	$1a_1$	2509.01	2509.17
2a'	558.62	558.51	$2a_1$	559.71	560.15
3a'	308.34	307.42	$1b_1$	559.71	560.15
1a"	308.32	307.42	$3a_1$	309.11	307.99
4a'	245.84	246.14	$1b_2$	309,11	307.99
5a'	183.26	183.59	$4a_1$	249.41	249.11
6a'	183.15	183.50	$2b_1$	186.85	186.66
2a"	183.15	183.50	$5a_1$	186.88	186.61
7a'	34.50	36.62	$2b_2$	186.74	186.55
8a'	31.18	31.43	$6a_1$	38.47	40.16
3a"	23.78	23.70	$3b_1$	35.13	37.01
9a'	23.59	22.77	$7a_1$	32.38	32.14
10a'	19.24	18.86	$3b_2$	25.01	24.82
11a'	17.31	17.28	$8a_1$	23.65	22.50
4a"	15.59	15.35	$4b_1$	19.92	19.37
5a"	13.88	14.83	$9a_1$	18.39	18.67
12a'	14.20	14.29	$4b_2$	17.06	17.71
13a'	12.63	13.82	$5b_1$	15.16	16.27
14a'	9.93	10.07	$1a_2$	16.60	16.14
6a"	9.66	9.99	$10a_1$	15.84	15.43
			$2a_2$	12.35	13.25
			$11a_1$	11.89	12.76
			$6b_1$	11.81	12.60
			$5b_2$	10.53	10.99

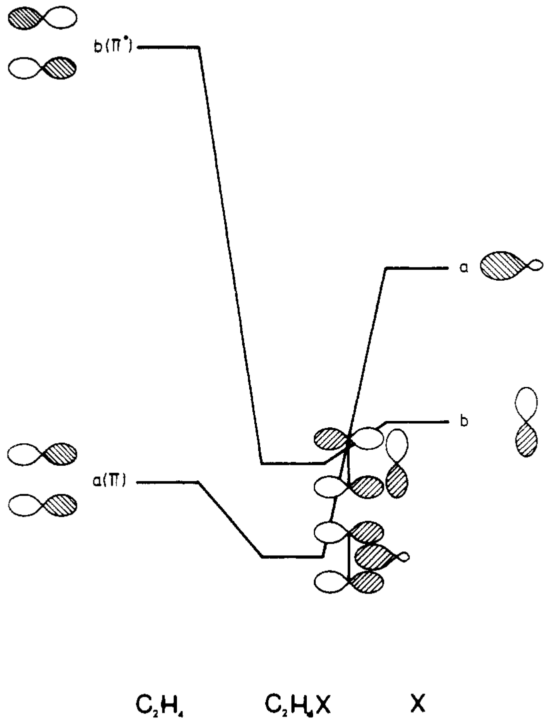

Figure 3. Interaction diagram for the formation of C_2H_4X from C_2H_4 in its ground state and the fragment X in a valence state with two electrons in an orbital of b symmetry.

fore corresponds to closed shell configurations and the 3p (3π) degeneracy in S (SO) is lifted.

The C_2H_4X system is in this picture treated as a donor–acceptor complex, with a donor orbital of symmetry b and an acceptor orbital of symmetry a on the fragment X. This interaction model is essentially the same as the one used by Hoffmann et al. in their discussion of the bonding mechanism,[4] but is here based on well-defined valence states of the interacting species, for which we can calculate the necessary orbital energies. This calculation was done using the same basis set as above.[16] The resulting orbital energies for the fragments S, SO, and SO_2 are shown in Figure 4 together with similar results for a number of other fragments X.

The CC bond in the ethylene fragment is weakened by two processes. Electrons are donated from the π orbital into the a orbital of the fragment X. The acceptor strength of the a orbital increases with *decreasing* orbital energy. There is also a reverse donation from the b orbital on X to the empty π* orbital on C_2H_4. The donator strength of the b orbital increases with *increasing* orbital energy.

The orbital energies shown in Figure 4 show that the donor strength of the b orbital increases continuously along the series X = S, SO, and SO_2. On the other hand, the acceptor strength of the a orbital first decreases (going from S to SO the orbital energy increases) and then increases again. This nicely explains the discontinuity in the CC bond length variations. The larger donor strength for X = SO, compared to X = S, is counterbalanced by a smaller acceptor strength, resulting in an almost unchanged CC distance. On the other hand, for X = SO_2 both the donor and the acceptor strengths are larger than for X = S, resulting in a considerable weaking of the CC bond.

A detailed analysis of the CC overlap population confirms this picture. This overlap population has in Figure 5 been divided into two parts: the binding populations from orbitals of symmetry a and the antibinding populations from orbitals of symmetry b (the latter is of course negative. For simplicity, the absolute value is given in the figure). We notice that the variation of these overlap popula-

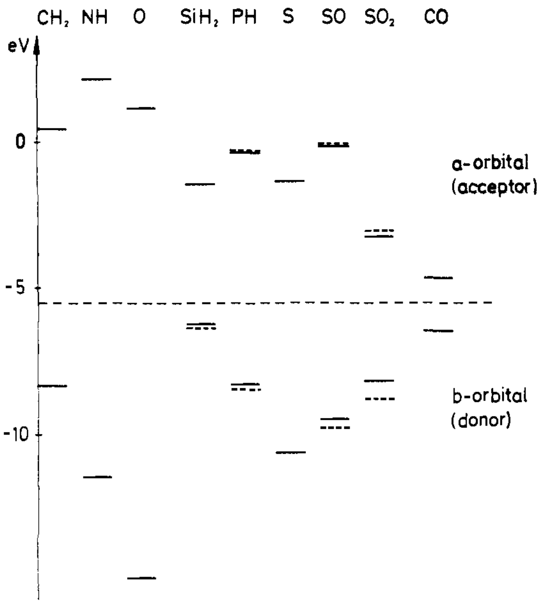

Figure 4. Orbital energies for the a and b orbitals in the fragments X in C_2H_4X. The orbital energies have been obtained from an SCF calculation on X in the valence state configuration $(b)^2(a)^0$. Dotted lines refer to calculations without 3d functions on the heavy atom in X.

tions closely parallels the variation of the orbital energies in Figure 4. While the population from b orbitals decreases continuously, the a orbital population first increases (from S to SO) and then decreases when going from SO to SO_2.

In order to further explore the present model we have also made calculations on the valence-state orbital energies for a number of other fragments X. The results of these calculations are also shown in Figure 4. For the series X = CH_2, NH, and O, the orbital-energy variations closely resemble the CC bond distance variations. The donor strength decreases continuously while the acceptor strength first increases and then decreases. Thus we would predict the longest bond distance for cyclopropane, and approximately the same distance for aziridine and oxirane. This conclusion is also confirmed experimentally, the CC distances being 1.525,[17] 1.480,[18] and 1.472 Å,[1] respectively. The same variations take place for the corresponding second-row compounds with X = SiH_2, PH, and S. The CC distances in phosphirane and thiirane are 1.502[20] and 1.492,[2a] respectively. If the compound $C_2H_4SiH_2$ existed, the present results would predict a CC distance much longer than in phosphirane. It is interesting to notice that various attempts to prepare a three-membered ring system with a silicon atom in the ring have failed.[21,22] Instead, silacyclopropanes have been found to undergo immediate rearrangement to vinylsilanes or larger cyclic organosilicon compounds.[21] Recently, however, a synthesis of some substituted 7-siladispiro[2.0.2.1]heptanes has been reported.[22] These compounds are believed to contain a silacyclopropane ring, even if the detailed structure is not yet known.

Calculations were finally also made for X = CO to see whether the model could predict the long CC distance (1.575 Å)[19] found in cyclopropanone. Since this molecule is planar, the corresponding valence state configuration for the CO fragment is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(2\pi_x)^2(5\sigma)^0$. The calculated values for the orbital energies for $2\pi_x$ (the b orbital) and 5σ (the a-orbital) are given in the last column of Figure 4. According to these results, one should expect the CC distance in cyclopropanone to be even longer than in ethylene episulfone. It should, however, be remembered that part of the explanation for the extraordinary long CC bond in the episulfone is the 3d-orbital participation. With

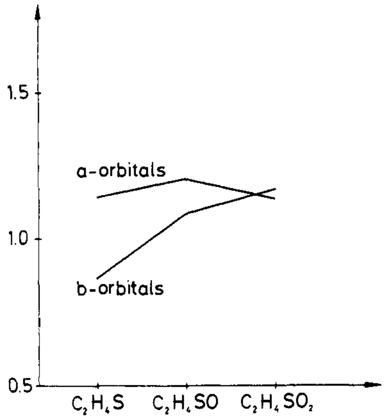

Figure 5. Contributions to the CC overlap populations from symmetric (a) and antisymmetric (b) orbitals. The absolute value of the negative contribution from the b orbitals is given.

these orbitals deleted from the basis set, the CC distance in $C_2H_4SO_2$ is predicted to be 1.548 Å, that is, considerably shorter than in cyclopropanone (cf. Table III).

5. Conclusions

The model used by Hoffmann et al. to discuss the bonding mechanism in ring-substituted cyclopropanes has in the present work been tested in a series of ab initio calculations. The conclusions to be drawn from the present results are in some respect different from those arrived at by Hoffmann et al. In agreement with their analysis, we find that two factors are important in order to explain the structural features in the molecules C_2H_4S, C_2H_4SO, and $C_2H_4SO_2$, namely the donor-acceptor strength of the fragment X (X being S, SO, and SO_2, respectively) and the 3d S orbital participation. Hoffmann et al. predicted, quite naturally, that the 3d S orbitals should have a larger influence on the structure of episulfone than on the two other molecules. The ab initio results also give a much larger 3d S population for this molecule than for the other two. This does not, however, lead to an increased effect on the CC and CS bond distances. Instead, the inclusion of 3d S functions in the basis set leads to almost the same increase of the CC distance, and to the same decrease of the CS distance, in all three molecules. Thus, while the explanation of the extraordinary long CC distance in episulfone must invoke 3d S functions, the variation of this distance in the series of molecules is not affected by the 3d S functions. Instead, this variation is explained by the variation of the donor-acceptor strength of the fragment X.

The present results do not give any evidence for an increased 3d S population in strained sulfur compounds. The 3d S population has actually been found to be almost the same in C_2H_4S and thiophene.

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Semiempirical Calculations of One-Bond Nitrogen-15–Hydrogen Coupling Constants and Inversion Barriers at Nitrogen[1]

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Abstract: The accuracy of several CNDO/2 methods is compared to INDO for the calculation of the Fermi-contact contribution to the one-bond ^{15}N–H coupling constant and the inversion barrier at nitrogen for molecules containing first-row atoms. The CNDO/2 methods use (i) the inversion-optimized parameter set of Rauk, Andose, Frick, Tang, and Mislow; (ii) two other inversion-optimized parameter sets (sets A and B), which parameterize on ammonia, and (iii) the standard Pople–Segal parameters. Parameters are reported for first-row atoms boron through fluorine. Comparisons of calculated vs. experimental barriers and coupling constants for the various parameter sets are made employing nonparametric statistical methods. From a comparison of the calculated and experimental coupling constants, it is concluded that results obtained from the CNDO/2 inversion-optimized parameter sets of Rauk et al. and set B are as accurate as INDO, while those obtained from the Pople–Segal parameters are not. Inversion barriers and their trends calculated from these inversion-optimized CNDO/2 parameters are as accurate as those obtained from INDO; a conclusion which disagrees with the work of Stevenson and Burkey. Suggestions are made for further experimental and theoretical work.

There is at present theoretical and experimental interest in the one-bond ^{15}N–H coupling constant, $^1J(^{15}N,H)$.[2] An objective of this paper is to compare the accuracy of semiempirical methods for the calculation of the Fermi-contact contribution to the coupling constant, which, in this case, is the principal contribution to the nuclear spin–spin interaction.[3]

Of the two commonly used semiempirical methods, CNDO/2[4,5] and INDO,[5,6] the former is apparently less effective because it ignores one-center exchange integrals, which are an important contribution to the coupling constant.[7] The suitability of the latter is at the cost of additional computer time.

Experimental evidence has indicated that the value of the one-bond ^{15}N–H coupling constant is markedly affected by the hybridization of the nitrogen orbitals.[8] In addition, due to the inflexibility of the CNDO/2 or INDO basis set, this hybridization is also an important ingredient in the inversion barrier at nitrogen; the barrier being largely governed by the energy associated with the hybridization changes that occur in the highest occupied molecular orbitals during inversion.[9]

Rauk, Andose, Frick, Tang, and Mislow[9] (RAFTM) have developed a revised set of CNDO/2 parameters which are specific for pyramidal inversion, and, by using these parameters, they have obtained good agreement between calculated and experimental barriers for some hundred structures. It is reasonable to hypothesize that these same parameters will assist in the calculation of $^1J(^{15}N,H)$ from CNDO/2, whenever nitrogen is a center of pyramidal inversion. This supposition is tested by calculations which are reported in the results and discussion section.

In the RAFTM paper, 1-methylaziridine is chosen as the molecule which is representative of inversion at nitrogen. However, for our purposes, which is the calculation of $^1J(^{15}N,H)$, a molecule with a directly bonded nitrogen and hydrogen may be more suitable. Thus the approach of RAFTM is repeated with ammonia as the representative molecule. Ammonia is chosen because it has both a well-studied inversion barrier and ^{15}N–H coupling constant, in addition to being economical to parameterize on.

In a recent paper Stevenson and Burkey[10] have studied inversion barriers at first-row elements using CNDO/2, INDO, and "CNDO–Mislow", the latter being the reparameterized CNDO/2 scheme of RAFTM. In a comparison of the three methods for inversion at nitrogen, they conclude that INDO is the most suitable method, closely followed by CNDO–Mislow. They infer this from calculations on six acyclic amines, where, for four of these, a tetrahedral ground state conformation is assumed. It is therefore important to determine if their conclusion is still valid for a wider variety of molecules, without assuming the value of the ground state out-of-plane angle.

In summary, the inversion barrier at nitrogen and the Fermi-contact contribution to the directly bonded ^{15}N–H coupling constant, $^1J(^{15}N,H)$, are calculated. For a variety