$K^+H_2CS(O)CH_3$ (1 equiv, 0.1–0.2 M in DMSO). The D_2O-phase neutral species were present in concentrations of 0.3 M (or 0.1 M as indicated); DSS (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt), an NMR reference, was present in concentrations of 0.05 M. Total NMR tube solution volumes were about 0.7 mL. The conjugate bases of the various nitrogen acids were generated by allowing, in the NMR tube, the respective acids to react with aqueous KOH (1 equiv, 2.5 M). All spectra were collected at 25 ± 1 °C.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the United States Army Research Office (Contract No. DAAL-03-90-G-0046), and the Southern Illinois University Materials Technology Center for support of this work.

Registry No. 1, 3232-84-6; 1 anion, 133476-04-7; 2, 34771-28-3; 2 anion, 133476-05-8; 3, 16312-79-1; 3 anion, 133476-06-9; 4, 5302-26-1; 4 anion, 133476-08-1; 5, 461-72-3; 5 anion, 133476-09-2; 6, 616-04-6; 6 anion, 133476-10-5; 7, 34771-26-1; 7 anion, 133476-07-0; 8, 6942-46-7; 8 anion, 135257-88-4; 9, 15988-11-1; 9 anion, 135257-89-5; 10, 34874-03-8; 10 anion, 135257-90-8; 11, 14500-23-3; 11 anion, 135283-77-1; 12, 28538-67-2; 12 anion, 135283-78-2; 13, 60-35-5; 13 anion, 31108-39-1; 14, 123-56-8; 14 anion, 28627-67-0; 15, 3148-73-0; 15 anion, 135257-91-9; 16, 29005-43-4; 16 anion, 135257-92-0; 17, 625-77-4; 17 anion, 93588-74-0; 18, 103-84-4; 1-methylhydrazine, 60-34-4; biuret, 108-19-0; 1,2-dimethylhydrazine, 540-73-8; diethyl carbonate, 105-58-8; 1-methyl-1-carbethoxyhydrazine, 760-81-6; methyl isocyanate, 624-83-9; 1-carbethoxy-2,4-dimethylsemicarbazine, 34771-20-5; 4-(4-methoxyphenyl)urazole, 13274-46-9; 4-(4-methylphenyl)urazole, 79491-05-7; 4-(3-chlorophenyl)urazole, 52039-91-5; methyl hydrazinecarboxylate, 6294-89-9; *p*-methoxyphenyl isocyanate, 5416-93-3; *p*-chlorophenyl isocyanate, 104-12-1; *m*-chlorophenyl isocyanate, 2909-38-8; *p*-methylphenyl isocyanate, 622-58-2; 4-(4-methoxyphenyl)semicarbazide, 62774-59-8; 4-(4-chlorophenyl)semicarbazide, 69194-89-4; 4-(3-chlorophenyl)semicarbazide, 51707-42-7; 4-(4-methylphenyl)semicarbazode, 62774-57-6; phenylhydrazine, 100-63-0; ethyl chloroformate, 541-41-3; 1-carbethoxy-2-phenylhydrazine, 6233-02-9; 1-carbethoxy-4-methyl-2-phenylsemicarbazide, 64739-43-1; diethyl dimethylmalonate, 1619-62-1; hydrazine, 302-01-2; barbituric acid, 67-52-7; uracil, 66-22-8; 4-(4-chlorophenyl)urazole, 52039-87-9.

Stability and Chemical Properties of Thiiranimine

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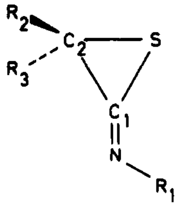
The stabilty and the molecular properties of thiiranimine are studied by using ab initio MO methods. Geometries are optimized at the HF/6-31G* and MP2/6-31G** levels while relative energies are estimated at the MP4/6-31G** level together with the zero-point energies. Our analysis points out that the interaction between the C=N moiety and the three-membered ring is responsible for several unusual properties of thiiranimine such as the high C=N stretching frequency, the relatively small ring strain (as compared with thiirane), and the large proton affinity at nitrogen. Our calculations also suggest that the first photoelectron band is due to an S ionization and that the first UV band arises essentially from an intraatomic sulfur transition. The fragmentation reaction is endothermic, but consideration of entropy terms modifies the picture significantly. The resulting free energies show that thiiranimine is quite stable towards fragmentation into hydrogen isocyanide plus thioformaldehyde in agreement with experiments on substituted thiiranimines. Finally, the regiochemistry of thiiranimine in cycloadditions is also discussed on the basis of the frontier orbitals.

Introduction

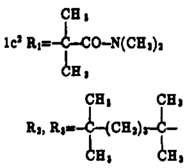
For 12 years now, thiiranimines (1), featuring three-membered rings with an exocyclic imine function, have been known as stable compounds.[1] The experimental geometry of some substituted forms (**1b**,[1] **1c**[2]) has been determined. In all cases the substituent R_1 on the nitrogen atom is in a cis position with respect to the sulfur atom.



1

1a $R_1=R_2=R_3=H$

1b[1] R_1=tosyl; $R_2=R_3$=phenyl



$$1c^2\ R_1 = -C(CH_3)_2-CO-N(CH_3)_2$$

$$R_2, R_3 = -C(CH_3)_2-(CH_2)_3-C(CH_3)_2-$$

As shown in a previous paper,[3] also the unsubstituted thiiranimine **1a** has been calculated with a small but definite cis preference. Other remarkable features of the geometry, such as the long C_2S bond and small bond angle at the sulfur atom, are well reproduced by ab initio Hartree–Fock calculations.[3] On the whole, the theoretical structure of **1a** more closely resembles **1c** than **1b**. This was attributed to the more perturbing nature of the tosyl group on the imine function in **1b** in comparison with the alkyl substitutent in **1c**.

In the previous paper the emphasis was mainly on the electronic structure and charge distribution in the prototype thiiranimine **1a**. In the present paper certain spectroscopic properties relevant to the vibrational and electronic spectra and several aspects of the thermochemical stability will be discussed in more detail. Finally, we will also consider the protonation as a model for electrophilic attack as well as the fragmentation of **1a** to isocyanide and thioformaldehyde. This latter reaction has been experi-

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[1] L'abbé, G.; Dekerk, J. P.; Declercq, J. P.; Germain, G.; Van Meerssche, M. *Angew. Chem.* **1978**, *90*, 207.

[2] Schaumann, E.; Nimmesgern, H.; Adiwidjaja, G. *Angew. Chem.* **1982**, *94*, 706.

[3] Vanquickenborne, L. G.; Vansweevelt, H.; Coussens, B.; Hajnal, M. R.; Delvaux, I.; Hendrickx, M. *J. Phys. Chem* **1990**, *94*, 1335.

Table I. Calculated and Experimental C=N Stretching Wavenumbers (cm^{-1})

	calculated[a]		
molecule	unscaled	scaled[b]	experimental
1a	2019	1742	**1b**: 1654–1673[6] **1c**: 1730[2]
$CH_2{=}NH$	1901	1640	1640,[7] 1638[8]
$CH_3CH{=}NH$	1922	1658	1651[8]
$HSCH{=}NH$	1873	1616	
$(CH_3)(SH)C{=}NH$	1899	1638	
$(CH_3)_2C{=}NH$	1925	1661	
$\overline{CH_2CH_2C}{=}NH$	2063	1780	

[a] At the HF/6-31G* level. [b] Employing a scaling factor 0.863, see text.

mentally shown[4] to be typical for oxiranimine, the oxygen analogue of thiiranimine,[4] but it has not been reported so far for the sulfur compound 1.

Method of Calculation

For the sake of simplicity, we considered only structures in which the imine hydrogen is situated in a cis configuration with respect to the sulfur atom, and, when there is no S group, in trans with respect to the group at the carbon atom C_2. All calculations were performed using the GAUSSIAN 86 set of programs.[5] The geometries were fully optimized at the Hartree–Fock (HF) level with the 6-31G* basis set and at the second-order Møller–Plesset perturbation theory (MP2) level with the 6-31G** basis set. Most of the structures were subjected to a vibrational analysis in order to characterize them. The harmonic vibrational wavenumbers and thermochemical properties were calculated at the HF/6-31G* level with corresponding equilibrium structures. The isodesmic reaction energies and proton affinities were determined using full fourth-order perturbation theory (MP4) with the 6-31G* basis set and HF/6-31G*-optimized geometries. The thermochemical parameters for the fragmentation reaction of **1a** were obtained at the MP4/6-31G** level and MP2/6-31G** geometries.

Results and Discussion

1. Wavenumbers of the C=N Stretching Mode.

The imine function attached to a three-membered ring is known to have a very high infrared CN stretching frequency.[6] This frequency is, however, shifted to lower wavenumber when a tosyl group is attached to the exocyclic nitrogen atom.[6] For the experimental values of thiiranimines, a similar trend has been observed. The C=N bond in **1c**, which has an alkyl substituent on the imine function,[2] vibrates at 1730 cm^{-1}, while **1b**, with a tosyl group, has a C=N stretching wavenumber lying between 1654 and 1670 cm^{-1}, depending on the solvent.[6] These observations confirm the classification of the tosyl group as the more perturbing substituent; the same result was already obtained on the basis of geometry considerations.[3] Therefore, we consider **1c** as the most appropriate species to compare with the theoretical values.

Some calculated CN stretching frequencies are listed in Table I. To obtain more insight into the factors influencing the vibrational frequency of the imine function, we include methylenamine ($H_2C{=}NH$) and some C-substituted forms, especially cyclopropanimine, which represents the closest parent molecule for **1a**. For the purpose of comparison, some experimental values are also given.

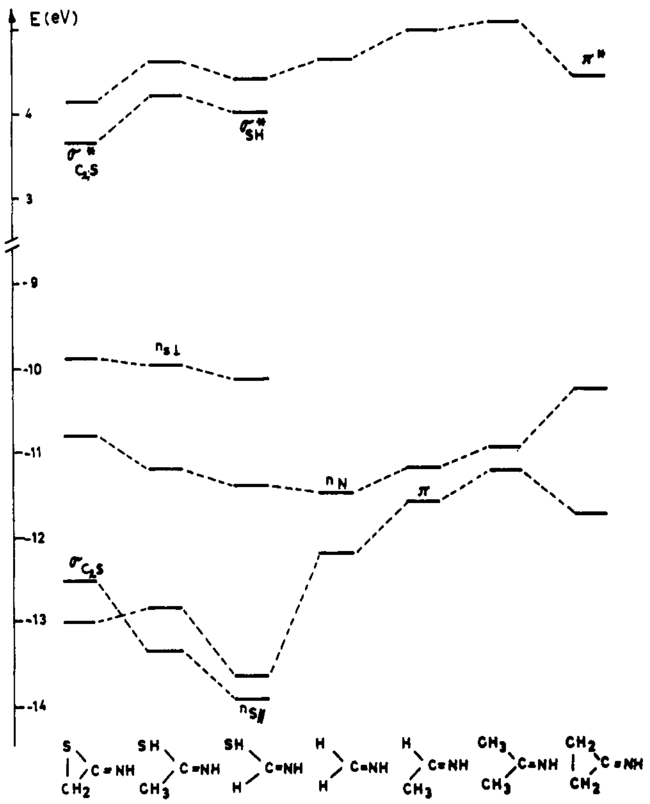

Figure 1. Molecular orbital energy levels for the various imines under consideration; related orbitals are connected; orbitals are labeled according to the most important contribution; the displayed MO energies were obtained from the HF/6-31G* wave function.

It is well known that wavenumbers calculated at the Hartree–Fock level tend to be about 10–15% too large.[7] Such an overestimation is not only due to the Hartree–Fock method as such, but also to the harmonic approximation employed in the calculations. To obtain an appropriate scaling factor for the C=N stretching mode, we used the ratio between the experimental and calculated values of methylenamine, which turns out to be 0.863. The scaled wavenumbers are also given in Table I.

The value for thiiranimine **1a** compares favorably with the experimental result for **1c**. The difference between the theoretical (1742 cm^{-1}) and experimental (1730 cm^{-1}) value is only 12 cm^{-1}. When a methyl substituent is attached to the carbon center of methylenamine, it causes a theoretical upward wavenumber shift of 18 cm^{-1} (Table I). The thiol group, on the other hand, decreases the C=N stretching wavenumber by a comparable amount (24 cm^{-1}). Accordingly, the resulting value for the thiol methyl C-substituted methylenamine turns out to be very close to the unsubstituted imine form, the difference being only 2 cm^{-1}. This suggests that the high wavenumber of the CN stretching mode in thiiranimine (102 and 104 cm^{-1} higher than that in $CH_2{=}NH$ and $CH_3(SH)C{=}NH$, respectively) arises from by the influence of the ring closure on the imine function.[6] This is confirmed by considering

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[4] Quast, H.; Meischner, G.; Seiferling, B. *Chem. Ber.* **1987**, *120*, 217, 225.

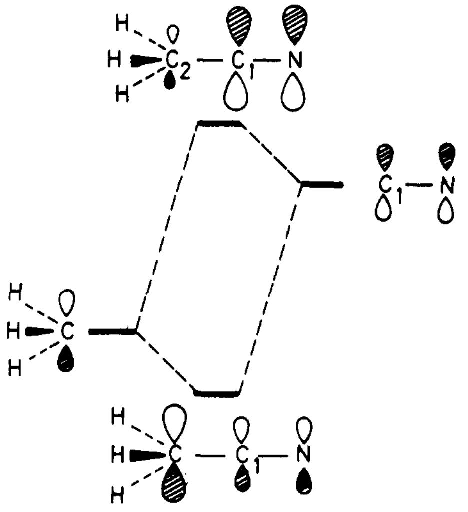
[5] Binkley, J. S.; Frisch, M.; Raghavachari, K.; Defrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Fox, D. J.; Head-Gordon, M.; Topiol, S.; Pople, J. A. GAUSSIAN 86, Release C, Carnegie Mellon University: Pittsburgh, PA, 1986.

[6] L'abbé, G.; Dekerk, J. P.; Martens, C.; Toppet, S. *J. Org. Chem.* **1980**, *45*, 4366.

[7] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[8] Bock, H.; Dammel., R. *Chem. Ber.* **1987**, *120*, 1961.

Scheme I



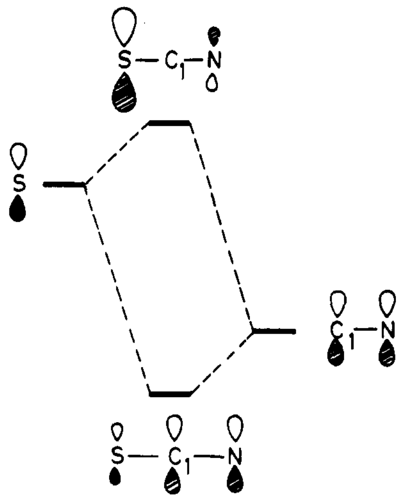
the CN stretching wavenumbers calculated for the ring cyclopropanimine (1780 cm^{-1}) and the open form dimethylmethylenamine (1661 cm^{-1}). Although the second methyl group has almost no effect compared with the single methyl-substituted methylenamine, an upfield shift of 119 cm^{-1} is again observed following ring closure (see Table I). Thus, results obtained for both cyclic molecules are similar and point toward a reinforcement of the strength of the C=N double bond by attaching it onto a three-membered ring.

2. MO Energy Levels. The MO energy levels for several imine molecules are depicted in the correlation diagram of Figure 1. As before we considered different substitutions of methylenamine. The MO's are labeled according to their most important contribution.

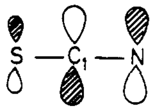
As seen in Figure 1, the π_{CN}-orbital is influenced rather thoroughly by the substitution; introduction of a methyl group raises its energy, whereas the thiol group has the opposite effect. This behavior can be rationalized from the total composition of the π-orbital. Indeed, the π-orbital of $CH_3CH{=}NH$ can be regarded as the antibonding combination of the π_{CN}-orbital of methylenamine and the parallel p_C orbital of the CH_3 group (Scheme I). Lower in energy (not shown in Figure 1) we find the corresponding bonding combination, which is composed predominantly of the p_c-methyl orbital, or rather of the CH_2 fragment orbital that goes with it. For the dimethylmethylenamine, the π-orbital is still higher in energy and is, as could be expected, an antibonding combination of the π_{CN}-orbital and the two CH_2 fragments. Similarly, the bonding combination (not shown in Figure 1) lies lower in energy than the corresponding orbital in the monosubstituted form.

The effect of the thiol group can also be explained by a similar consideration. Here, the interacting orbital represents a lone pair on the sulfur atom perpendicular to the molecular plane. Since the atomic S orbital can be expected to be higher in energy than the π_{CN}-orbital, the resulting MO with predominant π-character will be the bonding combination (see Scheme II), and we observe a decrease in π-orbital energy (Figure 1). As a consequence of this orbital mixing, the antibonding combination must be higher in energy. Indeed, in the sulfur-containing molecules, we see the appearance of a new HOMO, which consists essentially of a sulfur lone pair orbital perpendicular to the molecular plane (denoted as $n_{S\perp}$ in Figure 1). In the methyl thiol C-imine, the two effects tend to cancel, although the effect of the thiol group is slightly stronger than that of the methyl group. In marked contrast with the CN stretching frequencies, the closure of the ring has only a small stabilizing effect on the π-orbital energy, as well for thiiranimine as for cyclopropanimine.

Scheme II



Scheme III



The nitrogen lone pair of methylenamine is destabilized by all substituents considered and especially by the ring closure. Thus, ring closure induces two opposite effects on the C=N orbitals: stabilization of the π-orbital and destabilization of the lone pair, which result in an enlargement of the n-π energy gap.

In the virtual region, the evolution of the π^*_{CN}-orbital parallels that of the π_{CN}-orbital. Here also, the thiol group introduces a new orbital lying below the π^*_{CN}-orbital, the LUMO now being a σ^*_S-orbital. It is also worthwhile to take a closer look at the π^*-orbital of the sulfur-containing molecules. It consists of the antibonding combination of the lone pair on sulfur and the π^*_{CN}-component (see Scheme III). Together with the two above mentioned π and S lone pair orbitals (Scheme II), it completes the set of three allylic π-orbitals. This orbital structure suggests the possibility of resonance over the SC_1N moiety.

Based on the MO diagram it is clear that the frontier orbitals of thiiranimine are to a large extent determined by the sulfur atom. This should provide some insight into the photoelectron and electronic spectra of this class of molecules. The radical center in the thiiranimine radical cation is thus expected to be on S and this fact may lead to an eventual ring opening upon ionization. Similarly, the first UV absorption is likely to arise from an intraatomic sulfur transition. This preliminary conclusion should of course be confirmed by means of appropriate and more exact calculations of the relevant ionized and excited states.

On the basis of Figure 1, it is also possible to speculate on some of the reactivity patterns of thiiranimine. The HOMO energy is comparable to that of other conjugated π-systems (e.g. −10.5 eV for formamide[9]). Therefore, if a cycloaddition reaction with an unsaturated bond were to proceed in a concerted way, the most important interaction would normally be between the HOMO of thiiran-

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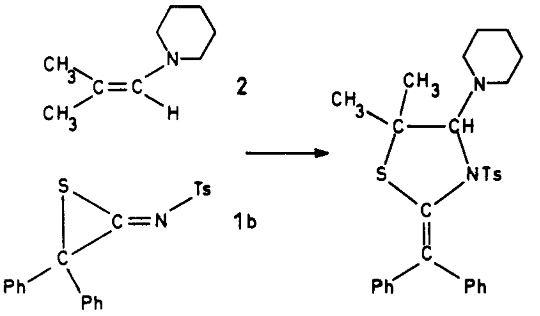
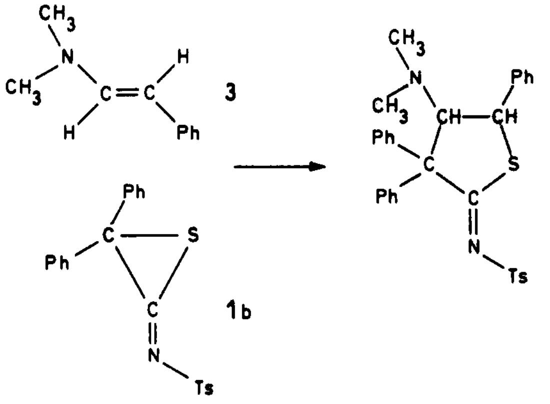
(9) Fleming, I. *Frontier Orbital Theory and Organic Chemical Reactions*; Wiley: New York, 1978.

imine and the LUMO of the partner. The addition would thus be expected to take place on the NC_1S system, where the HOMO has the largest components. In fact, this type of reactions has been observed experimentally,[6] as in the example of the addition of 1-piperidinoisobutene **2** with **1b**:



It has to be stressed, however, that a nonconcerted reaction path may also be probable in this particular case.

On the other hand, when the HOMO of the reaction partner raises in energy, the interaction of that orbital with the LUMO of thiiranimine ($\sigma^*_{C_2S}$) can become more favorable, implying an addition on the C_2S bond. This might be an explanation for the reaction between **1b** and *trans*-β-(dimethylamino)styrene **3**. The amino and the phenyl group on the double bond both tend to raise its π-HOMO energy[9] and indeed, a C_2S cycloaddition has been observed.[6]



Of course, these suggestions are only tentative, since they are based on unsubstituted thiiranimine and on qualitative considerations. Nevertheless, it seems that frontier orbital analysis, when more rigorously applied, can be a tool to rationalize and predict the chemical behavior of thiiranimines.

3. Ring Strain. We now analyze the stability of thiiranimine by using the isodesmic reaction technique. Isodesmic reactions[7] are, in general, reactions where the number of any kind of bond is conserved. Because there is no formal electron separation, the correlation effect is expected to have a rather small effect on the reaction energy. Therefore, the latter can be well predicted at the HF level. However, when considering molecules containing third-row elements, the above assumption may be no longer valid; the HF level may be insufficient for the calculation of isodesmic reaction energies (ref 7, p 306). Therefore, we have included electron correlation in the wave function by means of Møller–Plesset perturbation theory up to fourth order using the geometries optimized at the HF level.

In Scheme IV, eq a represents the bond separation reaction of **1a**. All formal bonds between the non-hydrogen atoms are separated from each other so as to generate the two heavy atom hydrides. The one heavy atom hydrides are added to maintain the stoichiometric balance. For comparison, the corresponding reaction for thiirane is given in eq b. The reaction energies are given in Table II. Both reaction energies are negative, indicating a stabilization on going to the separated products. This is typical for a strained molecule, the reaction energy being a measure of the ring strain. What is more surprising is that the value for thiiranimine is *less* negative than that for thiirane at all theoretical levels considered. By way of comparison, the isodesmic reaction energy for methylenecyclopropane is calculated to be, using a similar bond separation scheme, 21 kJ/mol *more* negative than that for cyclopropane at the HF/6-31G*//STO-3G of theory (ref 7, p 304).

Scheme IV

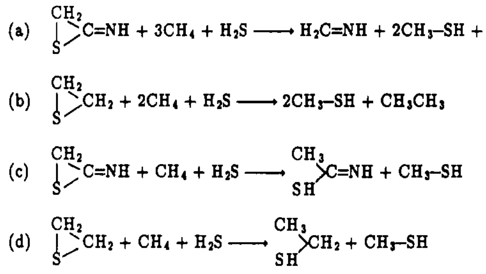


Table II. Isodesmic Reaction Energies (kJ/mol) Calculated Using the 6-31G* Basis Set[a]

reaction	energy[b] HF	MP2	MP3	MP4
a	−62	−14	−11	−20
b	−65	−45	−55	−49
c	−116	−95	−107	−98
d	−70	−58	−64	−60

[a] The reactions are listed in Scheme IV; the negative values of the different reaction energies correspond to a stabilization on going to the separated products. [b] At the indicated level with the geometry fully optimized at the HF/6-31G* level.

To account for this remarkable fact, we considered two other isodesmic reactions (Scheme IV, eqs c and d, Table II) in which the bonds are only partly separated and where the two reaction energies are almost entirely determined by the loss in ring strain. This time, the results are more in line with what can be expected intuitively. Therefore, in spite of the large intrinsic ring strain in thiiranimine, the unusual stability of this molecule is related to the interaction between the imine moiety and its neighbors. Apparently, a peculiar combination of a hyperconjugative effect with the methyl group and a conjugative effect with the sulfur lone pairs confers an extra stability to thiiranimine. Note that the same interaction is likely to be responsible for the extra stability of $CH_3(SH)C{=}NH$ and hence the large negative reaction energy of c. From a methodological view point, incorporation of electron correlation reduces systematically the reaction energies, especially for the reaction a; however, the energy order remains unchanged.

In summary, the intrinsic ring strain is definitely larger in thiiranimine than in thiirane (compare c and d), but the stabilizing interaction between the exocyclic imine function and the ring exceeds the destabilizing effect due to the ring strain (compare a and c).

4. Proton Affinities. The proton affinities of the imine nitrogen, listed in Table III, are obtained as the difference of the total energies of the neutral and protonated forms at the indicated level. Corrections for zero-point vibrational and thermal energies are not included. Also given are the changes of the CN and CS bond lengths upon

Table III. Proton Affinities[a] (PA, kJ/mol) and CN and CS Bond Length Changes (Δr, Å)

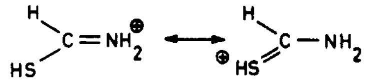
	PA[b]					
	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4/6-31G*	ΔCN[c]	ΔCS[c]
1a	941	920	932	928	0.038	−0.097
1a (on S)	912	851	866	860	*d*	*d*
CH_2=NH	932	906	914	910	0.013	
CH_3CH=NH	970	942	951	946	0.019	
SHCH=NH	946	929	936	933	0.037	−0.075
$(CH_3)(SH)C$=NH	972	950	959	955	0.040	−0.070

[a] On nitrogen, except otherwise indicated. [b] At the indicated level with the geometry fully optimized at the HF/6-31G* level. [c] At the HF/6-31G* level; positive values indicate an increase and negative values a shortening of the bond distance upon protonation. [d] Ring opening, see text.

protonation at the HF/6-31G*-level. These geometrical considerations can be of some help in the interpretation of the results.

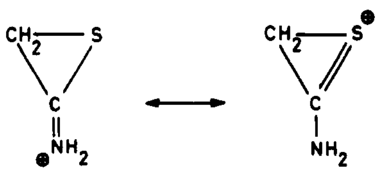
We note that the proton affinity ordering remains unchanged following incorporation of electron correlation. Again, the latter tends to reduce the calculated proton affinity. At the MP4/6-31G* level, the proton affinity at nitrogen of methylenamine amounts to 910 kJ/mol. Including a correction for zero-point energy of 41 kJ/mol,[10] the PA(CH_2=NH) is thus calculated to be 869 kJ/mol. This value compares favorably with the recent experimental value of 854 ± 8 kJ/mol determined by Fourier transform ion cyclotron resonance mass spectrometry.[11]

Table III shows that the substituents (CH_3 and SH) on methylenamine increase the proton affinity, the methyl group having the larger effect. For instance, the proton affinity increases by 36 kJ/mol (without zero-point correction, Table III). The corresponding change in experimental values is 41 kJ/mol (PA(CH_3CH=NH) being 895 ± 5 kJ/mol[11]). The inductive electron-donating capability of this group apparently makes the nitrogen more basic. On the other hand, a possible resonance of the sulfur lone pair with the imine group is much less pronounced due to the resulting weak π_{CS} bond, which accounts for its smaller effect on the proton affinity. This type of resonance, however, induces important geometrical changes following protonation. All molecules containing sulfur are in fact characterized by a nontrivial increase in the CN length and a shortening of the CS distance (Table III). The sulfur-protonated thioamide, form **4b**, is therefore likely to have a nonnegligible contribution into the protonated species.



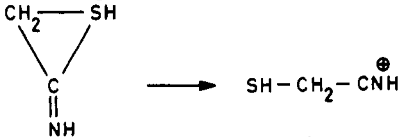
4a **4b**

Although thiiranimine contains a three-membered ring, its geometrical changes upon protonation are in agreement with a thioamide resonance form **5b**. This suggests that, in acidic medium, thiiranimine behaves rather as a thioamide, thereby making the C_1 atom the site of a subsequent nucleophilic attack.



5a **5b**

We have also considered the protonation at the sulfur atom of **1a**. Surprisingly, the ring opens by breaking the C_1S bond (and *not* the weaker C_2S bond), leading to a thiol–nitrilium cation **6**. Since the proton affinity at the



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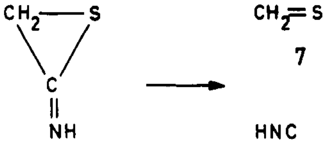
sulfur atom is much smaller than at the nitrogen atom (68 kJ/mol, Table III), it is likely that the protonation will actually take place on the imine group, without ring opening.

5. Fragmentation Reaction. In a study concerning the stability of thiiranimine **1a**, it is necessary to consider its fragmentation into thioformaldehyde **7** and hydrogen isocyanide **8**. To locate the transition structure **9** in Figure 2 for this reaction we started from *cis*-**1a** and increased the interfragment distance. The maximum along this path was used as starting structure for a transition structure optimization. The geometry obtained at the RHF/6-31G*-level is used as starting point for the MP2/6-31G** optimization. Our vibrational analysis was restricted to the uncorrelated level, but we can safely assume that the structure will remain a true transition state at higher levels as well.



7

1a **8**

We have also considered a structure with a short C_1C_2 bond length (1.40 Å) in search for a possible biradical intermediate or transition state. But, when optimizing toward a minimum we found the thiiranimine **1a** back and searching for a transition structure we arrived at a dissociation limit including the ketenimine and a sulfur atom, which is another mode of fragmentation of **1a**. This dissociation limit is found to lie higher in energy than the transition structure for thioformaldehyde loss. The geometrical parameters of the transition structure **9** connecting **1a** and the products **7** + **8** are depicted in Figure 2.

The transition structure is rather productlike: a nearly linear HNC fragment and planar H_2CS moiety. At the correlated level there is a geometrical shift to **1a**: a shorter interfragment distance, a larger C_1N and NH_1 bond, and a more bent isocyanide moiety.

Some energetic aspects of the fragmentation reaction are given in Table IV. We see that the inclusion of correlation to fourth-order Møller–Plesset perturbation theory at the

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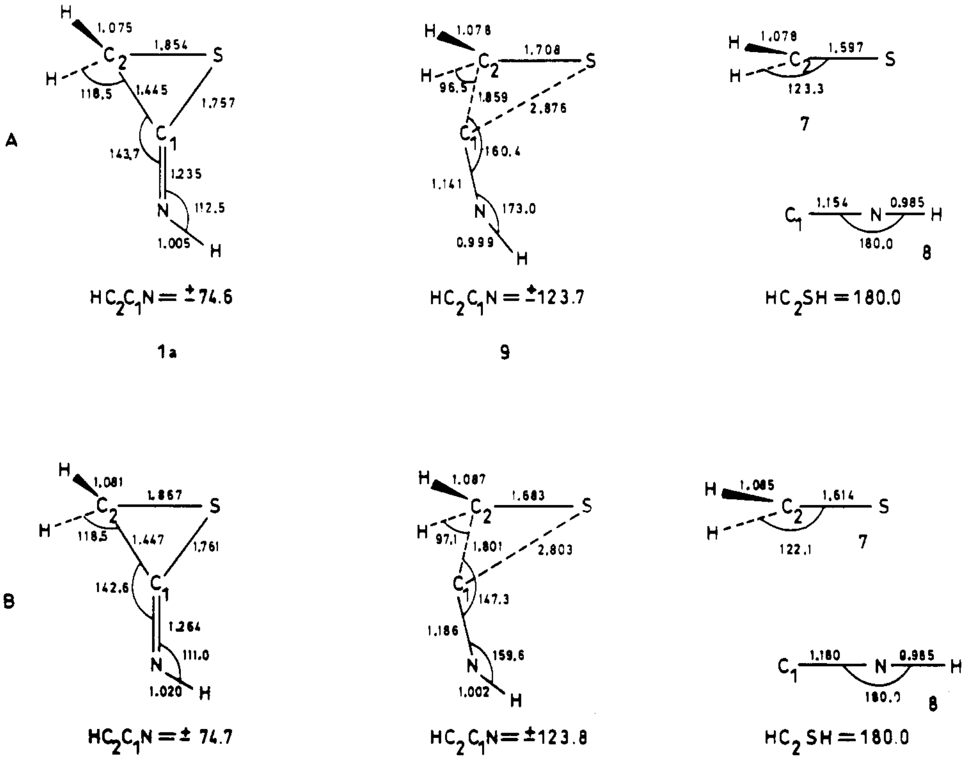

Figure 2. Optimized geometries for the stationary points along the fragmentation reaction at the HF/6-31G* (A) and MP2/6-31G** (B) levels, bond lengths are in angstroms bond angles in degrees.

Table IV. Total (Hartree) and Relative (in Parentheses, kJ/mol) Energies for the Stationary Points along the Fragmentation Path of 1a

method//geometry[a]	1a	TS (9)	products (7 + 8)
HF/6-31G*//HF/6-31G*	-529.38137 (0)	-529.32505 (148)	-529.36175 (51)
MP2/6-31G*//HF/6-31G*	-529.92177 (0)	-529.84668 (197)	-529.87762 (116)
MP4/6-31G*//HF/6-31G*	-529.97458 (0)	-529.90513 (182)	-529.93787 (96)
MP2/6-31G**//MP2/6-31G**	-529.94858 (0)	-529.87825 (185)	-529.90490 (115)
MP4/6-31G**//MP2/6-31G**	-530.00376 (0)	-529.93871 (171)	-529.96733 (96)

[a] Geometries are given in Figure 2.

HF geometry destabilizes the products as well as the transition structure relative to **1a**. Optimization at the correlated (MP2) level and using a slightly enhanced basis set has a similar effect, with a more explicit destabilization of the products. Single-point calculations including higher terms (MP4) again reduce the relative energy as compared with the MP2 values. The resulting values obtained at the MP4 level by employing either the HF or the MP2 geometries are close to each other, suggesting that inclusion of correlation in the optimization is less important for the relative energies than employ of higher Møller–Plesset terms.

Thermochemical parameters are listed in Table V. Inclusion of zero-point vibrational and thermal energy, leading to $\Delta H(298)$, induces a moderate decrease in the energy differences. Adding the entropy factor, on the other hand, has a dramatic effect on the products, as could be expected for a reaction going from one molecule to two fragments. The free energy of reaction is estimated at the highest level to be only 9 kJ/mol. The barriers for extraction and insertion remain however substantial, 146 and 137 kJ/mol, respectively. This is in line with the experimental fact that fragmentation of thiiranimine has not been observed.

Conclusions

The high CN stretching wavenumber in the IR spectrum of thiiranimine is especially due to the presence of the three-membered ring, which causes an important upfield shift. The interaction of the sulfur atom with the imine π-bond is shown to be responsible for several interesting effects. The first electronic transition is expected to correspond essentially to an intraatomic sulfur excitation, in contrast with methylenamine where one observes a n-π^* transition. Evaluation of a number of isodesmic reactions indicates that thiiranimine is at least as stable as thiirane, the unexpected stability of thiiranimine being due to the ring–imine interaction. Protonation can happen at two sites. On the sulfur atom it induces a ring opening at the C_1S bond; on the nitrogen, it leads to a thioamide-like structure. The nitrogen protonation is favored, and the corresponding proton affinity is larger than that of methylenamine. Frontier orbital considerations can partly explain the regioselectivity of the observed cycloaddition

Table V. Some Thermochemical Properties of the Fragmentation Reaction of 1a

property	activation 1a → TS 9a	reaction 1a → (7 + 8)
$\Delta H(0)$[a] (kJ/mol)	160	74
$\Delta H(298)$[b] (kJ/mol)	151	56
ΔS (J/mol.K)	20	16
$\Delta G(298)$ (kJ/mol)	146	9

[a] $\Delta H(0) = \Delta E^c - \Delta ZPE^d$. [b] Including thermal corrections. [c] At the MP4/6-31G**//MP2/6-31G** level (see Table IV). [d] The zero-point energies are as follows (kJ/mol): **1a**, 137; **9**, 126; **7**, 71; **8**, 45.

reactions. The ab initio results also confirm that thiiranimine is stable toward fragmentation (into an isocyanide plus a thioketon) in agreement with experimental findings for substituted thiiranimines.

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Registry No. 1a, 124604-18-8; (*Z*)-HSCH=NH, 135269-13-5; (*Z*)-Me(HS)C=NH, 135269-14-6; Me_2C=NH, 38697-07-3; (*E*)-MeCH=NH, 56003-81-7; H_2C=NH, 2053-29-4; cyclopropylimine, 54376-32-8.

Theoretical Studies of Transition Structures and Stereoselectivities of the [2,3]-Wittig Rearrangement of Sulfur Ylides

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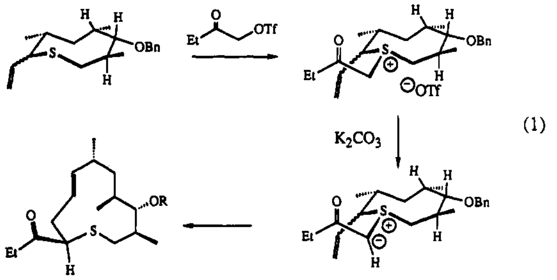
Transition structures of the [2,3]-Wittig rearrangements of allylsulfonium methylide and three substituted cases have been located with the 3-21G(*) and 6-31+G* basis sets. The transition structures have envelope conformations with the partially formed C–C bond nearly eclipsed with the partially broken C–S bond. The forming C–C bond is only formed to a small extent, corresponding to an early transition structure. The lone pair on sulfur prefers to be exo (away from the allyl fragment), primarily to minimize electrostatic repulsions. A formyl group at the anionic center is more stable in the endo configuration, while a methyl substituent prefers the exo configuration. The stereoselectivity of ring expansions of sulfur ylides can be rationalized by the combination of ring strain and the sulfur lone pair exo preference.

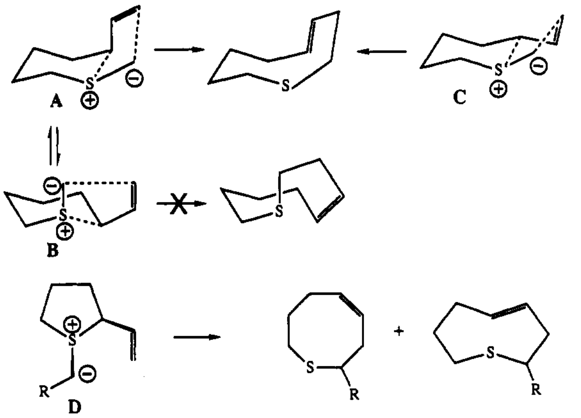
Introduction

The sulfur ylide mediated ring expansion involving the intramolecular [2,3]-Wittig rearrangement has been developed by Vedejs et al. as a useful method for medium-ring synthesis, as exemplified by eq 1.[1-3]



General stereoselectivity patterns have been established.[1,4,5] As summarized in Scheme I, six-membered reactants form nine-membered products with an (*E*)-alkene geometry, regardless of whether the reactant is cis (A or B) or trans (C).[4] The same stereoselectivity is observed for larger rings. With five-membered reactants, D, ring expansion occurs only when the two substituents are cis. Both *Z* and *E* products can be formed. The *Z* product is formed exclusively if the starting ylide is stabilized, while more *E* product is formed if the starting ylide is not stabilized. Several examples are given in the scheme. Stabilization is afforded by substitution of an electron-withdrawing group at the ylide anionic center.

Scheme I



R=H	6	1
R=Me	1	1.4
R=COPh	10	1
R=CO_2Et	exclusive	no

Fava et al. have qualitatively rationalized the stereoselectivities based on orbital overlap and ring-strain considerations.[4] Concerted transition states with envelope conformations were assumed to be involved in these reactions.[6,7] For example, conformer A is suggested to be more stable than B because A has good orbital overlap without geometrical distortion about the six-membered ring, while geometrical distortions are necessary for B to achieve good orbital overlap. The variation of stereoselectivity with R group in D was suggested to be the result

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