Chemistry of the Sulfur-Nitrogen Bond. X.[1] Barriers to Planar Inversion in *N*-(4,4′-Dimethylbenzophenylidene)arenesulfenamides and -selenenamides

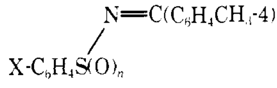
Sir:

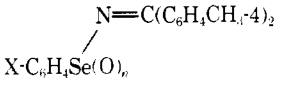
The importance of (p-d) π conjugation between sulfur and nitrogen in sulfenamides[2] and its effect on inversion barriers[3] in amines and phosphines have been the subject of considerable discussion.

Substituent effects on rotational barriers in sulfenamides[4] and inversion barriers in sulfenyl aziridines[5] have been attributed to both (p-d) π conjugation and negative hyperconjugation. However, a study of the rotational barriers in methyl *N*-arenesulfenyl-*N*-benzylurethanes concluded that the effect of (p-d) π bonding on the sulfenamide rotational barrier was insignificant.[6] A recent study of the transmission of electronic effects through the S-N bond suggested that sulfur was a much better transmitter of electronic effects when attached to an sp^2 rather than an sp^3 hybridized nitrogen.[1] Localized (p-d) π conjugation between sulfur and nitrogen was used to explain the mechanism of transmission. On the other hand, electronic effects have little effect on the barriers to inversion in *N*-isopropylideneareneesulfenamides[7] and -sulfinamides.[8] The importance of sulfur d orbitals in stabilizing α-thiocarbanions has been criticized.[9]

Inversion barriers in silylphosphines have been ascribed to (p-d) π conjugation[10] and negative hyperconjugation.[11] However, Mislow has shown that these barriers can adequately be accounted for on the basis of ligand electronegatively.[12] Ligand electronegatively also accounts for the low barrier in *N*-germylimine.[13]

In an effort to understand both the bonding between sulfur and nitrogen in sulfenamides and electronic effects on the barriers to stereomutation in imines we have prepared sulfenamides **1–3** and selenenamides **4–5** and measured their barriers to planar inversion.[14]


$X\text{-}C_6H_4S(O)_n\text{-}N{=}C(C_6H_4CH_3\text{-}4)_2$


$X\text{-}C_6H_4Se(O)_n\text{-}N{=}C(C_6H_4CH_3\text{-}4)_2$

1, $n = 0$
2, $n = 1$
3, $n = 2$

4, $n = 0$
5, $n = 1$

a, X = H
b, X = 4 = NO_2

Sulfenamides **1** and **3** were prepared by addition of the corresponding sulfenyl and sulfonyl chlorides to 1,1-di-*p*-tolymethenimine[15] in the presence of triethylamine. Oxidation of **1** with 1 equiv of MCPBA gave **2**.[16]

The selenamides were prepared in a similar manner from the corresponding seleneyl and seleninyl chlorides. All attempts to prepare **5b** by this method failed. Attempts to oxidize **4** to **5** with MCPBA also failed. These results are summarized in Table I.

Selenenamides **4** and **5** are the first examples of this class of compounds and are crystalline solids which decolorized on exposure to light. Compound **4** was stable when stored under N_2 in the dark whereas **5a** under similar conditions decomposed to an oil after several weeks.

The free energies of activation ($\Delta G^{\ddagger}$) were determined at the coalescence temperature of the diastereotopic methyl groups in **1–5** using the equation $K_c = 2.22\Delta\nu$[17] and the Eyring equation ($k = 1$). Within experimental error the energies of activation were found to be both concentration and solvent independent (Table I).

Table I. Properties of Sulfenamides and Selenenamides

Compound[a]	Mp, °C	Yield (%)	Solvent	$\Delta\nu$, Hz	K_c, s^{-1}	T_c, °C	$\Delta G^{\ddagger}$, kcal/mol
1a	78–79	64	*b*	2.3	5.1	58.0	18.4
			c	4.5	10.0	62.0	18.2
b	117 dec	42	*b*	2.5	5.6	63	18.6
			c	4.5	10.0	66	18.4
2a	118–189	55	*c*	5.0	11.1	−10	14.1
b	139–140	85	*c*	5.5	12.2	−27	13.1
3a	123–124	67	*c*	4.0	8.9	−32	13.0
b	140–142	32	*c*	3.8	8.3	−47	12.2
4a	65–66	88	*b*	4.0	8.9	101	20.5
			d	3.0	6.7	104	20.8
b	136–137	68	*b*	3.5	7.8	107	20.9
5a	125–129	30	*b*	4.0	8.9	100	20.4
			d	3.3	7.2	99	20.5

[a] All new compounds had satisfactory elemental analysis and/or mass spectra; ir and NMR spectra were consistent with their structures. [b] *o*-Dichlorobenzene. [c] Chloroform-*d*. [d] Chlorobenzene.

The barriers to planar inversion in phosphines[12] and imines[13] have been shown to correlate with the electronegativity of the ligand. The barriers increased as the electronegativity of the group attached to phosphorus or nitrogen increased. Since the electronegativity of sulfur in **1–3** increases in the order S < SO < SO_2 and the barriers decrease in the same order, ligand electronegativity cannot be a major factor determining the barriers in the sulfenamides.

The low barriers in **1–3** as compared to the corresponding oximes (18–13 vs. >39 kcal[18]) can be explained in terms of (p-d) π conjugation between sulfur and nitrogen. Calculations suggest that delocalization of a lone pair of electrons into an adjacent atom containing d orbitals will be at a maximum when the lone pair is in a p orbital[19] (the linear transition state). The lower barriers in **2–3** can be ascribed to more effective (p-d) π conjugation between sulfur and nitrogen. As the electronegativity of sulfur increases, the d orbitals contract, thus lowering their energy.[20]

The higher barriers observed for selenenamides **4** and **5** as compared to **1** and **2** support this argument, suggesting that (p-d) π conjugation is important in stabilizing of the transition state for stereomutation in **1–3**. The 4-d orbitals of selenium are of too high an energy to form effective p-d π bonds between nitrogen and selenium. Increasing the electronegativity of selenium (**5a**) has no effect on the barrier.

Neither the greater polarizability of selenium nor the longer Se-N bond length can account for the higher barriers for the selenenamides. Both these effects should lower the barriers in **4–5** compared to **1–3**. The electronegativity of selenium is also not a factor which can be used to explain the higher barriers in **4–5**, since sulfur and selenium have similar electronegativities.[21] Furthermore, increasing the electronegativity of selenium (**5a**) has no effect on the barriers in the selenenamides.

Negative hyperconjugation,[4,11] the transfer of electron density from the nitrogen lone pair into antibonding orbitals of sulfur, can be used to explain the difference in barriers between **1** and **4**, but is much less satisfying in explaining the difference between **1** and **3**. As the electronegativity of sulfur increases, the character of the antibonding orbitals change, and the capacity for overlap between nonbonding and antibonding orbitals decreases thus making the transition state for stereomutation less stable.

Steric effects could account for the observed trend in the barriers for **1–3** since the order of steric deceleration is expected to be SO_2 > SO > S. It is unlikely, however, that such effects are of major importance in determining the barriers in **1–3**. The difference between **1** and **2** is greater than between **2** and **3**. This is in accord with an electronic explanation.[22] A barrier of 20.3 kcal/mol has been reported for an *N-tert*-butyl ketimine of similar structure to **1–3**.[23] If steric factors were primarily responsible for the barriers in **1–3** the low barriers observed for **3** would not have been anticipated since a *tert*-butyl group is certainly larger than a sulfonyl group.

The barriers to planar inversion obtained for sulfenamides **1–3**, and selenenamides **4–5** clearly demonstrate that ligand electronegativity is unimportant in determining the barriers in these compounds. Although steric factors may account for a portion of the barriers in **1–3**, our results are best interpreted assuming that (p–d) π conjugation between sulfur and nitrogen is important in stabilizing the transition state to stereomutation.

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The Ground and Excited States of Trimethylenemethane

Sir:

Previous theoretical studies on trimethylenemethane diradical **1** have led to contradictory results. Most workers agree that for the planar geometry the lowest state is a triplet state; however, calculations of the lowest planar singlet state lead to energies of 21,[1] 68,[1] and 88 kcal/mol[2] from ab initio Hartree–Fock (HF) wave functions and 35 kcal/mol[3] from semiempirical Hartree–Fock wave functions. Part of the problem here is a special difficulty with spatial symmetry for the Hartree–Fock wave function of the lowest singlet state.[4] We report here the results of ab initio configuration interaction (CI) calculations based on generalized valence bond[5] (GVB) wave functions which eliminate this difficulty and provide a description of the other excited states, including the transition oscillator strengths.

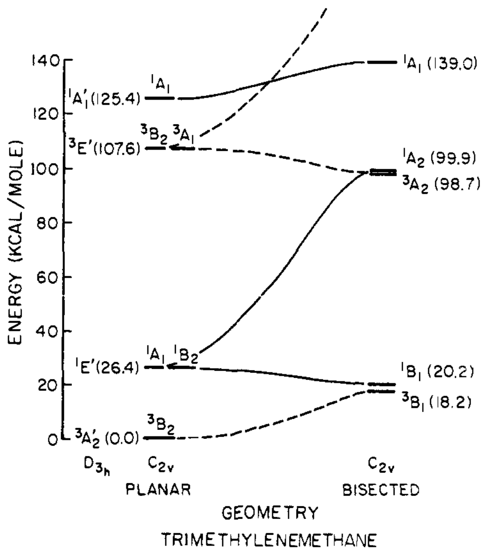
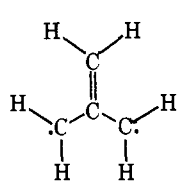


Figure 1

We carried out ab initio calculations on several excited states of both the planar (**1**) and the bisected (**2**) geometries[6] of trimethylenemethane using HF, GVB, and CI wave functions. For all calculations, Dunning's[7] "double zeta" contracted Gaussian basis set was used. In the GVB calculations, the orbitals corresponding to the CC and CH σ bonds and the carbon 1s core orbitals were not correlated. In the planar case the CI calculations utilized the full π-space but without excitations involving the GVB σ orbitals. The corresponding calculations were carried out for the bisected geometry. The excitation energies[8] from the CI calculations are listed in Figure 1.



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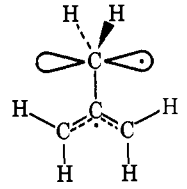

2

The first five states in Figure 1 for the planar geometry correspond to the two singlets and three triplets expected for a system with four singly-occupied orbitals (i.e., these are covalent states). The other state ($^1A_1$) is of ionic character. The calculated (vertical) ionization potential is 8.3 eV so that transitions to 3p Rydberg-like states are expected at ~5.6 eV (220 nm).

Carrying out a CI based on the GVB orbitals of the triplet state we encountered no spatial symmetry problems (correctly obtaining two degenerate components for the $^1E'$ state). Since we use the full self-consistent field equations for open-shell systems,[9] we have avoided the difficulties in-