

bonds are rather close to the pure quadruple bond model.
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Electronic Structures of Azolium Ions and Their Ylides. The Imidazolium, Oxazolium, and Thiazolium Ions

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Abstract: Semiempirical molecular orbital calculations of the imidazolium, oxazolium, and thiazolium ions and their conjugate bases are reported. The calculations predict that the carbon-2 proton is more acidic in the thiazolium ion than in the imidazolium ion, in good agreement with experimental evidence. Calculations were performed with and without extravalent 3d atomic orbitals on sulfur in order to establish the extent of their participation in resonance delocalization for the ground electronic state of the thiazolium ion and of the corresponding thiazolium ylide. These calculations indicate that the sulfur 3d orbitals are not necessary to describe either ground state. Polarization of the σ bonds is principally responsible for stabilizing the thiazolium ylide.

Introduction

The behavior of the thiazolium ion in thiamin (vitamin B₁) and its significance to the mechanism of action of thiamin pyrophosphate requiring enzymes^{2a} has been discussed by many investigators.^{2b,3-8} Deprotonation of carbon 2 of the five-membered ring with the resulting formation of an ylide is essential to the function of the thiazolium ion in enzymatic catalysis.

Rates of hydroxide-catalyzed proton exchange for hydrogens on carbon 2 of the imidazolium, oxazolium, and thiazolium ions have been determined and an unusually high exchange rate for the carbon-2 hydrogen of the thiazolium ring system has been noted.^{4,7} Deuterioxide abstracts the carbon-2 hydrogen of the thiazolium ion 3000 times faster than the carbon-2 hydrogen of the imidazolium ion.⁴ These relative rates are the reverse of that expected on the basis of the relative electronegativities of nitrogen and sulfur. Nitrogen, with the higher electronegativity, would be expected to stabilize the conjugate base of the imidazolium ion to a greater extent than sulfur would be expected to stabilize the conjugate base of the thiazolium ion.

Semiempirical molecular orbital calculations reported in this paper have been used to determine σ and π electronic structures and principal resonance forms for the imidazolium, oxazolium, and thiazolium ions and for the conjugate bases formed by deprotonation of the carbon 2 of these ions. One objective is to determine those factors that stabilize the conjugate base form of the thiazolium ion and thereby to gain insights into the function of thiamin pyrophosphate in enzymatic mechanism. The special ability of a sulfur atom to stabilize an adjacent negative charge has been noted;^{7,8} a comparison of the semiempirical molecular-orbital calculations performed on these three azolium ions should be able to define the electronic factors which are responsible for this special feature of sulfur.

Those structural features which stabilize the conjugate base form of these ions will also stabilize the transition state for removal of the carbon-2 hydrogen as a proton.⁴ A second objective of our calculations is to explain the order of the carbon-2 exchange rates: oxazolium > thiazolium > imidazolium.

Factors responsible for the relative stabilities of the transition states, and thus the relative exchange rates, may include both the σ and π electronic frameworks of the azolium ions and solvation energies. This study indicates that each of these factors may play a role in determining the relative exchange rates of these three azolium ions.

Theoretical Approach

The ARCANA semiempirical molecular orbital method, which was used for all calculations, has been described elsewhere.^{9,10} ARCANA is an iterative, charge self-consistent molecular orbital method which requires the following data for each valence atomic orbital: a Slater type orbital (STO) exponent for each n, l set, where n is an effective principal quantum number; an energy parameter, $1/R_i = \langle i | 1/r | i \rangle$, which characterizes how the STO is affected by isotropic and anisotropic charge distributions in a molecular environment; a neutral atom ionization potential for a doubly occupied atomic orbital.^{10,11,12}

The diagonal elements of the Hamiltonian matrix are computed according to the Cusachs approximation.⁹ The unique feature of the Cusachs approximation is the neighbor atom potential^{10,15} which contains all computed electron repulsion and nuclear attraction integrals. The off-diagonal elements of the Hamiltonian matrix are also calculated according to the Cusach approximation.^{16,17}

In this report, a comparison is presented between ground state one-electron properties of polar, heteronuclear ions and ylides. Iterative, semiempirical methods that contain two center terms in the Hamiltonian operator provide one-electron properties that are consistent with ab initio calculations. Thus, while an ab initio configuration interaction is preferable for potential energy surfaces involving chemical reactions, a semiempirical method, as noted above, gives a good accounting of ground state properties.

The ARCANA method has been applied to the calculation of ionization potentials,⁹ hydrogen bonding,¹⁸ and transition metals complexes.¹⁹ Calculations of bonding involving sulfur²⁰ and selenium²¹ have also been performed with this method.

Table I. Löwdin Net Atom Charges

	Imidazolium		Oxazolium		Thiazolium	
	Acid	Ylide	Acid	Ylide	Acid	Ylide
C ₂	0.243	-0.189	0.447	0.021	0.106	-0.344
H ₂	0.057		0.051		0.036	
N ₃	-0.051	-0.165	-0.062	-0.206	-0.047	-0.104
C ₄	0.093	0.085	0.099	0.107	0.123	0.151
C ₅	0.093	0.085	0.223	0.209	-0.083	0.098
X ₁	-0.051	-0.165	-0.219	-0.366	0.453	0.272

Calculated net atom charges and total overlap populations compare favorably with ab initio values.²²

Azolium Ion Geometries

The internal coordinates used for the azolium ions were literature values when possible. The thiazolium coordinates used were those of 2-(α -hydroxyethyl)-3,4-dimethylthiazolium bromide.²³ The imidazolium internal coordinates were derived from the crystal structure of histamine hydrochloride.²⁴ Final coordinates were the symmetrized values reflecting the C_{2v} symmetry. All carbon-hydrogen bond lengths were assumed to be 1.095 Å except C₂-H bond lengths, for which the literature value is 1.08 Å.²⁵ The oxazolium geometry is that of oxazole.²⁶ Vaughn et al.¹² have previously used idealized geometry for theoretical treatments of oxazolium ion.

Results

To discuss the bonding of the azolium ions and the conjugate bases, Löwdin net atom charges,⁴⁸ Q_{net} , and a Mulliken population analysis will be used. Net atom charges and σ - π bond densities have been included only for the atoms contained in the five-membered ring systems. Methyl substituents at the 3, 4, and 5 positions have been omitted from the analysis.

Table I contains Q_{net} values for each azolium ion and the corresponding conjugate base. Differences between charges for the azolium ion and the conjugate base reflect the abilities of nitrogen, oxygen, or sulfur adjacent to carbon 2 to absorb electron charge density and to stabilize the conjugate base. Charge polarization processes for the 1,3,4,5-tetramethylimidazolium, the 3,4,5-trimethyloxazolium ion, and the 3,3,5-trimethylthiazolium ion are very different as evidenced by Q_{net} values of Table I. In the following discussion, the charge patterns of the azolium ions of the conjugate bases and of "classical" ylide structures are compared.²⁷

Thiazolium Ion. The charge distribution of the 3,4,5-thiazolium ion is detailed in Table I. Mulliken σ and π bond electron densities are presented in Table II. The sulfur atom is positively charged in the thiazolium ion ($Q_{\text{net}} = 0.453$) while the carbon 2 is nearly neutral ($Q_{\text{net}} = 0.106$). Following deprotonation of the carbon 2, charge polarization is mostly confined to the N-C-S fragment of the ring. The sulfur takes up 0.181 units of electron density, but remains positive ($Q_{\text{net}} = 0.272$), while the carbon 2 becomes negative ($Q_{\text{net}} = -0.334$). The charge pattern of the deprotonated thiazolium ion is therefore that of a classical ylide.²⁷ Although depro-

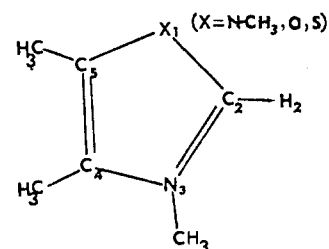


Figure 1.

tonation causes charge polarization, the basic charge pattern of the resulting ylide is like that of the parent thiazolium ion.

The π bonding for the five-membered thiazolium ring is extensively delocalized. The largest amount of π localization is in the C₄-C₅ bond with the N-CH-S fragment resembling a separate delocalized π network. Table II indicates that there is no one dominant resonance form for the thiazolium ion. The π electronic structure of the thiazolium system resulting from C-2 deprotonation is unique among the azolium ions investigated here. Although the removal of the carbon-2 hydrogen in the thiazolium ion cannot affect the π system because of symmetry considerations, the 2s and 2p orbitals on carbon 2 are destabilized in the ylide. Accordingly, a Mulliken population analysis shows that the carbon-2 p atomic orbital loses electron density after deprotonation. The values are 0.8907 for the thiazolium ion and 0.5088 for the ylide. The loss of 0.3819 units of electron density indicates that, although the π bond density for the N-CH-S and N-C-S fragments is nearly the same (Table II), the π bonds are polarized away from carbon 2 toward both the sulfur and the nitrogen atoms in the ylide. The sulfur 2p atomic orbital density increases by 0.1700 units of electron density in the ylide, while the nitrogen increases by 0.0905 units.

For the thiazolium ion the σ framework displays the greatest change upon deprotonation. The N₃-C₂ σ bond shows a loss of 0.201 units of electronic charge density upon ylide formation. This is a result of σ destabilization; the carbon-2 orbitals are all destabilized as both atomic centers, N₃ and C₂, have net negative charges (Table I). The electronic charge density lost from the N₃-C₂ bond is polarized away from the N₃-C₂ σ bond and contributes to the lone electron pair on carbon 2. The C₂-S σ bond is not greatly affected by the deprotonation process, showing a loss of only 0.024 units of electronic charge density. The σ C₂-S bond is polarized toward the sulfur, but not to the degree that the σ C₂-N₃ bond is polarized. The stability of the C₂-S bond in the thiazolium ylide is thus attributable to a polarization process involving the ability of sulfur to absorb electron density without significant destabilization of the 3s and 3p valence basis orbitals. The importance of sulfur 3d orbitals is discussed below.

Extravalent 3d Orbitals on Sulfur. The potential importance of sulfur 3d atomic orbitals in stabilizing the thiazolium ylide has been discussed by several groups.^{4,6-8,28,29} Table III contains the Mulliken σ and π bond populations for the thiazolium ion and the corresponding ylide where the sulfur valence basis

Table II. Mulliken Population Analysis

Bond	Imidazolium				Oxazolium				Thiazolium			
	Ion		Ylide		Ion		Ylide		Ion		Ylide	
	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π
C ₂ -X	0.717	0.267	0.515	0.271	0.6173	0.1964	0.3921	0.2060	0.632	0.249	0.608	0.237
C ₂ -N ₃	0.717	0.267	0.515	0.271	0.7341	0.3231	0.5310	0.3059	0.757	0.269	0.556	0.285
N ₃ -C ₄	0.705	0.179	0.705	0.141	0.6879	0.1350	0.6978	0.1049	0.718	0.173	0.720	0.136
C ₄ -C ₅	0.740	0.383	0.763	0.407	0.7743	0.4260	0.7898	0.4431	0.779	0.381	0.790	0.408
C ₅ -X	0.705	0.179	0.705	0.141	0.5649	0.1214	0.5447	0.0984	0.713	0.165	0.707	0.119

Table III

Bond	Thiazolium			Ionized thiazolium		
	Top ^b	π^a	σ	Top ^b	π^a	σ
S ₁ -C ₂	1.0230	0.2614 (0.0296) 0.1773	0.7320	0.7995	0.2521 (-0.0179) 0.1307	0.5653
S ₁ -C ₅	0.9416	(0.0346)	0.7297	0.7579	(-0.0109)	0.6381
C ₂ -N ₃	1.0093	0.2497	0.7596	0.8621	0.2840	0.5781
N ₃ -C ₄	0.9075	0.1811	0.7264	0.8666	0.1422	0.7244
C ₄ -C ₅	1.1404	0.3587	0.7817	1.2127	0.4039	0.8088

^a Value in parentheses is the p-d π overlap population. The total π bond population is the sum of both entries. ^b Top is the total overlap population between atoms.

have been augmented with sulfur 3d polarization Slater-type functions. The results of these calculations indicate that the degree of participation of the 3d orbitals is minimal. A comparison of Tables II and III shows that the bonding is not influenced by the sulfur 3d functions. The calculated destabilization energies⁴⁹ for carbon-2 deprotonation with and without extravalent 3d orbitals are very similar. The calculated change in destabilization energy is 15.00 kcal/mol. This is exaggerated owing to the single STO representation for the 3d functions. The sums of the 3d populations for the ion and the ylide are 0.2503 and 0.1883, respectively.⁵⁰

Imidazolium Ion. The 1,3,4,5-tetramethylimidazolium has a charge pattern characteristic of a symmetric azolium molecule. The two nitrogens have a net negative charge ($Q_{\text{net}} = -0.051$) with the positive charge of the azolium ion being dispersed to a large degree over the hydrogens of the *N*-methyl groups.⁵¹ The N-CH-N σ fragment of the imidazolium ion loses 0.201 units of electron density for each of the fragment CH-N bonds upon deprotonation of carbon 2 while the π bonding is only slightly perturbed. As in thiazolium ion, the π bond density remains nearly constant, though the bonds are more polar in the conjugate base than in the imidazolium ion. The carbon-2 P- π atomic orbital shows a 0.3504 loss of electron density upon deprotonation, while the nitrogen P- π atomic orbitals reflect an accompanying increase. The π bonds of the N-C-N fragment are thus polarized toward the nitrogens. Carbon 2 has a partially positive charge ($Q_{\text{net}} = +0.243$) in the imidazolium ion and a partially negative charge after deprotonation ($Q_{\text{net}} = -0.189$). The conjugate base again has ylide character.²⁷

Oxazolium Ion. The net atom charges of 3,4,5-trimethyloxazolium and its conjugate base (Table II) reveal some significant differences relative to the other azolium ion-conjugate base pairs. The carbon-2 net atom charge is more electropositive in the oxazolium ion ($Q_{\text{net}} = 0.447$). Following deprotonation, the carbon 2 absorbs considerable electron density, but remains positive ($Q_{\text{net}} = 0.021$). The charge patterns of the oxazolium ion and the oxazolium conjugate base are uncharacteristic of ylide charge patterns.²⁷ The net positive charge of carbon 2 may significantly influence the conjugate basis stability in polar solvents as charge controlled nucleophilic hydrolysis could result.³⁰ Furthermore, carbon 2 of the deprotonated oxazolium ion could not be expected to function as a nucleophile as does the thiazolium ylide. The charge pattern helps explain the unsuitability of the oxazolium structure to serve as a biological cofactor, an observation which has been previously analyzed by Duclos and Haake.³⁰

The gross Mulliken atomic orbital population for the lone pair was 1.5005. The C₂-H σ bond density (0.7772) is principally absorbed as the lone pair. The change in σ and π structure accompanying lone pair formation reflects destabilization of the O₁-C₂-N₃ fragment. There is a loss of 0.2156 units of electron density from the C₂-O₁ bond and a corresponding loss of 0.2203 units of electron density from the C₂-N₃ bond upon deprotonation. The decrease in bond density

is due primarily to σ destabilization (Table II). The C₂-O₁ and N₃-O₂ π bonds are polarized following deprotonation even though the total π bond density remains constant. Gross Mulliken atomic orbital populations for the oxazolium ion π atomic orbitals change upon deprotonation and reflect polarization away from carbon 2.

Discussion

Of the three azolium ions, the thiazolium ion undergoes the least amount of charge rearrangement upon carbon-2 deprotonation. The thiazolium conjugate base has the greatest amount of ylide character and the thiazolium ion ground state bears the strongest resemblance to its corresponding ylide. On the basis of a bonding and charge analysis, the thiazolium should experience the least amount of destabilization upon deprotonation and exchange at a faster rate than either of the other azolium ions. The relative destabilization energies (eV) calculated for the thiazolium and imidazolium are 1.000:1.098. The destabilization energies for the two azolium ions substantiate the bonding analysis trend and can explain the observation of Haake and co-workers⁴ that the carbon-2 hydrogen of the thiazolium ion exchanges 3000 times faster than that of the imidazolium ion.

Our analysis of the tabulated charges and bond densities (Tables I and II) indicates that molecular relaxation should occur and affect the oxazolium ion differently than the imidazolium and thiazolium ions. However, molecular relaxation has not been considered here. According to the tabulated charges and bond densities (Tables I and II) molecular relaxation should have opposite effects upon the stabilities of the oxazolium conjugate base and upon the stabilities of imidazolium and thiazolium ylides. The lack of an established reference structure for the oxazolium ion has prohibited calculation of an accurate destabilization energy.

It is possible that solvation effects could have an important, even a dominant, role in determining the relative exchange rates of the azolium ions. The calculated charges for the carbon-2 protons indicates that the oxazolium ion should hydrogen bond much more strongly than the other two azolium ions. This calculated difference between the azolium ion structures is consistent with the higher $J(^{13}\text{C}-^2\text{H})$ coupling values observed by Haake et al.⁴ for the oxazolium ion. Earlier studies concerning the interaction of ions and zwitterions have revealed that large stabilization energies may be involved.³¹ If the oxazolium ion forms a significantly more stable hydrogen bond, this could favor deprotonation of the oxazolium ion through the preexponential factor. Such a possibility is supported by kinetic studies for thiazolium ion carbon-2 deprotonation where the mechanism at high pH involves direct solvent or base abstraction of the proton.²⁹ The ability of the carbon-2 proton of these azolium ions to participate in hydrogen bonding with water is presently being investigated.

The calculated charge distributions of the azolium ions and the conjugate bases reported here are consistent with the experimental data concerning vitamin B₁. The stability of the

C-S bond, and ease of deprotonation of carbon 2, and the observed stability of the thiazolium conjugate base may all be related to the electropositive nature of the sulfur atom in the azolium ring. The ground state for the thiazolium ion has ylide character with the C₂-S bond being stabilized mainly by σ bond polarization.

The observation that the thiazolium sulfur remains positively charged following deprotonation explains the lack of severe destabilization. The charge distribution reported here is also consistent with thiamin crystal structures where the thiazolium sulfur to hydroxy oxygen separation of 2-(α -hydroxyethyl)-3,4-dimethylthiazolium bromide is 0.43 Å shorter than the sum of the van der Waals radii for sulfur and oxygen.²³ The electropositive nature of sulfur has been previously reported.^{21,32} The net positive charge of the thiazolium ion is an important factor in producing the high acidity of the thiazolium carbon-2 hydrogen.³⁴

Gallo and Sable^{42,43} have pointed out that the ¹³C chemical shifts for the thiazolium carbon atoms of thiamin do not correlate with previously calculated π charge densities.^{44,45} The Löwdin net atom charges calculated by the ARCANA method provide a better correlation with the experimentally determined ¹³C chemical shifts. Both C₂ and C₄ are calculated to have positive net charges and C₅ to have a net negative charge (Table I). This is consistent with the chemical shifts of C₂ and C₄ relative to C₅. The net positive charge at C₂, however, is calculated to be less than that at C₄, while the assigned ¹³C resonance for C₂ is at lower field than that for C₄.⁴² To the extent that a correlation between the ¹³C chemical shifts and the net atom charges is to be expected,⁴⁶ the ARCANA results reported here seem to be as successful at predicting the relative ¹³C chemical shifts of the thiazolium ring atoms as the CNDO/2 calculations carried out by Jordan.^{33,37}

Some analyses have stressed the potential importance of sulfur 3d orbitals in explaining the reactivity of thiazolium ion and of the thiamine pyrophosphate coenzyme structure.^{4,6-8,28,29} For example, the greater stability of the thiazolium ylide relative to the imidazolium ylide indicated by kinetic exchange rates has been attributed, at least in part, to "d- σ overlap-stabilization through interaction of a d orbital (or a mixed orbital with considerable d character) at sulfur with the σ orbital directed away from the ring at the 2 carbon".⁴

The contention that d-p π bonding might play a significant role has been supported by rate studies for H-D exchange in thiazolium ions and thiazoles.^{7,8} Molecular orbital calculation of the potential importance of the sulfur 3d orbitals in thiazolium acidity, however, have yielded conflicting results. Ab initio calculations for an α -sulfinyl carbanion led to the conclusion that there were no d-orbital contributions to the higher occupied molecular orbitals.³⁵ Ab initio calculations for the thiomethyl anion and its conjugate acid led Streitwieser and Williams to conclude that sulfur 3d orbitals stabilize the acid and base to the same degree, and that sulfur stabilized carbanions by polarization rather than by d-orbital conjugation.³⁶ A similar conclusion was drawn from ARCANA calculations on the structures of thione esters.²¹ On the other hand, Hückel studies of the thiamin and thiamin pyrophosphate structures by Jordan indicated a large 3d orbital participation.³⁷

As shown by the comparison of Tables II and III, the ARCANA calculations indicate that the sulfur 3d orbitals are not significantly involved in the bonding structure of the thiazolium ion or the corresponding ylide. Our conclusions in this regard are therefore in accord with the conclusion of ab initio calculations performed on simpler sulfur-containing anions.^{35,36}

Kinetic studies have clearly shown that the oxazolium ion deprotonates at a much faster rate than the thiazolium ion.⁴ However, according to these ARCANA calculations, the oxazolium conjugate base does not possess classical ylide char-

acter and would not function as the thiazolium ion in the vitamin. The magnitude of the carbon-2 positive charge in the oxazolium ion and its conjugate base should also make these structures susceptible to charge-controlled nucleophilic hydrolysis, an observation in agreement with the data from experimental observations of hydrolysis.^{30,34}

As previously mentioned, the charges at the carbon-2 hydrogens of the oxazolium ion favor hydrogen bond formation (Table I). This has been verified by hydrogen bonding calculations in which the magnitude of the hydrogen bond stabilization energy for the oxazolium ion exceeds that of the other azolium ions by approximately 3 kcal/mol.⁴⁷ The deprotonation of the oxazolium ring appears to proceed by a direct abstraction by hydroxide ion.⁴ The great stability of the oxazolium/H₂O hydrogen bond (-19 kcal/mol) is indicative of the role that may be played by a polar solvent. The relative rate of proton exchange of the three azolium ions investigated here is paralleled by the calculated relative hydrogen bonding stabilization energies, oxazolium > thiazolium > imidazolium.⁴⁷ Thus, in addition to those electronic features which stabilize the developing lone pair on carbon 2 in the transition states, the relative rates of proton exchange observed in this series of azolium ions may be influenced by the relative hydrogen bonding (solvation) energies.

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 (49) Destabilization energies are calculated as the difference in total energy (eV) between the azolium ion and conjugate base. Relative destabilization energies reflect the positive change in internal energy that accompanies deprotonation.
 (50) The average d population for each orbital was 0.0501 and 0.0377, respectively.
 (51) The average Q_{net} value for the *N*-methyl protons of the imidazolium is 0.0341, while the average *C*-methyl proton charge is 0.0435. The average Q_{net} of imidazole *N*-methyl protons is 0.0114.

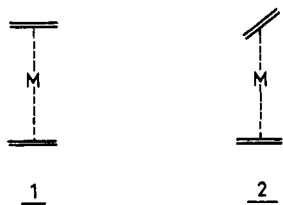
Stereochemistry of *trans*- $\text{MoX}_4(\text{C}_2\text{H}_4)_2$ and $\text{MoX}_4(\text{O}_2)_2$ Complexes

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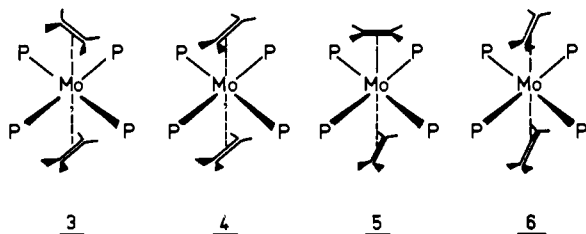
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Abstract: The relative energies of the different conformations for the complex $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ are discussed on the basis of ab initio LCAO-MO-SCF calculations of double- ζ quality at the level of the valence shells. The most stable conformation has the two ethylene ligands mutually perpendicular and eclipsing the Mo-P bonds. This is rationalized on the basis of the metal-ligand electronic interactions $4d-\pi^*$ and $4d-\pi$ and of the steric effects. The computed barrier of 16 kcal/mol for the rotation about the metal-olefin bond compares well with the reported experimental value of 15.3 kcal/mol. The relative stabilities of the various conformations are also discussed as a function of the number of d electrons and of the nature of the equatorial ligands (with CO replacing PH_3). Similar arguments are used to rationalize the stereochemistry of the diperoxomolybdenum-(VI) porphyrin.

Transition metal complexes with *trans* olefinic ligands may show a variety of structures, with the olefinic ligands either eclipsed (**1**) or staggered (**2**). Furthermore, if the metal



atom is hexacoordinated with a quasi-octahedral structure, the relative orientation of the axial olefinic ligands with respect to the equatorial ligands may be either eclipsed or staggered as in the four structures 3-6. We denote these structures *se* (for



staggered-eclipsed, **3**), *ee* (eclipsed-eclipsed, **4**), *ss* (**5**), and *es* (**6**). Osborn et al. assigned a *se* structure to the molecule *trans* $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$ (diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) on the basis of the ^1H and ^{31}P NMR spectra, with the ethylene ligands staggered but eclipsing the *trans* P-Mo-P vectors.¹ They reported an estimated barrier of 15.3 kcal/mol for the

rotation about the metal-olefin bond, but did not specify the nature of the rotation motion (one may consider either a process where the two ethylene ligands remain mutually staggered such as **3** \rightarrow **5** or a process where each ethylene ligand rotates independently, for instance, **3** \rightarrow **4**). A *trans* structure has been assigned to $\text{W}(\text{CO})_4(\text{C}_2\text{H}_4)_2$ on the basis of the infrared spectra,² but detailed information regarding the stereochemistry of the ethylene ligands is lacking to our knowledge. The matrix synthesis of $\text{Cu}(\text{C}_2\text{H}_4)_2$ and $\text{Ni}(\text{C}_2\text{H}_4)_2$ has been reported recently but their structure remains unknown.^{3,4} Rösch and Hoffmann addressed the question of the relative orientation of the two ethylene ligands in bis(ethylene)nickel(0).⁵ They found the D_{2d} structure **2** favored over the D_{2h} structure **1** by 1.5 kcal/mol on the basis of an extended Hückel calculation, a consequence of the fact that the stabilization produced by the two interactions of **7** is slightly greater than the stabilization associated with **8**. However, the lack of discrimination

