Acknowledgment. This research was supported by a grant from the National Science Foundation.

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Torsional Potentials of Methyl Rotors Attached to Polar Linkages

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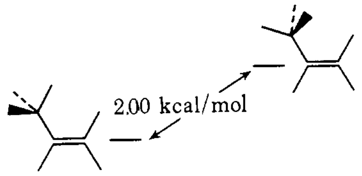
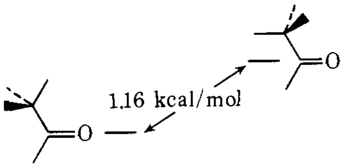
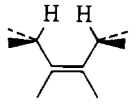
Abstract: The qualitative orbital arguments presented earlier as one possible rationalization for the observed conformational preference in propene are extended to the case of rotation of a methyl group about a polar double bond. The conclusions of this simple model, regarding variations in the torsional potential of the methyl group, are fully substantiated both by experimental data and by the results of quantitative ab initio molecular orbital calculations. Brief consideration is also given to variation in the barriers of methyl rotors in other molecular environments.

It is generally accepted that a methyl group attached to an unsaturated linkage will adopt a conformation in which one of its CH's eclipses the multiple bond. For example, propene is known to exist in such a methyl-eclipsed equilibrium conformation[2] with a barrier to rotation—through a methyl-staggered form—of some 2.0 kcal/mol.[3] Similarly, one of the C–H bonds in acetaldehyde prefers to eclipse the carbonyl linkage.[4a] In this instance, however, the potential hindering free rotation is considerably smaller than it is in propene.[4] Even the individual methyl rotors in a molecule like *cis*-2-butene prefer to be oriented so as each to eclipse the carbon–carbon double bond, although in doing so one would seem to maximize the steric repulsion between the pair of in-plane methyl hydrogens. Indeed, the barrier to rotation here (0.73 kcal/mol)[3a,5] is far smaller than that found for propene.







We,[6] and others,[7] have already pointed out possible explanations for this preference of *vinylic methyl groups* to eclipse unsaturated linkages. Consider, if you will, the consequences resulting from the interaction of the valence orbitals of a methyl rotor[8] and the π system of a double bond (Figure 1). Restricting ourselves only to the highest occupied and lowest vacant molecular orbitals on each of the two fragments, we see that four interactions result.[9] The first is between filled valence shells. The net repulsion which results—akin to that experienced between approaching rare gas atoms—is greater for the staggered rotamer than it is in the eclipsed. This is because overlap between the two fragments is most effective (and hence destabilization at a maximum) in the arrangement where the out-of-plane methyl hydrogens are positioned directly over the double bond, rather than being trans disposed. It should be emphasized that the diagram below and the ones which follow are constructed to represent individual interactions between specific orbitals on a methyl group and a polar unsaturated linkage. They should not be taken as representations of the total molecular orbitals which result. In this regard it is important to realize that the *energy of interaction* is proportional to the square of the overlap between fragments

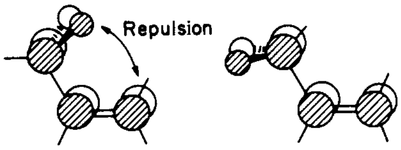
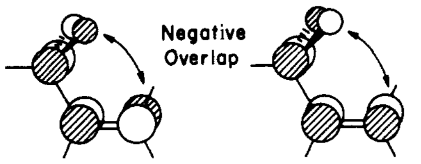


Table I. Theoretical Geometry and Energy Data for Unsaturated Compounds

Molecule	Eclipsed		Staggered	
	α[a] (deg)	E[b] (hartrees)	α[a] (deg)	E[b] (hartrees)
Propene	124.7	−116.90322	124.3	−116.90034
syn-Acetaldimine	120.6	−132.86482	120.5	−132.86261
anti-Acetaldimine	126.8	−132.86386	126.2	−132.86187
Acetaldehyde	123.8	−152.68555	123.6	−152.68409
1-Fluoroethyl cation	122.4	−176.91897	122.3	−176.91831
N-Methylformaldimine	115.1	−132.84888	114.4	−132.84541
trans-Methyldiazene	111.2	−148.78950	111.0	−148.78693
cis-Methyldiazene	117.3	−148.77609	116.4	−148.77284
Nitrosomethane	112.3	−168.56307	112.1	−168.56123

[a] Angle $H_3C{-}X{=}Y$ resulting from optimization at the minimal basis STO-3G level.[13] Except for the cases of propene and the 1-fluoroethyl cation where complete geometrical optimization has been performed on both eclipsed and staggered structures, this is the only parameter for which energy minimization has been carried out, all others constrained to take on standard model values.[12] The hydrogens bonded to the central carbon in acetaldimine and acetaldehyde have been constrained to bisect the angle made by the three heavy atoms. [b] 4-31G at optimum STO-3G geometry.

and not to the overlap itself. Hence, the relative signs of the orbital on the two fragments are unimportant. Interaction 2 (between π^* and the highest occupied π symmetry function on methyl) and 3 (between π and $\pi^*_{CH_3}$) both involve two electrons, and hence may be considered to lead to energetic stabilization. Here the conformer—eclipsed or staggered—in which the total overlap is the greater will be preferred. Again this is the eclipsed arrangement, in this instance because overlap between the out-of-plane methyl hydrogens and the π linkage—significant only in the staggered geometry—is of opposite sign from the main component—that between atoms which are already σ bonded—and hence subtracts from the total. The final interaction, between the lowest empty orbitals on each fragment is of no consequence energetically. If, however, either of these functions were to be populated—for instance by electronic excitation—the net effect of the interaction would be to favor the staggered over the eclipsed arrangement.[10]



The simple orbital picture should also be capable of providing qualitative information about the variation in torsional barriers for vinylic methyl groups as a function of detailed molecular environment, in particular, to changes in the nature of the unsaturated linkage. This is the subject of the present manuscript.

Results and Discussion

The conformational preferences and rotational barriers of many of the molecules we shall discuss in order to test our extensions of the qualitative orbital model have as yet to be determined experimentally. Thus, we have supplemented what data there are available with theoretical ab initio molecular orbital calculations. Here we shall employ the 4-31G extended Gaussian basis set,[11] the ability of which to describe rotational potentials has been adequately documented in earlier publications. Standard model bond lengths and bond angles have been employed,[12] except for the single angle involving the heavy atom skeleton. This has been optimized at the minimal basis STO-3G level[13] for both staggered and eclipsed conformations of the methyl group. All calculations have been carried out using the GAUSSIAN 70 series of computer programs.[14]

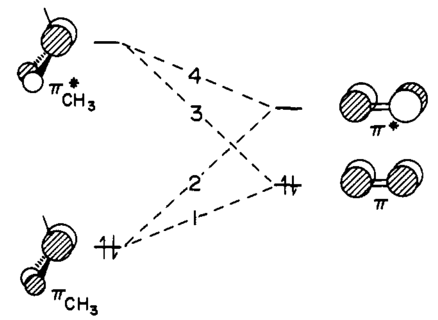
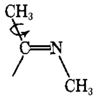


Figure 1. Interaction of the π system of a nonpolar double bond with the valence orbitals on a methyl group.

Table II. Barriers to Rotation of Vinylic Methyl Groups (kcal/mol)

Molecule	4-31G[a]	Exptl
Propene	1.81	2.00[b]
syn-Acetaldimine	1.39	(1.642[c])
anti-Acetaldimine	1.25	...
Acetaldehyde	0.92	1.16[d]
1-Fluoroethyl cation	0.41	...
N-Methylformaldimine	2.18	1.970,[e] (2.109[f])
trans-Methyldiazene	1.61	...
cis-Methyldiazene	2.04	...
Nitrosomethane	1.15	1.137[g]

[a] Theoretical energies taken from Table I. [b] Reference 3. [c] Value for C–C rotational barrier in i; ref 16.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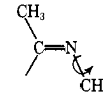

ii

[d] Reference 4. [e] Reference 15. [f] Value for C–N rotational barrier in ii; ref 16. [g] D. Coffey, Jr., C. O. Britt, and J. E. Boggs, *J. Chem., Phys.*, 49, 591 (1968).

The diagram in Figure 1 was explicitly constructed to represent interaction between the valence orbitals on a methyl group and those of a nonpolar double bond. If we assume that the energy spacings depicted in this figure were specifically adjusted for a carbon-carbon double bond (e.g., propene), we may then go on to consider what changes might be expected in the rotational potential due to replacement of the atoms involved in the unsaturated linkage by ones of lesser or greater electronegativity. If the nonpolarity of the unsaturated linkage is maintained, the only change which occurs is a lowering (or raising) of both π and π^* energy levels as the carbons are replaced by atoms of greater (lesser) electronegativity. In the case of methyldiazene, for example, movement of these two orbitals to lower energy would lead to an increase in interaction 2, and a furthering of the tendency of CH_3 to eclipse the double bond, but at the same time to a decrease in 3—that between the NN π linkage and the empty orbital on methyl—and hence a lessening of this preference. The gap between the two filled levels decreases on account of such an electronegativity perturbation, but because the magnitude of the four electron interaction is independent of energy separation this should be of little consequence. Thus, one is unable to draw a clear-cut prediction of the methyl rotational barrier relative to that in propene. Rather, all that might be concluded from the simple model is that any differences, one way or the other, should be small. This is apparently the case as our theoretical ab initio calculations attest (Table II). Whereas the rotational barrier in *trans*-methyldiazene is slightly smaller than that in propene (1.61 kcal/mol vs. 1.81) that in the cis isomer is somewhat larger (2.04 kcal/mol). One

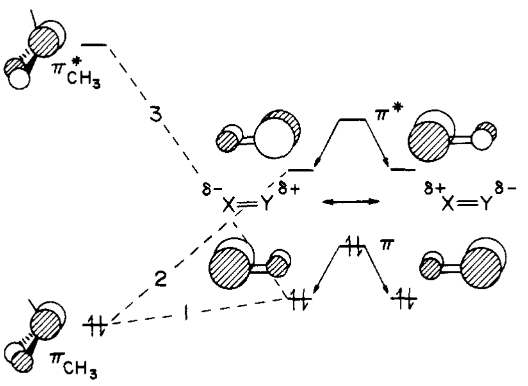
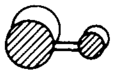
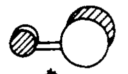


Figure 2. Interaction of the π system of a polar double bond with the valence orbitals on a methyl group. See text for discussion.

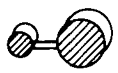
would anticipate a similar result for methyl rotation about a double bond composed of atoms less electronegative than carbon (silicon for example), though we have not carried out calculations to substantiate such a conclusion.



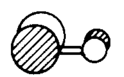
$\pi_{x=y}$



$\pi^*_{x=y}$

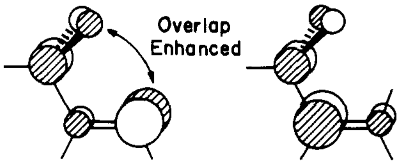


$\pi_{x=y}$

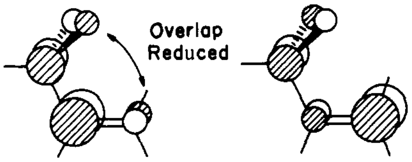


$\pi^*_{x=y}$

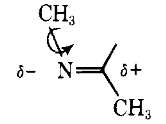
Let us now consider the more general situation of a methyl rotor attached to a polar double bond. In this instance not only do we have to contend with shifts in energy levels as a function of electronegativity but also with changes in the basic structure of the filled π and empty π^* double bond orbitals. Consider an unsaturated linkage X═Y. If X is the more electronegative atom, then the filled π orbital will be heavily localized here, and the empty π^* function mainly on Y. For the converse situation (Y more electronegative than X) the opposite pattern of localization will be observed. Figure 2 provides a composite representation of electronegativity and localization effects upon the interaction of methyl group and double bond fragments. Here, we have used the vertical (energy) axis to provide indication of the effect of replacing one or both of the double bond's carbons by atoms of different electronegativity. The horizontal scale depicts the direction of localization of the double bond π and π^* orbitals. To the left of center are molecules CH_3—X═Y, X being the more electronegative atom; to the right systems where Y is more electronegative than X. Recall that for X and/or Y more electronegative than carbon, the energy separation between the double bond π orbital and the lowest empty function on the methyl group increases (relative to its value in propene) while that between π^* and π_{CH_3} is lessened. Hence, according to the simple perturbation model, interaction 2 takes on added importance at the same time as the significance of interaction 3 is diminished. The gap between the two filled levels also decreases on account of an electronegativity perturbation in this direction, but we shall again assume in the discussion which follows that any effect which arises because of this is dwarfed by comparison to shifts in the magnitudes of the two electron components 2 and 3. If X is at the negative end of a polar double bond then localization effects will tend to reinforce the energy level shifts, and lead to increased preference for methyl eclipsing. That is to say, the negative secondary overlap contribution, involving the out-of-plane methyl hydrogens and the far end of the double bond has been enhanced between the π_{CH_3} and π^* fragment orbitals. Hence, the total (positive) overlap between these fragments is decreased and the stabilization is then less. Since the energies of these fragment orbitals have come closer together on account of electronegativity perturbations, this effect dominates. The complementary interaction 3 (between π and $\pi^*_{CH_3}$) is already weakened due to widening of the corresponding energy separation. The overall effect, therefore, is to *increase* the rotational barrier.

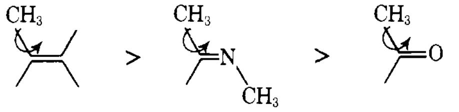


If, on the other hand, the double bond is polarized in the opposite manner, $X^{\delta+}$-$Y^{\delta-}$, then energy and localization effects work against each other, and a reduction in conformational preference for the eclipsed arrangement should be observed. Here, interaction between π_{CH_3} and π^*, strengthened because of decreased energy separation, looses some of its ability to distinguish between the staggered and eclipsed conformers. The selectivity of interaction 3, between the π orbital and the lowest empty function on methyl, increases because of polarization of charge density in the double bond towards the far terminus. The energy splitting between these two orbitals has increased, however, and the interaction no longer plays a dominant role in influencing the conformation of the molecule. The overall effect is to *decrease* the rotational barrier.



The available experimental data and our theoretical 4-31G calculations largely support the contentions of the simple model. Experimentally, whereas the barrier to rotation in *N*-methylformaldimine[15] is nearly identical with that in propene, that of the *N*-methyl group in *anti*-*N*-methylacetaldimine is 2.109 kcal/mol,[16] 0.1 kcal/mol greater than the propene value. Our calculations indicate the difference in barriers between *N*-methylformaldimine (2.18 kcal/mol) and propene (1.81 kcal/mol) to be even greater. As anticipated, the rotational barriers in the systems decrease with increasing electronegativity of the atom at the far terminus of the double bond. Our theoretical calculations concur fully, suggesting in addition that the 1-fluoroethyl cation, where polarization is extreme, exhibits only a slight (0.41 kcal/mol) preference for an eclipsed conformation.[17]





2.00 kcal/mol[3] 1.642 kcal/mol[16] 1.16 kcal/mol[4]

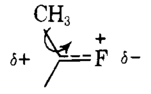


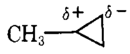
Table III. Theoretical Energy Data for Small Ring Compounds[a]

Molecule	*E* (hartrees)	
	Bisected	Straddled
Methylcyclopropane	−155.86317	−155.85828
2-Methylaziridine	−171.80369	−171.79964
Methyloxirane	−191.61018	−191.60622
N-Methylaziridine	−171.78646	−171.77863

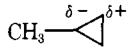
[a] Molecular geometries used correspond to the attachment of a "standard" methyl group (C–H = 1.09 Å, tetrahedral angles) to the STO-3G equilibrium structures for the parent 3-membered rings (W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Fortschr. Chem. Fortsch.*, 40, 1 (1973)). Bond angles remain the same as those for hydrogen in the unsubstituted rings and connecting bond lengths as follows: C–CH_3, 1.52 Å; N–CH_3, 1.47 Å.

The similarity of the Walsh orbitals in a 3-membered ring[18] to the valence functions of a double bond prompted us in an earlier publication to[19] suggest that the same model used to rationalize the conformational preference in, say, propene should apply as well to molecules such as methylcyclopropane. The arguments, which lead to the favoring of the conformation in which one CH bond bisects the small ring, rather than straddling it, closely parallel those made for vinylic methyl rotors, and will not be repeated here. It is reasonable to anticipate that the conclusions we have reached regarding changes in rotational barrier in response to the introduction of a heteroatom into the unsaturated linkage will carry over to like substitution on the small ring.

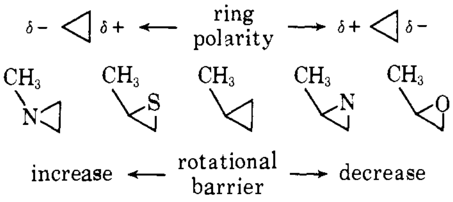
In particular, polarization of the ring



should result in a decrease in rotational barrier, while charge distribution in the opposite manner



should lead to an increase. Both the theoretical (4-31G) calculations and the available experimental data (Table IV) concur fully, showing a close parallel between the barrier heights and the polarity of the small ring.



It is, of course, tempting to pursue the model one step further and to consider possible rationalizations for the observed variations of methyl torsional barriers in saturated acyclic molecules of the form $CH_3\text{—}C\text{—}X(Me)_2$. All that is required is the realization that the valence orbital description around the central carbon in, say, isobutane is qualitatively very similar to that in methylcyclopropane. Here again, application of the simple arguments would suggest a close parallel between the polarity of the skeleton to which the rotor is affixed (i.e., the electronegativity of X) and the potential hindering torsion. The available experimental data (Table V) concur fully. However, part of the barrier increase in a molecule such as trimethylamine is probably due to direct overlap effects involving the hydrogens on different methyl groups.

Table IV. Barriers to Rotation of Methyl Groups Attached to 3-Membered Rings (kcal/mol)

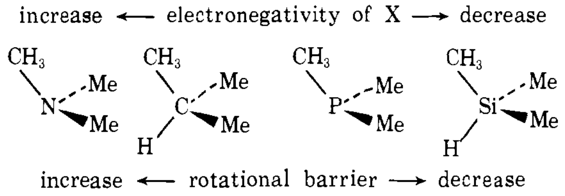
Molecule	4-31G[a]	Exptl
N-Methylaziridine	4.91	3.462[b]
Methylthiirane	. . .	3.240[c]
Methylcyclopropane	3.07	2.860[d]
2-Methylaziridine	2.54	2.608[e]
Methyloxirane	2.48	2.560[f]

[a] Theoretical energies taken from Table III. [b] M. D. Harmony and M. Sancho, *J. Chem. Phys.*, 47, 1911 (1967). [c] S. S. Butcher, *J. Chem. Phys.*, 38, 2310 (1963). [d] R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, 48, 4671 (1968). [e] Y. S. Li, M. D. Harmony, D. Hayes, and E. L. Beeson, Jr., *J. Chem. Phys.*, 47, 4514 (1967). [f] J. D. Swalen and D. R. Herschbach, *J. Chem. Phys.*, 27, 100 (1957).

Table V. Barriers to Rotation of Methyl Groups Attached to Saturated Systems (kcal/mol)

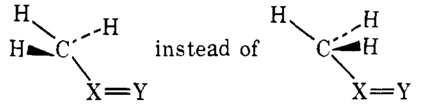
Molecule	Exptl
Trimethylamine	4.40[a]
Isobutane	3.90[b]
Trimethylphosphine	2.60[b]
Trimethylsilane	1.83[c]

[a] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, 28, 572 (1958). [b] D. R. Lide, Jr., and D. E. Mann, *ibid.*, 29, 914 (1958). [c] L. Pierce and D. H. Petersen, *ibid.*, 33, 907 (1960).

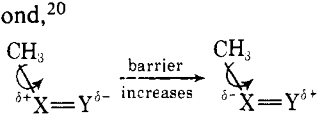


Conclusion

Qualitative arguments based on the interaction of fragment orbitals have been applied to the problem of preferred conformation and variation in rotational barrier of a methyl group attached to a polar unsaturated linkage. The conclusions of the simple model, both with regard to conformation



and shifts in torsional potential upon changes in the polarity of the double bond,[20]



are completely borne out both by experimental observation, where available, and by quantitative molecular orbital calculations at the ab initio split valence shell level.

It needs to be emphasized that the model we have proposed here is based on the hypothesis that π effects dominate. That is to say, it completely ignores the possibility of repulsive (or attractive) interactions within the σ framework. If this assumption is realistic, then it follows that the barriers hindering methyl rotation systems such as *syn*- or *anti*-acetaldimine

or in *cis*- or *trans*-methyldiazene

be of similar magnitude. Although there are no experimental data available for these particular systems, the results of our ab initio molecular orbital calculations largely support the notion that σ effects here are not of primary importance.

References and Notes

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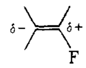

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Photoelectron Spectra and Molecular Properties. LI.[1-3] Ionization Potentials of Silanes Si_nH_{2n+2}

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Abstract: The low-energy photoelectron spectra (PES) of silanes Si_nH_{2n+2} (n = 1-5) are reported. Their assignment is achieved by spectral comparison, by parametrization of MO models using PES data, and by modified CNDO calculations, which have been used in addition to examine the conformational dependence of the ionization potentials. The unsymmetrical splitting pattern observed in the σ_{SiSi} ionization region of the silane PES stimulates a rediscussion of bond-bond interaction models for permethylated silanes or alkanes.

Photoelectron spectra (PES) of permethylated linear and cyclic silanes display isolated bands in the 8-10 eV region, which are readily assigned to ionizatiions from the silicon framework.[5] The corresponding spectroscopic splitting patterns can be rationalized within a simple LCBO (linear combination of bond orbitals) model, which only considers the silicon bonds and their topology as shown in Figure 1.

Assuming validity of Koopmans theorem,[6] $IE_n = -\epsilon_J^{SCF}$, and some approximate proportionality, $\epsilon_J^{SCF} \propto \epsilon_J^{HMO}$, the linear regression of Figure 1 yields the parameters $\alpha^R{}_{SiSi}$ = 8.7 eV and $\beta^R{}_{SiSi/SiSi}$ = 0.5 eV.[5] Extended models, incorporating the unoccupied molecular orbitals, render possible an understanding of other properties of the alkylsilanes, e.g., the decrease in first excitation energies with increasing silicon chain length[7] or the ESR spectra of their radical anions.[8] Nevertheless, the neglect of the methyl groups in a simplifying bonding model for methylsilanes $-[Si(CH_3)_2]_n-$ (Figure 1) needs further elaboration.

Hydrocarbons C_nH_{2n+2} have been repeatedly investigated using photoelectron spectroscopy, e.g.,[9-12] and analogous bonding models[12-16] seem well-suited to interpret many of their molecular properties. Although alkanes are smaller in molecular size than corresponding methyl silanes of the same chain length, n, in general numerous bands overlap in their PES and often render difficult unequivocal assignments[9-12] as well as comparative discussion.[12] The PES of silanes Si_nH_{2n+2} (n = 1,[9,17,18] 2,[9] 3, 4, 5) have been recorded, because increased PE band separation and consequently more obtrusive assignment were expected, shedding more light also on the applicability of bond orbital models to both methyl silanes as well as alkanes.

Experimental Section

Preparation and Purification of Silanes. The silanes Si_nH_{2n+2} (n = 2, 3, 4, and 5) have been prepared—in the course of investigations to determine their molecular properties[2]—by a technical scale hydrolytic decomposition of 160 kg of Mg_2Si[19] with diluted phosphoric acid,[20] yielding 5 l. of a mixture containing, among other isomers as well as higher silanes, 5.5% disilane, 34.8% trisilane, 29.2% n-tetrasilane, and 15.5% n-pentasilane. The rather dangerous mixture of the gaseous hydrolysis products, monosilane, hydrogen, and uncondensed disilane was cautiously blown off via a water siphon. Separation and purification of the liquid silanes were achieved by fractionate distillation over a 1.5-m column filled with