Photoelectron Spectroscopy of Heterocyclobutanes: Electronic Structure of Small Ring Compounds and Ramifications for Reactivity

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Abstract: The highest occupied molecular orbitals of cyclobutane are the degenerate pair of Walsh σ orbitals, which account for the conjugative ability of four-membered rings. In heterocyclobutanes, the degeneracy is lifted, and the presence of the heteroatom perturbs both the energies and the shapes of these MO's. The photoelectron spectra of oxetane, thietane, and azetidine have been measured, and assignments have been made by comparison with minimal basis set STO-3G ab initio calculations, and by correlations with spectra of acyclic analogues and three-membered ring heterocycles. The resulting patterns of orbital energy shifts in heterocyclopropanes and heterocyclobutanes (containing C, O, N, S, and Si) are interpreted using two models: one which considers orbital energy changes as a function of cyclization and ring size, and the second which views these changes as a function of interactions occurring upon union of heteroatom and alkyl fragments. Reactivities of molecules containing these small-ring heterocycles are discussed in terms of the ionization potentials and orbital shapes now available for these systems.

Since the discovery at the turn of the century of the facile cleavage of cyclopropane single bonds, strained rings have elicited interest on gradually increasing levels of sophistication. In addition to the unusual reactivity of these species, their spectral and conjugative properties prompted comparisons with alkenes.[2] In 1949, electronic structural hypotheses for three-membered rings were proposed.[3] Those models are still in current use, and have been extended to cover four-membered ring systems.[4-6]

While the conjugative abilities of cyclopropane and cyclobutane are qualitatively understood and frequently invoked to explain certain chemical phenomena,[4,7] the electronic structures of heterocyclopropanes and cyclobutanes have been delineated less thoroughly, and the conjugative capacities of these systems have not been subject to experimental scrutiny. Numerous semiempirical and ab initio calculations on small ring systems have been carried out to explore the electronic structures of these molecules,[8,9] and in the case of three-membered rings, photoelectron spectra have been compared with calculated orbital energies.[10] However, ab initio calculations of various kinds give rather poor agreement with the photoelectron spectrum of oxirane,[9,10] and an ab initio calculation on thiirane[11] is in extraordinary disagreement with the experimental spectrum. In the latter case, assignments have been made by comparison with CNDO/2 calculations.[12] Because of the difficulties encountered with the three-membered ring molecules, we felt that ionization potential data for the four-membered ring compounds would be of value not only because of inherent interest in these molecules, but because insight into the nature of the orbitals of three-membered ring compounds might also be obtained thereby.

In order to provide correlative evidence for the radical-cation state energies, and, assuming Koopmans' theorem, the orbital energy ordering in small-ring compounds, we have measured the photoelectron spectra of oxetane, azetidine, and thietane. These results, along with data in the literature, constitute a complete set of ionization potential data for acyclic and three- through five-membered ring alkanes, ethers, amines, and sulfides. We have also carried out ab initio calculations on acyclic, three-, and four-membered heterocycles containing O, N, S, and Si. With these data in hand, orbital assignments for the whole series may be confirmed. Applications to the explanation of reactivity are discussed at the end of this paper.

Results and Discussion

Molecular Orbitals of the Small-Ring Heterocycles. The highest occupied Walsh orbitals of cyclopropane and cyclobutane are depicted in Figure 1. The degenerate, highest occupied orbitals of these molecules are quite similar in energy, as determined from their ionization potentials: 10.9 eV for cyclopropane, and 11.0 eV for cyclobutane.[10,13] Cyclobutane, like cyclopropane, is capable of symmetry-correct interaction with π-type orbitals of appropriate substituent groups, e.g., the vacant p orbital of a carbonium ion center (Figure 2). However, in conformations optimally disposed for overlap of a Walsh orbital of a small ring and an appended p orbital, the conjugative interaction in cyclopropylcarbinyl is considerably stronger than that in cyclobutylcarbinyl.[4] In this case, then, the disparity in the strengths of the otherwise comparable interactions is ascribable to differences in overlap: the relevant Walsh orbital of cyclopropane is more localized at the site of interaction than is the corresponding orbital of cyclobutane. Thus, the conjugative ability of a cyclobutyl group is less than that of cyclopropyl, but greater than that of methyl.[14,15]

In heterocyclopropanes and heterocyclobutanes, the degeneracy of the Walsh orbitals is lifted, and the presence of the heteroatom perturbs not only the energies, but also the shapes of these molecular orbitals. In the planar (C_{2v}) oxetane molecule, for example, the highest occupied a_1 and b_2 orbitals are derived from the degenerate e_u pair of cyclobutane. Various molecular orbital calculations suggest that these orbitals retain much of the form of their homocyclic counterparts: both are lowered in energy, and the a_1 orbital is reinforced at oxygen, and the b_2 in the vicinity of the transannular carbon (Figure 3). However, calculations sometimes disagree on the relative energies of these orbitals, semiempirical methods predicting a_1 to lie below b_2,[16] with ab initio calculations reported here predicting the opposite.

In the cases of interest here, as the symmetries of the parent molecules (D_{3h} for cyclopropane, D_{4h} for planar cyclobutane) are lowered to C_{2v} or lower by incorporation of a heteroatom, orbital mixing gives rise to new MO's for the perturbed system. The incorporation of the heteroatom has been simulated in earlier work[17] by two simple perturbations:[18] (1) raising the basis orbital energy for a pair of geminal protons causes the electron density in the two C–H bonds to drift toward the ring atom, thereby allowing the development of "lone pairs" (one

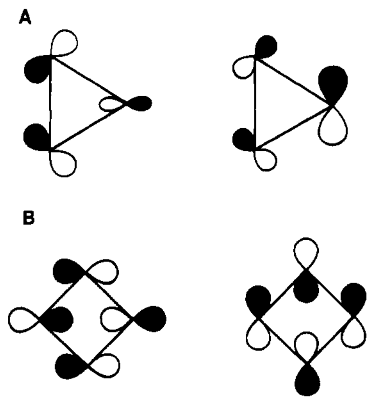


Figure 1. The degenerate highest occupied Walsh orbitals in (A) cyclopropane (e′ in D_{3h}), and (B) cyclobutane (e in D_{2d}, e_u in D_{4h}).

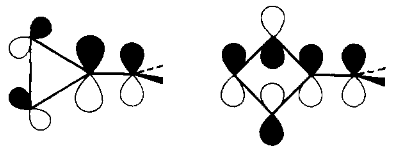


Figure 2. The optimal conjugative interactions between a carbon p orbital and the appropriate Walsh orbitals in cyclopropylcarbinyl and cyclobutylcarbinyl.

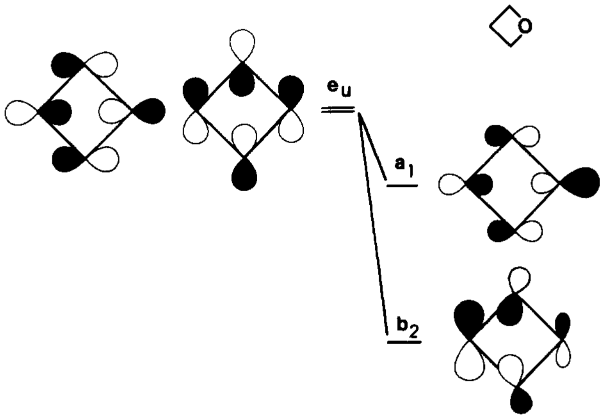


Figure 3. The e_u orbitals of cyclobutane and the corresponding a_1 and b_2 orbitals of oxetane.

p-type b_1, and one σ-type, a_1); (2) changing the basis orbital energies of the ring carbon at the corresponding site simulates the electronegativity effect of the heteroatom (Figure 4). Alternative models are discussed in later sections of this paper.

Photoelectron Spectra of Heterocyclobutanes. Oxetane, thietane, and azetidine were obtained as high-purity commercial samples. The photoelectron spectra were recorded on a Perkin-Elmer PS-18 Spectrometer employing a 127° electrostatic deflection analyzer and a He I source, with xenon and argon gases as calibrants. All values reported are for vertical ionization potentials, which are measured as the position of the strongest vibrational band, or for broad bands, the maximum in the Franck-Condon vibrational envelope.

The photoelectron spectra of cyclobutane, oxetane, thietane, and azetidine are presented in Figures 5-8, and the vertical ionization energies for these compounds are listed in Table I. The first two peaks in the spectrum of the parent hydrocarbon are the Jahn-Teller split components of the band due to ionizations arising from the degenerate Walsh σ orbitals.[13] They can be correlated with the second and third ionization energies of the heterocyclobutanes, as shown in Figure 9 (vide infra).

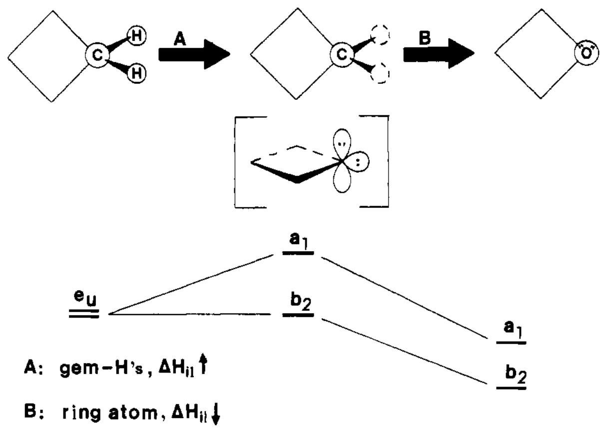


Figure 4. Stepwise perturbations simulating the conversion of cyclobutane to oxetane.

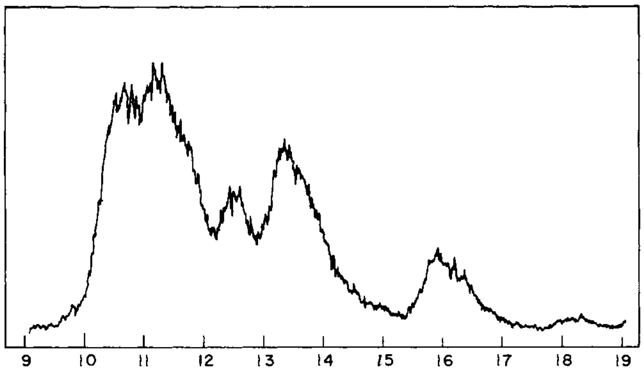


Figure 5. The photoelectron spectrum of cyclobutane (Courtesy of E. Heilbronner).

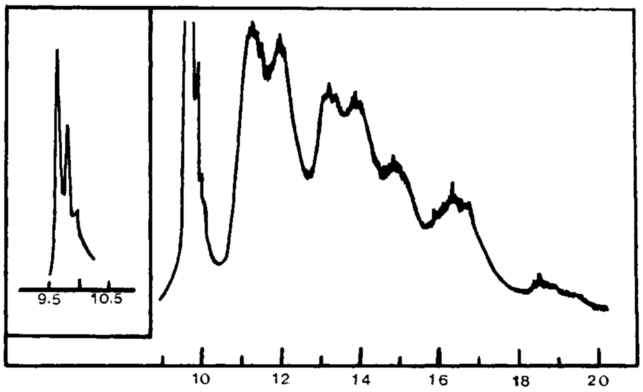


Figure 6. The photoelectron spectrum of oxetane.

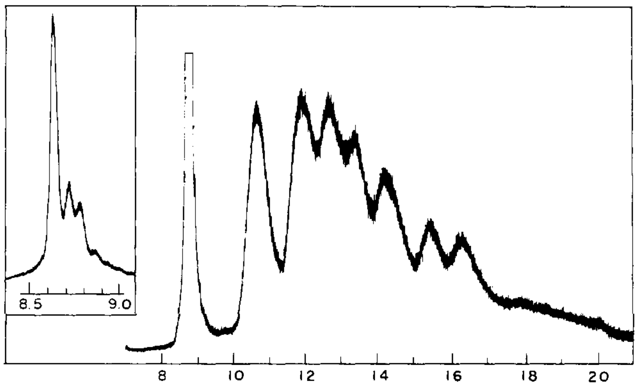


Figure 7. The photoelectron spectrum of thietane.

Table I. Vertical Ionization Energies (eV) of Heterocyclobutanes

Compd	IE_v (b_1–π)	IE_v (a_1)	IE_v (b_2)	Higher IE_v						Ref
Cyclobutane		10.7^a	11.3^a	12.2	12.5	13.4, 13.6	15.9	18.2		13
Oxetane	9.63	11.32	11.98	13.4	14.0	14.8	16.4	16.7	$18._5$	This work
Thietane	8.65	10.60	11.89	12.60	13.27	14.13	15.38	16.27		This work
Azetidine	8.93	11.40	12.03	12.9	14 (3 bands)		16.1_2	17.0_7	18.6_5	This work
Silacyclobutane		10.05	10.60	11.3	12.0	12.3	13.4	14.7	15.5	34

[a] Jahn–Teller split components of the degenerate e_u Walsh orbitals.

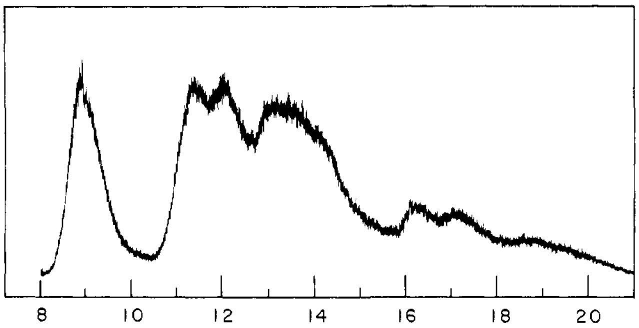


Figure 8. The photoelectron spectrum of azetidine.

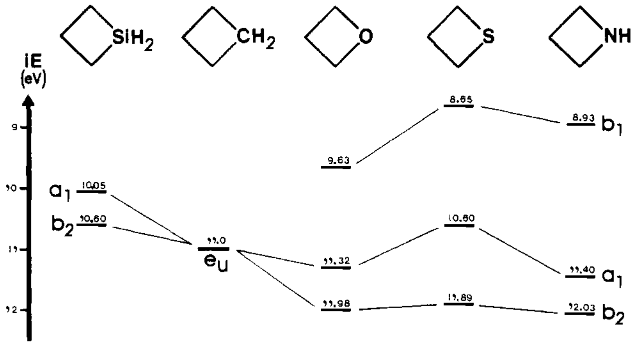


Figure 9. Assignment and correlation of the low-energy ionization potentials of cyclobutane and its hetero analogues. (Note: The symmetry designations are those which the orbitals would have were the molecules planar (C_{2v}). Silacyclobutane, thietane, and azetidine actually belong to the point group C_s, under which a_1 transforms as a′, and b_2 as a″.)

The first ionization energies of the heterocycles may be assigned to "lone pairs" on the heteroatoms. In the case of oxetane (IE_1 = 9.63 eV),[19] the band shape (a very strong adiabatic transition, followed by rapidly diminishing intensity 0-1, 0-2, and 0-3 transitions) is typical of p-type nonbonding electron pairs. The vibrational fine structure (ν = 1210 cm^{-1}) arises from the hyperconjugation of the "lone pair" with its neighboring methylene groups; the small difference between the ion frequency and neutral molecular frequency ($\nu \sim$ 1340–1460 cm^{-1})[20] attests to the nonbonding character of this, the highest occupied orbital.

Likewise, the first band of thietane (IE_1 = 8.65 eV)[21] is indicative of a nonbonding pair, highly localized in a sulfur 3p orbital. The vibrational fine spacings of 650 ± 40 and 1120 ± 60 cm^{-1} observed in this band probably correspond to the symmetric C–S stretching, ν = 698 cm^{-1}, and CH_2 wagging, ν = 1226 cm^{-1}, modes observed in the ground state of thietane.[22] The vibrational spacings found in this PES band are slightly smaller than the average vibrational spacings (698 and 1175 cm^{-1}) found in the Rydberg spectra of thietane.[21] (For comparison, the first PES band of dimethyl sulfide has vibrational spacings of 660, 990, and 305 cm^{-1}, the last corresponding to CSC bending[22]). Again, the quite small shift in the frequencies of these modes would suggest an essentially nonbonding molecular orbital.

In contrast to the needle-like peaks of the first bands of oxetane and thietane, that of azetidine (IE_1 = 8.93 eV) is quite broad, and the adiabatic transition is no longer the vertical transition. Its shape, of course, reflects the fact that the pyramidal form of the nitrogen center allows considerable admixture of other bond components and concomitant delocalization; the result is loss of nonbonding character. The difference between the adiabatic and vertical IE's arises from the large difference in ground state (pyramidal) and radical cation (planar) geometries about nitrogen. Both the band shapes and the pattern of energy differences in this series find parallels in the first ionizations of water, hydrogen sulfide, and ammonia.[25]

Ab Initio STO-3G Calculations on Heterocyclopropanes, Heterocyclobutanes, and Their Acyclic Analogues. Although a variety of calculations on many of the molecules studied here have been reported, including extended basis double ζ ab initio SCF calculations on some of the three-membered ring compounds,[10] we felt it important to have a consistent set of high quality calculations on the entire series of molecules to give confident assignments. For this purpose, the GAUSSIAN 70 system of programs devised by Pople and coworkers,[26] and the well-tested and relatively economical minimal STO-3G[27] basis set were used. The results of these calculations are shown in Table II, which gives the first few topmost occupied orbital energies and symmetries. The geometries used in these calculations are experimental where available, and the references to structural data, or geometrical parameters used, are given in ref 28. The correlation between these calculated orbital energies and experimental vertical IE's are moderately satisfactory, giving the following least-squares correlation:

$$\text{IE (exptl)} = 0.677\text{IE (STO-3G)} + 4.43 \qquad (1)$$

which has a correlation coefficient of 0.954, and a standard error of ±0.4 eV. In Figure 10, the experimental ionization potentials, and STO-3G calculated ionization potentials (corrected by eq 1) are shown for the acyclic, three-, and four-membered alkanes, amines, ethers, sulfides, and silanes. The experimental values used in Figure 10 are from this work or from the literature[29-34] (Table III). Correlations and assignments are shown for the experimental ionization potentials, but except for the lone pair ionizations for which assignments can be made on the basis of band shapes and vibrational structure, the remaining assignments are based on the STO-3G calculations, using Koopmans' theorem.[35] That is, the lowest three IE's were assumed to be in the same order as the top three calculated orbital energies. Because of the lack of experimental data on silanes, correlations are shown for the calculated IE's.

The assignments made here for the acyclic and three-membered ring compounds agree in most cases with assignments made in the literature.

Ab initio and semiempirical methods of various kinds on propane,[9,29] cyclopropane,[10] and cyclobutane[5,13] are in agreement with those reported here. For the amines, calculations on aziridine by two different double ζ[10,36] and one minimal basis STO[37] ab initio SCF techniques have been reported,

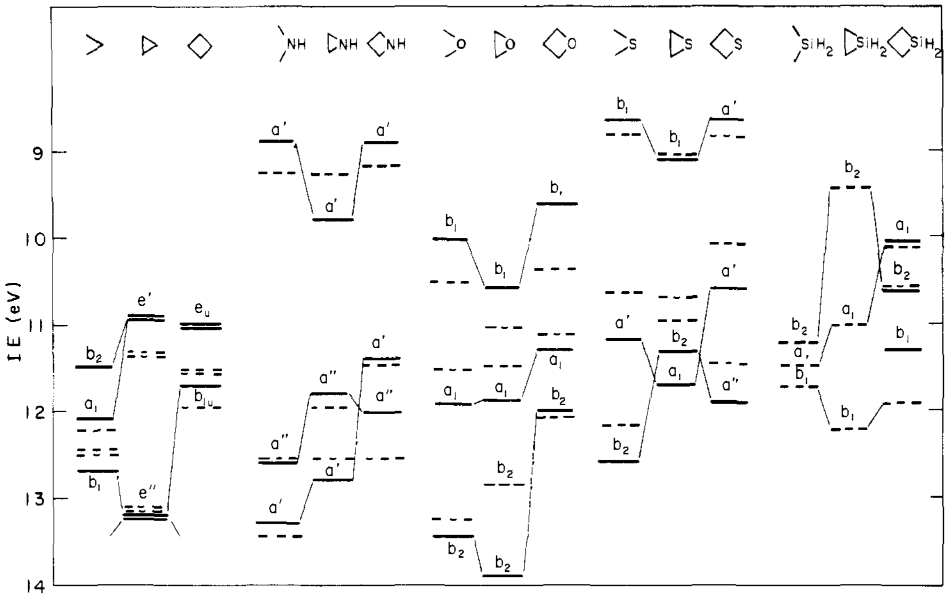


Figure 10. Correlations between the lower ionization potentials of the alkanes, amines, ethers, sulfides and silanes obtained from PES (—) and from corrected STO-3G calculations (- - -).

Table II. STO-3G Orbital Energies (eV)

Propane (C_{2v})[a] −11.64 (b_2) −12.00 (a_1) −12.07 (b_1)	Cyclopropane (D_{2h}) −10.37, −10.37 (e') −13.05, −13.05 (e'') −15.88 (a_1')	Cyclobutane (D_{4h})(D_{2d}) −10.64, −10.64 (e_u)(e) −11.25 (b_{1u})(a_1) −12.33 (b_{1g})(b_1)
Dimethyl ether (C_{2v})[a] −9.13 (b_1) −10.60 (a_1) −13.15 (b_2)	Oxirane (C_{2v}) −9.91 (b_1) −10.54 (a_1) −12.54 (b_2)	Oxetane (C_{2v}) −8.93 (b_1) −10.03 (a_1) −11.43 (b_2)
Dimethylamine (C_s) −7.25 (a') −12.16 (a'') −13.45 (a')	Aziridine (C_s) −8.92 (a') −11.21 (a'') −12.16 (a')	Azetidine (C_s) −7.15 (a') −10.46 (a') −12.10 (a'') −12.51 (a'')
Dimethyl sulfide (C_{2v}) −6.59 (b_1) −9.30 (a_1) −11.57 (b_2)	Thiirane (C_{2v}) −6.92 (b_1) −9.39 (b_2) −9.70 (a_1)	Thietane (C_s) −6.62 (a') −8.47 (a') −10.51 (a'')
Dimethylsilane (C_{2v}) −10.18 (b_2) −10.55 (a_1) −10.91 (b_1)	Silacyclopropane (C_{2v}) −7.37 (b_2) −9.74 (a_1) −11.51 (b_1)	Silacyclobutane (C_{2v}) −8.51 (a_1) −9.21 (b_2) −11.18 (b_1) −11.57 (b_2)

[a] Warren G. Hehre, unpublished results referred to in ref 6.

Table III. Vertical IE's for Acyclic and Three-Membered Compounds

Compd	IE_1	IE_2	IE_3	Ref
Propane	11.5	12.1	12.7	29
Cyclopropane	10.53, 11.30	13.2	15.7	10
Dimethylamine	8.9	12.6	13.3	30
Aziridine	9.8	11.8	12.8	10
Dimethyl ether	10.04	11.93	13.42	31
Oxirane	10.57	11.71	13.7	10
Dimethyl sulfide	8.67	11.17	12.57	32 (33)
Thiirane	9.05	11.32	11.72	12

while the results reported here for dimethylamine and azetidine are apparently the first reported for these compounds.

Whereas a variety of calculations gives the STO-3G[38] orbital ordering shown for dimethyl ether,[31] the assignments for oxirane have been problematical. Basch and coworkers[10] found that double ζ ab initio SCF calculations predict the b_1 and a_1 orbitals to be of equal energy, and the b_2 of lower energy, while calculations of differences in energy between the ground and radical cation states predict the order of radical cation states to be $^2B_1 < {}^2A_1 < {}^2B_2 < {}^2A_2$—that is, the order predicted by STO-3G (Figure 10), using Koopmans' theorem.[35] Taking changes in correlation energy into account, Basch and coworkers again found the latter order. Pople and coworkers[9] have carried out ab initio 6-31G* calculations on oxirane, and the descending orbital energy order, $a_1 > b_1 > a_2 > b_2$ is found, in variance with all previous results. The greatest discrepancy in the prediction of IE's using Koopmans' theorem is the prediction that the lone pair (b_1) ionization will be 0.16 eV higher than the a_1 ionization, whereas the experimental spectrum clearly indicates the lone pair ionization to be 1.3 eV lower in energy than any other. The difficulty here clearly arises from the much greater electronic reorganization which occurs upon ionization of localized b_1 lone pair electron as compared to that for the more highly delocalized a_1 orbital, as revealed by the calculations of Basch et al.[10] The disagreement between 6-31G* and STO-3G or Basch et al.'s calculations is less surprising, all giving predictions of nearly equal energies for these orbitals.[39] Minimal basis STO calculations[37] agree with our results.

The discrepancies extend to the oxetane series, where CNDO/2 and EHT calculations give the descending order $b_1 > b_2 > a_1$,[16] rather than that reported here, which is also obtained by 4-31G calculations.[38]

The assignments for dimethyl sulfide agree with various semiempirical calculations,[9,40,41] and CNDO/2 and CNDO/BW calculations on thiirane,[12] as well as minimal basis or double ζ[42-44] ab initio calculations with or without 3d orbitals on sulfur, agree with the STO-3G values reported here. The same thietane order reported here is also given by CNDO/2 calculations we have performed.

Finally, in the silane series, the topmost two occupied orbital energies of silacyclobutane obtained by EHT calculations have

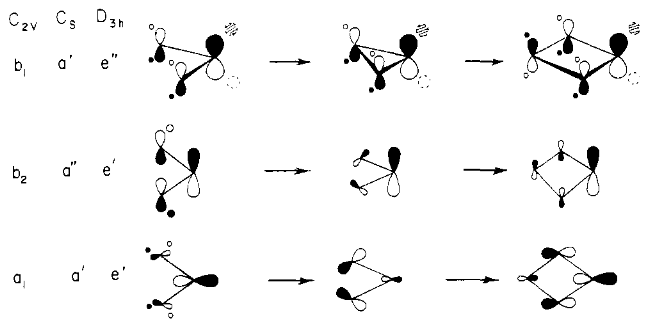


Figure 11. The b$_1$, b$_2$, and a$_1$ orbitals of acyclic, three-, and four-membered ring compounds.

been reported,[34] and the order is the same obtained by STO-3G calculations. EHT calculations also predict the order b$_2$ > a$_1$ > b$_1$, as found here by STO-3G, for silacyclopropane.[45]

Discussion of Calculations and Ionization Potential Changes. For all five series shown in Figure 10, there is a regular pattern observed for the b$_1$ orbitals—the lone pair, or π_{CH_2}, orbitals, Cyclization of the acyclic to the three-membered ring causes a considerable lowering of this orbital energy, and expansion to the cyclobutane causes destabilization. Figure 11 shows the b$_1$ orbital for the acyclic systems. In the cyclopropanes, the b$_1$ orbitals are stabilized relative to the acyclic compounds, because the symmetric combination of π_{CH_2} orbitals of the ethano group is more bonding than the symmetric combination of π_{CH_3} orbitals in the acyclic molecule. Thus, hyperconjugation is less able to destabilize the b$_1$ orbital in the cyclopropanes than in the acyclic compounds. For example, the degenerate π_{CH_3} orbitals of methane give an IE of 14.2 eV, while the π_{CH_3} + π_{CH_3} orbitals of ethane give rise to an IE (the third in this molecule) of 15.4 eV.[29] This difference is also reflected in the photoelectron spectrum, where the extent of admixture of π_{CH_3} or π_{CH_2} orbitals with the lone pair can be qualitatively determined by the intensity of contributions of vibrational levels other than 0-0 to the b$_1$ ionization. By this measure, the extent of "purity" of the lone pair ionization is S > O > NH.

Upon conversions of the cyclopropanes to cyclobutanes, the b$_1$ IE decreases, and becomes equal to, or lower than that in the acyclic compound. According to the previous model, this arises from a decrease in π_{CH_2} bonding between the π_{CH_2} groups, so they can mix with the lone pair orbital more, and an increase in the number of atoms provides a third π_{CH_2} group which further raises the π_{CH_3} + π_{CH_3} orbital energy by hyperconjugation. In the cyclobutanes, a propane $\pi_{CH_3} - \pi_{CH_2} - \pi_{CH_3}$ orbital (IE = 11.5 eV)[29] of higher energy than that of ethane can mix with the lone pair orbital.

If this explanation accounts for the b$_1$ orbital energy changes, then differing amounts of π_{CH_3} or π_{CH_2} character in the topmost orbitals should be reflected in the calculations. The extent of mixing will depend upon the energy of the "isolated" lone pair orbital relative to the π_{CH_3} or π_{CH_2} orbitals, as well as the extent of overlap of the interacting orbitals. The smallest changes in IE's are observed in the sulfide species, and the b$_1$ orbital is "least contaminated" by π_{CH_2} contributions in this species as compared to the others. In dimethyl sulfides, 6.2% of the b$_1$ orbital density is contributed by C and H, and this drops to 4.6% in thiirane. Similarly, the S-CH$_2$ π-electron population decreases from −0.47 in dimethyl sulfide to −0.44 in thiirane. By comparison, the b$_1$ orbitals of dimethyl ether and oxirane contain much more significant contributions from other orbitals.

In addition to the importance of the energy of the isolated lone pair or analogous orbital and its overlap with π_{CH_2} orbitals, the extent of the mutual overlap of the π_{CH_3} groups in the acyclic compounds will be of importance. Pople and coworkers have discussed the importance of this type of overlap in determining the barrier to rotation in geminally dimethyl substituted compounds.[46] For those acyclic compounds with relatively large $\pi_{CH_3} - \pi_{CH_3}$ overlap, and, therefore a relative low-lying b$_1$ combination, cyclization will not appreciably decrease the energy of the $\pi_{CH_2} - \pi_{CH_2}$ b$_1$ combination, and the lowering of the lone pair b$_1$ orbital upon cyclization will decrease. Thus, the ethers show less decrease in b$_1$ energy than the amines, in spite of the lower energy of the oxygen lone pair orbital. In the cases of relatively small b$_1$ stabilization upon cyclization, a large destabilization upon ring expansion is observed. Here, the b$_1$ orbitals are relatively strongly π_{CH_3} + π_{CH_3} or π_{CH_2} + π_{CH_2} bonding in the acyclic and cyclic cases, respectively, but insertion of an additional π_{CH_2} orbital in an antibonding fashion between the π_{CH_2} orbitals has a larger destabilizing effect.

The b$_1$ (or a'') and a$_1$ (or a') orbitals show less consistent patterns upon conversion from acyclic molecule to cyclopropane to cyclobutane. In all cases except the oxide case, the b$_2$ (or a'') orbital is destabilized upon conversion from acyclic to three-membered ring compound, and then stabilized to a lesser extent upon conversion of the cyclopropane to the cyclobutane. Figure 11 shows the qualitative changes which occur. Destabilization upon cyclization is expected, since the b$_2$ (or a'') orbitals have antibonding interactions between the methyl groups in the acyclic compounds, and these antibonding interactions are exacerbated in the three-membered ring compounds, as shown in Figure 11. Insertion of another methylene group relieves this antibonding, and introduces additional bonding interactions.

Why does oxirane deviate from this pattern? One explanation is that the assignments for oxides are incorrect: there might be an additional ionization at an energy between the 10.57- and 11.7-eV bonds. In the published spectrum of oxirane, after the sharp 0-0 band due to the b$_1$ (lone pair) ionization and the accompanying vibrational structure, there is a broad band assigned as a single vertical ionization.[10] In fact, it is easy to imagine a second maximum in this region, which would bring the b$_2$ ionization of oxirane into pattern exhibited by all the other series. This possibility is made less attractive by calculations, which also indicate that the b$_2$ orbital of oxirane is anomalously stable as compared to other three-membered rings, just as Basch et al.'s photoelectron assignments do. The question of assignments in oxirane apparently has not been definitively settled, and we intend to study substituted derivatives to trace the IE changes as a function of substitution, and thus to make a definite assignment.[47]

The a$_1$ (or lower energy a') orbital is destabilized considerably upon conversion of propane, dimethylamine, or dimethylsilane to the corresponding three-membered ring compound, but is essentially unchanged in dimethyl ether, and is stabilized in dimethyl sulfide. The conversion to the four-membered ring results in destabilization of this orbital for all molecules except cyclopropane itself, where there is very little change. The a$_1$ orbital, as shown in Figure 11 for all three types of compounds, is rather heavily localized on the central atom, and conversion to the three- or four-membered rings results in substantial changes in shape. Perhaps no simple pattern is expected here, since the mixing of all the a$_1$ orbitals in these molecules upon cyclization will ultimately determine the energy changes observed. A similar statement may be made for the b$_2$ orbital.

An alternative useful method for the analysis of orbital energies and shapes is to consider uniting ethylene π and π^* orbitals with p orbitals of the heteroatom. Hoffmann and coworkers have applied this model to thiirane and its oxides,[48] and Rohmer and Roos have discussed bond lengths in other three-membered ring heterocycles by the method.[42] These workers considered a model where the occupied a$_1$ (or a') or-

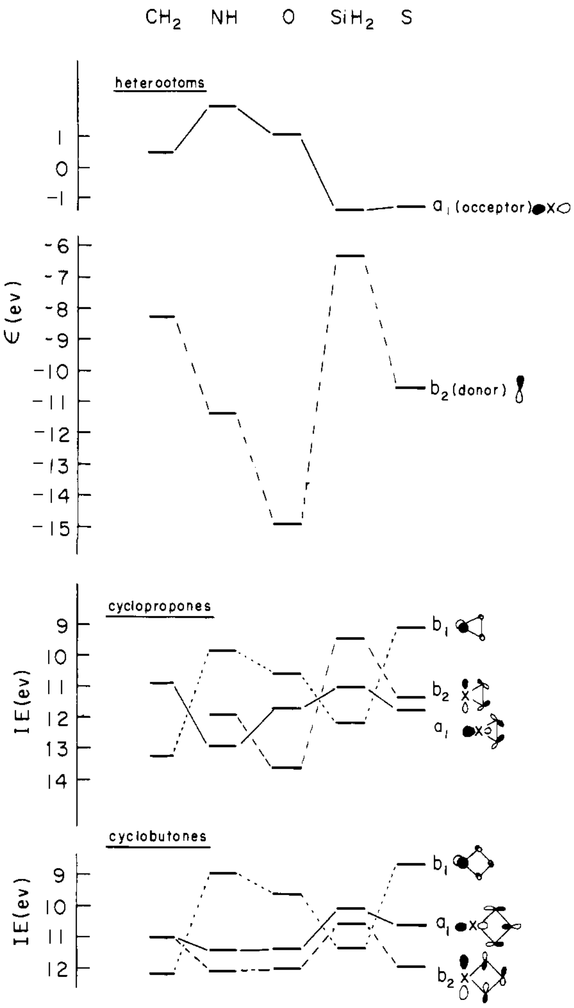


Figure 12. Top: calculated values of heteroatom fragment orbital energies. Middle: experimental IE's of heterocyclopropanes (values for silacyclopropane are calculated). Bottom: experimental IE's of heterocyclobutanes.

bitals of three-membered ring heterocycles result from the interaction of the π orbital of ethylene and a vacant orbital of a_1 (or a′) symmetry on the heteroatom, while the b_2 (or a″) orbital arises from the interaction of a filled b_2 (or a″) orbital on the heteroatom and the vacant π orbital of ethylene.

The model was applied by these authors to the explanation of the trends in CC bond lengths in three-membered ring heterocycles. This model accounts well, in part, for the trends in orbital energies in the three-membered ring heterocycles.

There is, indeed, a close parallel between Rohmer and Roos calculated values of the donor (b_2) orbital of the heteroatom fragment, and the experimental IE's of the b_2 (or a″) orbitals of the heterocyclopropanes, as shown in Figure 12. In the top part of this figure, the calculated values of the b_2 acceptor orbital are plotted. The b_2 IE's of the heterocyclopropanes (shown in the middle of Figure 12) parallel the energies of the b_2 fragments quite closely. The damping of the b_2 energy changes in the heterocyclopropane must arise from the mixing of the fragment b_2 orbital with the ethylene π^* orbital.

The heterocyclobutane b_2 orbitals may be considered to arise from mixing of a filled b_2 heteroatom fragment with a vacant trimethylene diradical level. Because other lower lying filled orbitals of the trimethylene fragment interact with the b_1 level, the heterocyclobutane b_1 IE changes are highly damped, but still follow the heterocyclopropane changes.

The a_1 orbital IE's of the heterocyclopropanes are roughly the mirror image of the a_1 (acceptor) fragment orbital energies.

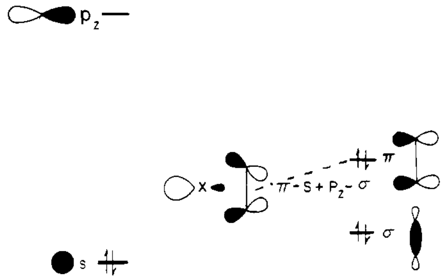


Figure 13. Genesis of the a_1 orbital of heterocyclopropanes from the a_1 orbitals (in C_{2v}) of the heteroatom fragment and ethylene.

This does not fit well with the simple model described above, in which the lower in energy the acceptor fragment, the greater the mixing with the ethylene π orbital should be, and the lower in energy the resulting a_1 orbital should be. The apparent deviation of orbital energy changes from those expected from the simple model is undoubtedly due to the fact that the donor has a filled orbital, which will mix with the π orbital of ethylene. The heteroatom filled and vacant orbitals are the valence s and p orbitals, respectively, or, alternatively may be considered as two sp hybrids. In either case, the filled orbital of the heteroatom apparently dominates the heterocyclopropane a_1 energy. Figure 13 shows how the a_1 orbital derives from the corresponding a_1 orbitals of the fragments. As the energy of the s (or filled sp hybrid) orbital is lowered, the extent of mixing with π decreases, and the energy of the resultant a_1 heterocyclopropane orbital will decrease, due to less extensive mixing of the s (or sp) orbital with the ethylene orbital. If the differences in energies of the s (or sp hybrid) orbitals of the heteroatom are the mirror image of the Rohmer-Roos vacant orbital energies, the trends in Figure 12 can be explained.

For the heterocyclobutanes, the same trends in a_1 energies are observed, but are highly damped due to the presence of several a_1 orbitals on the trimethylene fragment, and probably also due to the more nearly equal mixing of the trimethylene a_1 highest occupied orbital with the filled and vacant donor a_1 orbitals.

Finally, the extremely close parallel between the heterocyclopropane and heterocyclobutane b_1 orbitals is apparent in Figure 12.

Intramolecular Rearrangements Involving Small-Ring Carbocycles and Heterocycles. Hoffmann and co-workers have analyzed substituent effects on cyclopropane structures and reactivity in some detail.[48,49] Donor substituents on the cyclopropane weaken the remote (C(2)-C(3)) cyclopropane bond by donation of the electron density into a C(2)-C(3) antibonding orbital, while acceptors should strengthen this bond by withdrawing electron density from the high-lying filled b_1 orbital, which is C(2)-C(3) antibonding. These agreements have been used to explain the position of equilibrium in substituted norcaradiene-cycloheptatriene interconversions, and to explain rate of Cope rearrangements.[49] These types of arguments can be applied to heteroatom systems.

The rates of Cope rearrangements of 1,5-hexadienes are extraordinarily sensitive to groups substituting or bridging the 3 and 4 positions. While the activation enthalpy for the Cope rearrangement of 1,5-hexadiene through a boat-like transition state (Figure 14, where two hydrogens replace X) is about 41 kcal/mol,[50] that for the cyclobutyl bridged compound (X = CH_2CH_2-) is 23.1 kcal/mol,[51] and that for the cyclopropyl compound (X = CH_2-) is only 17.8 ± 2 kcal/mol.[52] For the heterocyclopropane compounds, the rates of rearrangement fall in the order, X = $CH_2 > NR \gg O > S$.[53] Thus the carbon and nitrogen compounds rearrange instantly below room temperature, the oxide at 60 °C, and the sulfide at 100 °C.

Table IV. Coefficients and Calculated Reactivities

	$\sum c^2$	IE	$\sum c^2$/IE	$\sum c^2$/(IE − 5)
Silacyclopropane	0.3094	9.4	0.0329	0.0703
Cyclopropane	0.3132	10.9	0.0287	0.0531
Aziridine	0.2115 0.1007	12.8 8.9	$\left.\begin{matrix}0.0165\\0.0113\end{matrix}\right\}0.0278$	$\left.\begin{matrix}0.0271\\0.0258\end{matrix}\right\}0.0529$
Oxirane	0.2630	11.9	0.0221	0.0381
Thiirane	0.2490	11.7	0.0213	0.0372
Cyclobutane	0.1731	11.0	0.0157	0.0289
Ethane	0.5440	13.5	0.0403	0.0640

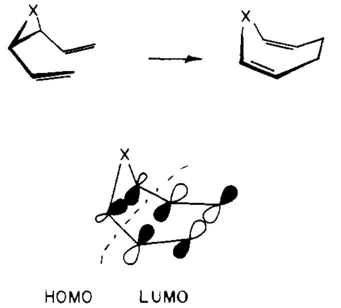
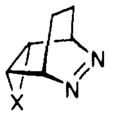


Figure 14. The boat transition state of the Cope rearrangement and the relevant frontier molecular orbitals of the heterocycloalkyl and homodiene fragments.

Comparisons of rearrangements involving cyclopropyl or cyclobutyl bond cleavage are quite common, and Jorgenson has recently summarized a number of these.[54] In a variety of reactions in which the cyclopropyl group and cyclobutyl groups are compared as donors, the cyclopropyl group is vastly superior, causing rate accelerations of 10^{10}–10^{13} in many cases, as compared to cyclobutyl. For these two all-carbon rings, the differences in donor ability have been well worked out. The relevant a_1 orbital of cyclobutane is of only slightly lower energy than that of cyclopropane, but can overlap less effectively with a nearby electron-deficient center.[54]

A simple MO model for the Cope rearrangements shown in Figure 14, which can be extended to consider stabilization of cations formed by solvolysis of systems such as **1** (L = leaving group) and extrusion of nitrogen from compounds such as **2**, can be built by considering the Cope rearrangement to be formally the result of interaction of a donor orbital (the HOMO) of the strained single bond and the low-lying vacant orbital (the LUMO) of the homodiene system. The better the interaction of the high-lying donor single bond with the homodiene acceptor orbital, the more stabilized the transition state of the Cope rearrangement. The extent of interaction, in the usual perturbation approximation, will be directly proportional to the square of the overlap between the donor and acceptor orbitals, and inversely proportional to the difference in energy of these two orbitals. Thus, the facility of rearrangement should be proportional to both the energy of the appropriate CC donor orbital and to the coefficients of this CC orbital, which determine the extent of interaction possible with the homodiene system. That this interaction, rather than the CC LUMO, homodiene HOMO interaction is most important is supported by the treatment shown below and by the observation that alkylation of the homodiene slightly raises the activation energy for rearrangement of the *cis*-divinylcyclopropane system.[54]

1



2

Table IV gives the vector sum of the coefficients at one of the carbons in the highest a_1 (or a′) orbital for ethane, cyclobutane, and the heterocyclopropanes. For aziridine, the HOMO, which is formally identified as the lone pair on nitrogen, has a substantial contribution from the carbon orbitals, whereas the other three-membered rings have no such mixture because of the C_{2v} symmetry of these molecules. Thus, the sum of the interactions due to the two a′ orbitals of aziridine are used as a theoretical reactivity index.

The use of the vector sum of the C a_1 (or a′) coefficients is crude, since this assumes that overlap of these orbitals with the homodiene LUMO depends only on the total density at the carbons, whereas the type of atomic orbital contributions, as well as the net density, will be important. However, since the exact geometry of the Cope rearrangement transition state is not known, we choose to use this crude index rather than some more exact, but also more speculative model. Two reactivity indices are listed in Table IV. The first uses the sum of the squares of the coefficients at the carbon in the a_1 or a′ orbital to measure the relative values of H_{ij}^2, the numerator of the perturbation expression for interaction of the donor HOMO with the homodiene LUMO, and EA as the denominator, which is the difference in energy between the two interacting orbitals. The reactivity index in the last column used IE − 5 eV as the denominator. The denominator of the perturbation expression can be considered to be the energy required to transfer an electron from the donor orbital to the acceptor orbital in the geometry of the transition state.[56] The denominators used in the last column should be reasonable approximations to these quantities for the rearrangement in question. For the solvolysis of **1**, which involves the interaction of the donor HOMO with very low-lying carbonium ion center LUMO, the denominators would be smaller, while for the reactions of **2**, a larger denominator would be appropriate. In the former case, the order of predicted reactivities may vary somewhat from the order given here.

Either of the last columns accounts reasonably well for the observed relatives rates of Cope rearrangements of the *cis*-divinylheterocyclopropanes. However, the parent system is calculated to react too fast. This indicates that ring strain relief in the transition state, as well as HOMO–LUMO interactions of the type discussed here, are important in the Cope rearrangement. A combination of considerations of the donor ability of the σ orbital, as measured by the IE, and the density at the relevant carbons, as measured by calculated coefficients, provides some insight into the order of reactivity of these compounds. The necessity of using coefficients is particularly well demonstrated by the case of aziridine, where use of the first IE would predict far too great reactivity, while the use of only the third would predict far too low reactivity.

Although the IE of silacyclopropane is only estimated, it is clear that this molecule should serve as a donor par excellence; rearrangements such as those of the hypothetical *cis*-divinylcyclopropane should occur very rapidly at low temperatures; reactions of **1** and **2**, where X = SiR_2, would be extremely fast. The high reactivity of silacyclopropanes is undoubtedly due to both the high nucleophilicity of these species, as reflected by the low calculated IE, as well as by the high electrophilicities of these species.

Either of the Hoffmann models provide alternative ways of looking at these effects.[48,49] The cyclopropanes with the weakest C(2)-C(3) bonds are those with the lowest a_1 and b_2 IE's, assuming that the Hoffmann-Rohmer-Roos model for genesis of these orbitals follows. The average of the a_1 and b_2 orbitals for these molecules (first three IP's for aziridine) follow the order: silacyclopropane (10.2 eV, calcd) < cyclopropane (10.9 eV) < cyclobutane (11.0 eV) < aziridine (11.5 eV) < thiirane (11.5 eV) < oxirane (12.7 eV) < ethane (<13.5 eV).

This order is nearly the reverse of that observed for rearrangement, except that S and O are in the wrong order. Nevertheless, there is a surprisingly good correlation between the IE's (which presumably indirectly reflect the C(2)-C(3) bond strengths) and rates of rearrangement.

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