

The sums over vibrational quantum number \mathbf{n} may be approximated as before,² but, because we consider cases of small J , the discrete sum over K is retained. Analogous to eq 4 the classical approximation to the sum over \mathbf{n} in eq 4.2 thus gives

$$N(E, J) = \sum_{K=-J}^J \frac{(E - V_0 - W_{J,K}^\ddagger)^{s-1}}{(s-1)! \prod_{i=1}^{s-1} (\hbar\omega_i^\ddagger)} \quad (\text{A.5a})$$

$$N_0(E, J) = \sum_{K=-J}^J \frac{(E - W_{J,K})^s}{s! \prod_{i=1}^s \hbar\omega_i} \quad (\text{A.5b})$$

so that the classical rate expression which replaces eq 5a is

$$k(E, J) = A \frac{\sum_{K=-J}^J (E - V_0 - W_{J,K}^\ddagger)^{s-1}}{\sum_{K=-J}^J (E - W_{J,K})^{s-1}} \quad (\text{A.6})$$

A being the frequency factor of eq 5b. Note that, for $J = 0$, eq A.6 reduces to eq 5a.

The effect of tunneling along the reaction coordinate is included in the same manner as before, by replacing $N(E, J)$ by $N_{\text{QM}}(E, J)$:

$$N_{\text{QM}}(E, J) = \sum_{K=-J}^J \sum_{\mathbf{n}} P(E - \epsilon_{\mathbf{n}, J, K}^\ddagger) \quad (\text{A.7})$$

where again $P(E_1)$ is the one-dimensional tunneling probability. The expression for the tunneling rate constant which

generalizes eq 11 by including rotation is thus

$$k_{\text{QM}}(E, J) = \frac{(s-1)! \prod_{i=1}^s \hbar\omega_i}{2\pi\hbar} \times \frac{\sum_{K=-J}^J \sum_{\mathbf{n}} P\left[E - V_0 - W_{J,K}^\ddagger - \hbar\omega^\ddagger \cdot \left(\mathbf{n} + \frac{1}{2}\right)\right]}{\sum_{K=-J}^J (E - W_{J,K})^{s-1}} \quad (\text{A.8})$$

with the rotational energies $W_{J,K}$ and $W_{J,K}^\ddagger$ given by eq A.4. One notes that for the case $J = 0$ eq A.8 reduces to the result in the text (eq 11) that ignores rotation altogether.

References and Notes

- (1) See, for example, (a) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, 1966, pp 37-47; (b) P. Pechukas in "Modern Theoretical Chemistry", Vol. 2, "Dynamics of Molecular Collisions", Part B, W. H. Miller, Ed., Plenum Press, New York, 1976, pp 269-322; (c) W. H. Miller, *Acc. Chem. Res.*, **9**, 306 (1976); R. A. Marcus, *J. Chem. Phys.*, **45**, 2138 (1966).
- (2) (a) P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, 1972; (b) Wendell Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973.
- (3) $N_0(E)$ was actually computed using the more accurate Whitton-Rabinovitch formula (cf. ref 2a, pp 131-137), but this makes only a few percent difference in the present applications.
- (4) See: (a) E. S. Yeung and C. B. Moore, *J. Chem. Phys.*, **58**, 3988 (1973); (b) P. L. Houston and C. B. Moore, *ibid.*, **65**, 757 (1976); and many other references cited therein.
- (5) J. D. Goddard and H. F. Schaefer, *J. Chem. Phys.*, **70**, 5117 (1979).
- (6) M. J. H. Kemper, J. M. F. Dijk, and H. M. Buck, *J. Am. Chem. Soc.*, **100**, 7841 (1978).
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Substituent Effects on Strain Energies¹

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Abstract: Ab initio calculations employing the STO-3G basis set have been performed on numerous substituted derivatives of the strained (or unsaturated) molecules ethylene, cyclopropane, cyclobutane, acetylene, spiropentane, bicyclobutane, cyclopropene, tetrahedrane, and cubane. Substituents investigated include Li, BeH, BH₂, BH₃⁻, CH₃, CH₂⁺, CH₂⁻, CN, CF₃, NH₂, NH₃⁺, OCH₃, OH, O⁻, and F. Stabilization of strained molecules is achieved with σ -donating, π -withdrawing, and most π -donating substituents. σ withdrawal destabilizes unsaturated linkages. Effects decrease in the order of increasing saturation, e.g., ethynyl > vinyl > cyclopropyl. The stabilizing effects of Li and O⁻ substituents are particularly striking. The strain in tetralithiotetrahedrane is calculated to be less than one-fourth of that in tetrahedrane.

The concept of strain in small-ring organic compounds, originally introduced by Adolph von Baeyer in 1885, has remained fundamentally unchanged since its inception. It is generally accepted³ that (Baeyer) strain energy is associated with compression of bond angles at saturated carbon centers below the ideal tetrahedral angle. This view assumes electronic effects other than those resulting from angle bending to be unimportant; in particular it allows for no influence of substituents. This view is also implicit in the widely accepted group-increment scheme for calculating molecular heats of formation,⁴ in which the strain energy of a substituted small ring is taken to be equal to that of the unsubstituted parent. A recent, comprehensive review of strained molecules⁵ questions this view after examining the small body of available ther-

mochemical data on substituted ring systems. It is the purpose of this paper to supplement published data with quantities derived from theoretical calculations, and demonstrate that, contrary to the established view, appropriate substitution can indeed have dramatic effects on the magnitudes of strain energies.

Interactions between substituents and strained ring systems have been examined in other contexts. It has been noted^{6,7} that substitution on cyclopropane can result in changes in the geometry of the ring. Substitution at the 7 position of 1,3,5-tropyliene (**1a**) alters the position of the equilibrium with the more strained norcaradiene (**1b**) isomer.⁸⁻¹¹ Similarly, a substituent's electronic character determines whether it occupies the 1 or the 5 position on semibullvalene (**2**).^{11,12} Cy-

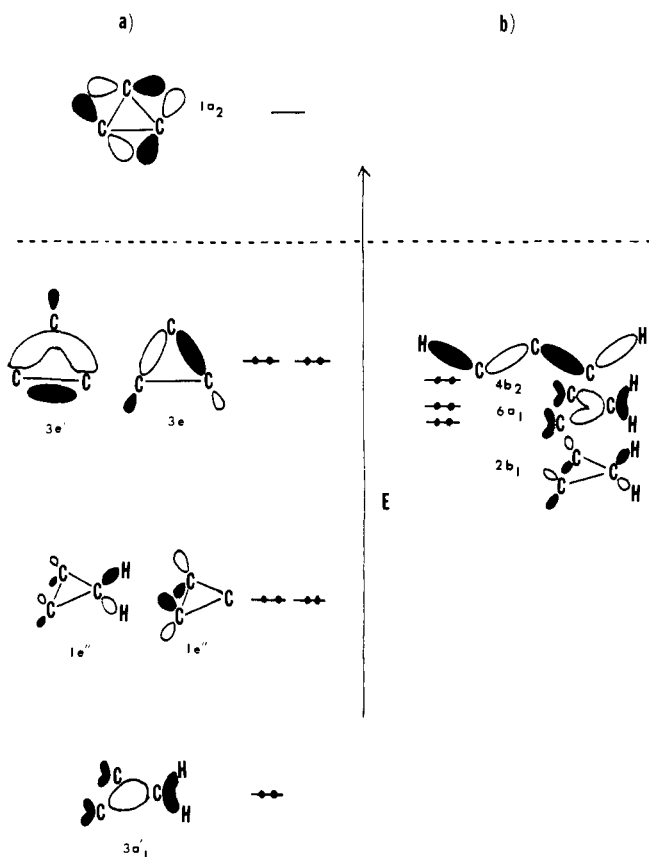


Figure 1. Molecular orbitals of propane relevant to interaction with a substituent at the 2 position, and analogous molecular orbitals of cyclopropane (only one of each set of degenerate orbitals of cyclopropane should be considered; cyclopropane's low-lying π^* -type orbital is also included).

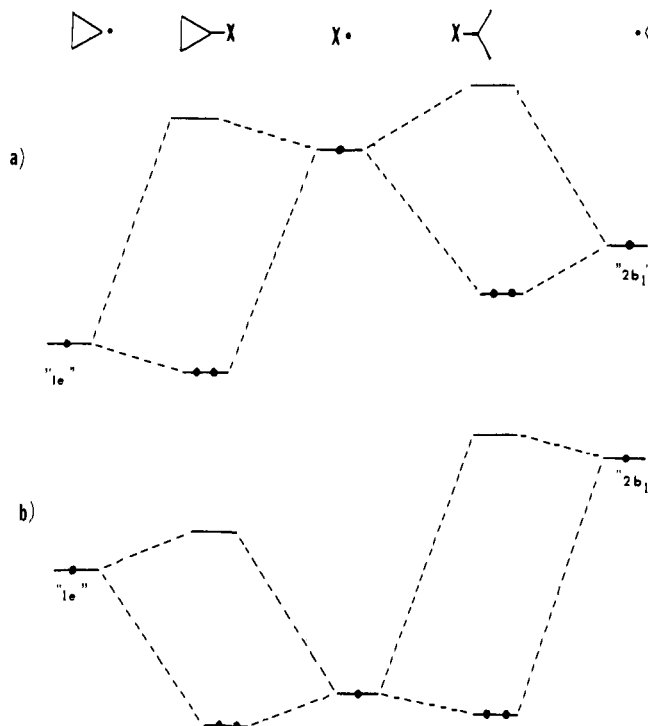
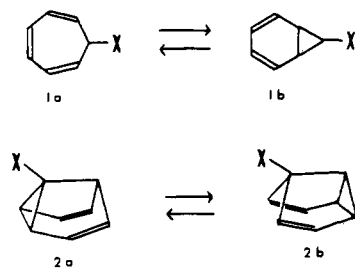


Figure 2. Comparisons of the σ interactions of cyclopropyl and isopropyl substituents with "localized" exocyclic (i.e., C-H) orbitals: (a) X is an electropositive substituent; (b) X is an electronegative substituent.

Relevant molecular orbitals for cyclopropane and its acyclic model propane are depicted for reference purposes in Figure 1.

Component a above has its origin in conventional views of the hybridization of "localized" exocyclic ring orbitals and is illustrated in Figure 2. It is the major determinant of substituent inductive effects on strained rings. The exocyclic cyclopropane molecular orbital is significantly lower in energy than the corresponding propane orbital consistent with the view that the former is of higher s character. If we "conceptually" cleave C-H bonds homolytically, then the approximate singly occupied molecular orbitals depicted in Figure 2 are obtained. If an electropositive substituent (e.g., Li or BH_2) has a single electron in a σ orbital, then formation of a bond with cyclopropane is more stabilizing than it would be with propane since the substituent electron will "drop" into a σ orbital of lower energy in the first case (Figure 2a). For an electronegative substituent (e.g., F or NH_3^+), it is the electron "localized" in the exocyclic ring carbon orbital which "drops" into an orbital largely localized on the substituent upon bond formation (Figure 2b). The "drop" in energy is greater for the electron localized in the propane orbital. Substituent effects based upon hybridizations of "localized" exocyclic carbon orbitals should be dominant where σ effects predominate. Thus, a pure σ -donating substituent will stabilize strained rings and a pure σ -withdrawing substituent will destabilize strained rings relative to unstrained model compounds.

The second component, b, is based upon concepts introduced by Hoffmann.⁶ Again consider cyclopropane as an example. In the Walsh picture¹⁶ two types of molecular orbitals describe the electron distribution among the carbon framework.¹⁷ In the first, a " σ -type" orbital ($3a_1'$),^{17b} overlap occurs in the center of the ring; this type of orbital is strongly bonding in character. In the second, a " π -type" orbital ($3e'$),^{17b} overlap occurs outside the ring and is poor owing to nonoptimal directionality of the atomic orbitals involved. This MO is weakly bonding in character. In cyclopropane itself, one such " σ -type" and two " π -type" orbitals are occupied and these are depicted

cyclopropane exhibits a strongly stabilizing interaction with an adjacent carbocation center.^{13,14} In these and other¹⁵ examples, while stabilizing interactions may occur, variations in the magnitude of the strain energy in the ring have not been explicitly considered. In part, this is because a convenient, unambiguous scheme for assessing stabilization of strain in a substituted ring system has not been presented. Such a scheme is proposed in this paper.

Theoretical Considerations

The theoretical basis of electronic substituent effects on strained and unsaturated molecules such as cyclopropane and ethylene has two main components: (a) σ interaction of the substituent with the "localized" exocyclic ring carbon orbital bonded to the substituent; (b) σ and π interactions of the substituent with orbitals delocalized over the carbocyclic network. Since changes in strain energies are defined here relative to acyclic model compounds (see discussion of strain energies below), the two components above each refer to differences in the substituent interactions with the strained (e.g., cyclopropyl-X) and unstrained (e.g., isopropyl-X) molecules.

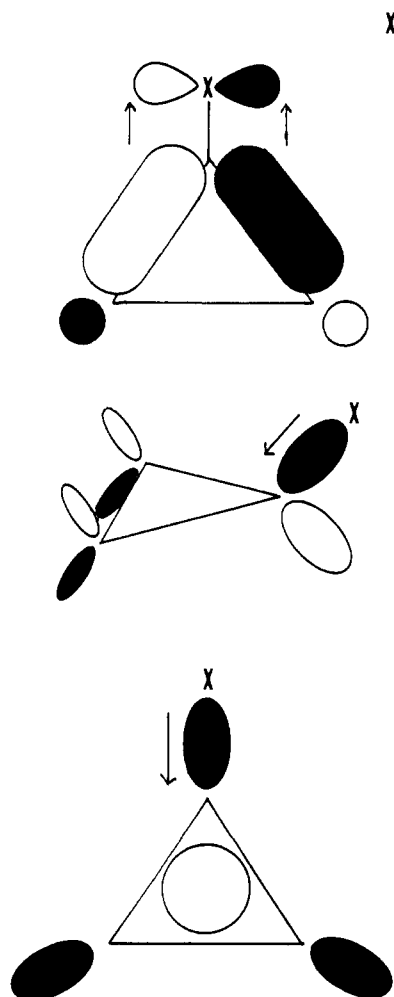


Figure 3. Interactions of an electropositive substituent having a vacant p orbital with the highest energy occupied σ - and π -type molecular orbitals of cyclopropane.

in Figure 1. The result is relatively weak binding between the carbon nuclei; hence the molecule is "strained" compared to an acyclic analogue in which electrons occupy more strongly bonding conventional CC orbitals. If one regards ethylene as "cycloethane", then this molecule can also be regarded as strained since it possesses an occupied relatively high energy π orbital in place of a σ orbital.

A substituent with a vacant p orbital or low-lying π^* orbital will have a stabilizing interaction with cyclopropane's " π -type" molecular orbital; there will be a decrease in the ring coefficients in the latter and withdrawal of some electron density from the ring. In the case of an electropositive substituent such as BH_2 , the shift in electron density is mitigated by inductive release of electrons to the ring which would have the effect of increasing the coefficients of the carbon orbitals comprising the " σ -type" molecular orbital. The net effect is a shift of ring electron density from higher energy " π -type" orbitals to lower energy " σ -type" orbitals with a concomitant decrease in ring strain. This is depicted in Figure 3. Of course, superimposed on the above is the transfer of electron density from the substituent to the "localized" exocyclic ring carbon orbital which should increase stability while not affecting strain. The fact that strained molecules such as cyclopropane have relatively high energy " π -type" molecular orbitals as well as low-energy " σ -type" molecular orbitals (both delocalized on the carbon framework and "localized" in exocyclic ring orbitals) compared to unstrained analogues explains stabilization by substituents such as BH_2 or Li.

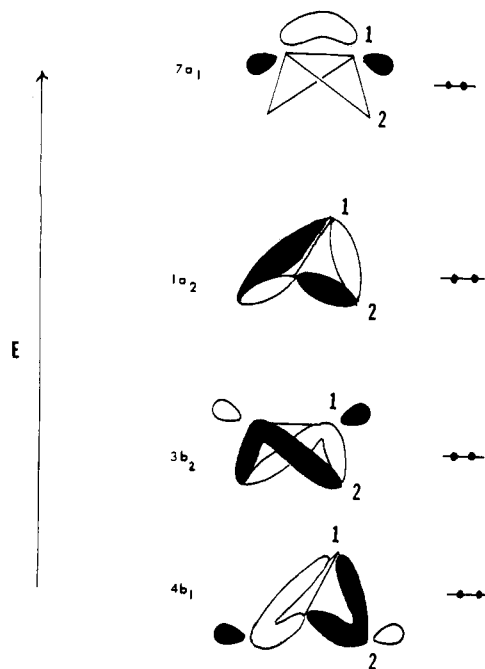


Figure 4. Highest occupied molecular orbitals of bicyclobutane relevant to interactions with substituents at the 1 and 2 positions.

A substituent that is an electronegative π withdrawer (e.g., CN or NO_2) will have inductive and resonance effects which are opposed. If the resonance effect dominates, as is usually the case, the substituent is stabilizing. Although withdrawal of σ and π electron density from the ring to the substituent has the effect of slightly increasing ring strain, the buildup of exocyclic π bond order will stabilize the substituted molecule.

If the substituent is a π donor, it will again stabilize strained ring derivatives since it will interact with low-lying π^* -type ring orbitals which are essentially absent in unstrained hydrocarbons. Population of a ring π^* orbital will "loosen up" bonding, thus effectively increasing ring strain. However, this is more than compensated for by an increase in the exocyclic π bond order. If the substituent is electropositive (e.g., CH_2^- or O^-), the π donor effect is particularly large and is reinforced significantly by net transfer of electron density from the substituent to the localized exocyclic ring carbon orbital. For a π donor, σ withdrawer (e.g., NH_2 , CH_3O , or F), the inductive and resonance effects are opposed with the latter usually dominating and providing net stabilization. However, if the σ effect dominates, then the strained molecule is destabilized relative to saturated model compounds.

In comparing stabilizations afforded by a substituent upon different molecular frameworks, the key factor is the energy difference between the appropriate highest occupied σ - and π -molecular orbitals of the parent hydrocarbon of interest. Large differences are usually, but not always, associated with high-lying π orbitals (low-lying π^* orbitals) and low-lying σ orbitals of both ring delocalized and localized exocyclic types. This is obviously true in the comparison of propane and cyclopropane. The greater σ - π split in acetylene relative to ethylene is, however, due entirely to particularly low-lying σ orbitals in the former. It makes the σ component of the substituent effect more important for acetylenes than it is for ethylenes and is the reason why BH_2 is more stabilizing for ethynyl than for vinyl, while F destabilizes ethynyl while it stabilizes vinyl (see later discussions).

An appropriate hydrocarbon molecular orbital is one having significant electron density at the substituent-bearing carbon and is of proper symmetry for mixing with the substituent's orbitals. Thus, the highest occupied MO of bicyclobutane

Table I. STO-3G Calculated Strain Energies (kcal/mol) of Monosubstituted Strained (Unsaturated) Molecules

substituent	vinyl	cyclopropyl	cyclobutyl	ethynyl	bicyclobutyl		cyclopropenyl		spiropentyl	cubyl	tetrahedryl
					1-	2-	1-	3-			
H	22.3	27.4	26.4	58.4	65.6	65.6	75.0	75.0	63.6	164.3	148.8
Li	3.3	19.5	23.8	10.4	40.7	53.3 exo ^a	35.2	68.2	51.8	147.9	112.6
BeH	8.2										
conj BH ₂	9.6	18.4		36.0	47.1						
nonconj BH ₂	16.2	24.1			56.2						
CH ₃	16.4	25.0	24.9	48.6	64.1	63.2 exo					
CN	12.1	21.6	21.9	53.2	59.7	60.8 exo ^b					
CF ₃	20.1	26.0			57.1						139.4
pyr, conj NH ₂	14.5	24.5		53.8	63.8 ^c						
trig, conj NH ₂	8.9			52.1	64.5						
trig, nonconj NH ₂	18.7										
OH	11.8	28.0		53.1	64.0						
OCH ₃	12.5	25.0									
F	16.6	26.6	22.9	59.6	65.4	63.8 exo	71.0	69.7	63.1	158.0	153.1
BH ₃ ⁻	9.1	18.8			46.5						
ideal, conj CH ₂ ⁺	-2.2	3.7	20.2	47.9	37.3						130.9
ideal, nonconj CH ₂ ⁺	30.0	30.0	24.3		69.2						
ideal, pyr CH ₂ ⁻	-22.8	10.7									
ideal, trig, conj CH ₂ ⁻	-34.0	9.7		-2.1	31.6						
ideal, trig, nonconj CH ₂ ⁻	6.8				35.2						
NH ₃ ⁺	25.9	30.8		83.8	74.3						
O ⁻	-19.5	11.6		1.5	32.2						

^a Calculated strain in endo isomer is 58.3. ^b Calculated strain in endo isomer is 60.9. ^c Structure is NH₂ anti to C₁C₃; syn isomer calculated to be 1.5 kcal/mol less stable.

(7a₁,^{17b} see Figure 4) is appropriate for π interaction with a substituent at C₁ but not for a substituent at C₂. For π interaction with a substituent at C₂ the 1a₂ molecular orbital^{17b} must be employed.

In evaluating the effects of a substituent upon a strained molecule, it is crucial to assess whether σ or π effects are dominant. One of the major goals of the present study is such an assessment for each of a variety of substituents. It is true that for a given substituent the relative σ and π effects change somewhat when the hydrocarbon framework is varied, but such effects are almost always smaller than changes in the σ - π balance accompanying variations of substituents on a given framework.

Methods

The data on which this paper is based are the strain energies listed in Table I as well as Table II. The molecules investigated include a variety of highly strained ring systems with groups of differing electronic characteristics. Molecules for which reliable experimental data exist were included wherever possible. Since such data are available for a number of substituted ethylenes and acetylenes, many of these, which may be regarded as strained "cycloethanes" and "bicycloethanes", were included for calibration and comparison. The substituents on molecules for which thermochemical data exist are almost universally σ donors lacking appreciable π effects (e.g., CH₃), σ acceptor- π donors (e.g., NH₂), or σ acceptor- π acceptors (e.g., CN). Molecules calculated theoretically were chosen so as to fill in gaps, especially to examine the effects of model substituents not well studied experimentally. Among these are the strong σ donor- π acceptors Li, BeH, and BH₂, σ donor- π donor O⁻, σ donor BH₃⁻, and the σ acceptor NH₃⁺. In a few cases polysubstituted ring systems were included in order to assess additivity and positional dependencies of substituent effects. However, in order to avoid complications due to strong interactions between substituents, no geminally disubstituted molecules were examined.

The strain energies in Table I are derived from experimental heats of formation taken directly from the literature and es-

Table II. STO-3G Calculated Strain Energies (kcal/mol) of Polysubstituted Molecules^a

molecule	strain
1,2-dilithiocyclopropane	20.8
1,2-difluorocyclopropane	28.0
1,2-dilithiobicyclobutane	37.3
1,3-dilithiobicyclobutane	24.0
2,4-dilithiobicyclobutane	45.2
1,2-difluorobicyclobutane	65.5
1,3-difluorobicyclobutane	68.0
2,4-difluorobicyclobutane	64.1
1,2-dilithiocyclobutane	23.0
1,3-dilithiocyclobutane	21.5
1,2-difluorocyclobutane	21.0
1,3-difluorocyclobutane	21.0
1,2-dilithiospiropentane	50.1
1,3-dilithiospiropentane	45.9
1,2-difluorospiropentane	63.8
1,3-difluorospiropentane	62.0
dilithiotetrahdrane	82.4
trilithiotetrahdrane	56.4
tetralithiotetrahdrane (corner lithiated)	33.4
difluorotetrahdrane	157.1
trifluorotetrahdrane	161.7
tetrafluorotetrahdrane	166.8

^a For strain energies of parent hydrocarbons, see Table I.

timated heats of formation obtained by theoretical methods. In the following sections we discuss the sources of these heats of formation and the methods used to obtain strain energies.

Experimental Heats of Formation

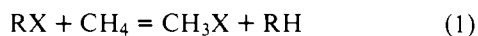
The experimental data used in this study are tabulated in supplementary Table 1, both for strained ring systems and strain-free reference compounds. All refer to the gas phase at 298 K. For neutral molecules, wherever possible, values were taken from a recent compilation of internally consistent computer-analyzed thermochemical data.¹⁸ For charged species, gas-phase proton affinity,^{19,20} ion molecule,²⁰ and

ionization appearance potential²¹ data were employed. To maintain consistency, where necessary heats of formation were derived with reference to other values given in this table. For example, all heats obtained from proton affinities refer to the single listed value for $\Delta H_f^\circ(\text{H}^+)$. Thus, some of the values may differ slightly from those given in the original publications. For error limits on the reported values, original sources or referenced compendia should be consulted.

Ab Initio Calculations

Theoretically calculated quantities fall in several categories. First, for several three-heavy-atom compounds estimated heats of formation have been reported in the literature, typically from 4-31G bond separation energies.²² These heats are reported in supplementary Table 1 for certain species without specifying the total energies or details of the calculations, for which original sources should be consulted. Second, in several cases total energies calculated at STO-3G or 4-31G levels have been taken from the literature, combined with appropriate other energies, and used to compute heats of formation as described below. Total energies for these entries are given in supplementary Table 1, but geometries and calculational details are to be found elsewhere. Finally, by far the largest body of calculated data is from this work. To obtain the total energies listed in this table, calculations were carried out employing the GAUSSIAN 70 package²³ at the STO-3G level²⁴ using standard geometries²⁵ wherever possible. As standard geometries do not exist for small-ring compounds, experimental geometries of parent hydrocarbons were employed with substituents replacing hydrogen affixed at standard bond distances.²⁵ References to the geometries of parent hydrocarbons are specified in supplementary Table 1.

The general aim of the theoretical work was not to obtain the energies of completely geometry-optimized molecules, but rather to obtain an extensive, consistent, and reasonably accurate set of heats of formation and strain energies within computer time and expense limitations. We have also listed calculational results published by others for geometry-optimized molecules at the next higher level of theory (4-31G). In order to derive heats of formation from isodesmic²² reactions, it is required that all molecules in a given reaction be calculated at the same level of theory and modeled similarly. Thus, for example



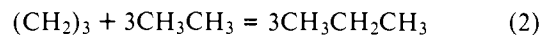
In the isodesmic comparison, typically all four species are calculated at the STO-3G level, both RX and RH are modeled with standard geometries, and both CH₄ and CH₃X are taken at optimized geometries if available. This approach follows that used in ref 26. In this approach errors due to basis set deficiencies and correlation energy differences are expected to largely cancel,²² so that reaction energies calculated at the STO-3G level should be reasonably accurate regardless of the nature of R. In a number of cases, most notably for substituted ethylenes, geometry-optimized data are published and these data were employed.

For the 19 molecules listed in supplementary Table 2, use of isodesmic eq 1 provides very satisfactory agreement of experimental and theoretical data (usually within 5 kcal/mol). Furthermore, the CH₃X model of eq 1 is seen to provide better numerical agreement than other models such as CH₃CH₂X.

Strain Energies

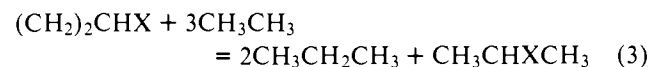
The approach to assessing strain energies devised here was independently arrived at elsewhere,²⁷ but its application to substituted ring systems was not discussed. This method involves a series of isodesmic reactions, termed "group separation reactions", which compare a strained ring system with the appropriate sum of its strain-free component groups, each

expressed as a neutral molecule. For example, cyclopropane contains three equivalent disubstituted methylene groups, C(H)₂(C)₂.²⁸ The smallest acyclic molecule containing this group is propane, so the group separation reaction for cyclopropane is



Note that balance is achieved by adding the appropriate number of ethanes on the left-hand side. The exothermicity of this reaction (the "group separation energy") is simply the strain energy of cyclopropane as is seen by comparing the group separation approach with the conventional group-increment method⁴ of strain-energy calculation. In the latter, strain is given as the difference between the heat of formation of cyclopropane and that of three strain-free C(H)₂(C)₂ groups. In the group-separation reaction, the left-hand side contains three strained C(H)₂(C)₂ and six C(H)₃(C) groups; the right-hand side also contains three C(H)₂(C)₂ plus six C(H)₃(C), but here the methylenes are strain-free. The negative energy of the reaction (GSE) is therefore equal to the total strain. In ref 27, strain energies calculated by group separation and conventional group increment approaches are compared quantitatively for a number of hydrocarbons.

Extension to substituted (and polysubstituted) ring systems is straightforward. The group separation reaction for a substituted cyclopropane is



where each molecule on the right-hand side contains one of the "corners", or groups, of the substituted cyclopropane. A disubstituted cyclopropane would have two (CH₂)₂CHX and two propanes in eq 3. The isopropyl-X molecule is employed to model all secondary derivatives such as spiropentyl, cyclobutyl, 2-bicyclobutyl, and 3-cyclopropenyl, as well as vinyl. For tertiary derivatives including 1-bicyclobutyl, tetrahydryl, and cubyl, as well as ethynyl and 1-cyclopropenyl, (CH₃)₃CX and isobutane are employed in eq 3. In all cases the strain energy of the ring system involved is given by the negative energy of the reaction as written. Strain energies calculated in this manner are collected in Table I. Polysubstituted molecules are listed in Table II.

At this point we note one ambiguity in our approach. The group separation reactions (eq 3) actually give rise to overall *stabilization* energies. In fact, we can imagine stabilization to arise not only from reduction in ring strain but also through buildup of bonding character between the unsaturated unit and its substituent. A substituent whose dominant effect is donation into a π^* -like orbital on the hydrocarbon may provide net stabilization by increasing the exocyclic bond order at the expense of increased antibonding character (i.e., strain) in the ring.

Discussion of Effects of Specific Substituents

We have earlier outlined some of the unifying theoretical aspects of substituted ethylenes and cyclopropanes. These apply to the other strained species examined here. We will discuss our results on a per substituent basis saving additional unified conclusions for the end. We remind the reader that inductive electron release stabilizes strained (or unsaturated) linkages and electron inductive withdrawal is destabilizing; π withdrawal is stabilizing and π release is almost always stabilizing.

Lithium (Li) Substituent. Lithium is calculated to reduce the strain of a vinyl derivative by 19.3 kcal/mol, a cyclopropyl derivative by 7.9 kcal/mol, and a 1-bicyclobutyl derivative by 24.9 kcal/mol (refer to Table I). Its dominant effect is σ donation but a calculated charge of -0.1 in the p_z orbital of

Table III. Values of $J(^{13}\text{C}-\text{H})$ in Parent Hydrocarbon at Carbon upon Which Lithium Substitution Is Made, Associated s Characters of External Carbon Orbitals, and Strain Reductions (Stabilizations) Calculated from Table I for Lithiated Hydrocarbons^{a-c}

molecule	$J(^{13}\text{C}-\text{H})$, Hz	% s character	strain redn
methyl lithium	125	25	0 (assumed)
lithiocyclobutane	136	27	2.6
<i>exo</i> -2-lithiobicyclobutane	153	31	12.4
lithioethylene	156.2	31	19.3
lithiocubane	160 ± 5	32	16.2
lithiocyclopropane	160.5	32	7.9
lithiospiropentane	160	32	11.8
<i>endo</i> -2-lithiobicyclobutane	169	34	7.3
1-lithiobicyclobutane	205	41	24.9
1-lithiocyclopropene	221	44	36.6
lithioacetylene	248.7	50	48.0

^a G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972. ^b J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972. ^c L. N. Ferguson, "Highlights of Alicyclic Chemistry", Part 1, Franklin Publishing Co., Palisade, N.J., 1973, pp 101-102.

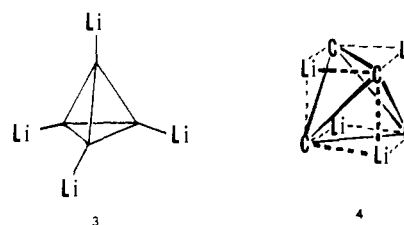
idealized lithioethylene suggests that it is at least a weak π acceptor. (STO-3G calculations apparently overestimate π conjugation by Li.²⁹) Lithium is a very unusual substituent reflected in the unconventional structures of the organic molecules containing it. Such species are electron deficient and compensate by forming as many bonds as possible by bridging and/or coordination.³⁰ For example, methyl lithium is a non-volatile solid known to occur as the tetramer (CH_3Li)₄ while its more volatile relative ethyllithium is tetrameric in the solid state and hexameric in the gas phase as well as in hydrocarbon solution.³¹ (Even upon electron impact "clusters" are still dominant among the resultant ions.³²) Monomeric CH_3Li has been observed at low temperature in an argon matrix.³³ A geometry-optimized STO-3G study finds the methyl group to be highly pyramidal.³⁴ There continues to be debate over whether the bonding between carbon and lithium in species such as monomeric CH_3Li is polar covalent³⁵ or ionic.³⁶ Bridged compounds are best regarded as held together by multicenter covalent bonding.³⁴ Additional examples include dilithioacetylene (C_2Li_2),³⁷ C_3Li_4 ,³⁸ and cyclopentadienyllithium ($\text{C}_5\text{H}_5\text{Li}$),^{39,40} which are calculated to have structures containing two, four, and four C-Li-C bridges, respectively. (Experimental solution-phase studies on the last species corroborate this geometry where the structure has been described as a contact ion pair.⁴¹) The compounds CLi_2F_2 , 1,1-dilithiocyclopropane, and 3,3-dilithiocyclopropene are calculated to contain planar tetracoordinate carbon,⁴² while stabilized perpendicular singlet and triplet structures are calculated for 1,1-dilithioethylene.^{29,43}

Results calculated at the STO-3G level are in good agreement with those obtained at the 4-31G level (5-21G for Li and Be⁴⁴). The enthalpies of formation calculated for (idealized) vinyl lithium according to eq 1 are 62.8 (4-31G) and 54.6 kcal/mol (STO-3G). For cyclopropyllithium the calculated heats of formation are 69.0 (4-31G) and 63.6 kcal/mol (STO-3G).

A clear correlation exists between the percent s character on the parent hydrocarbon's external C-H orbital (localized hybrid orbital on carbon attached to H) and the strain reduction (stabilization) in the corresponding lithiated derivative. This is shown in Table III. These results also support the view that lithium's dominant effect is through the σ framework. One would expect this trend if the carbon-lithium bond were ionic or polar covalent.

Another interesting observation is that the strain-energy reduction of 3-lithiocyclopropene is calculated to be smaller than that of lithiocyclopropane. This appears to reflect a "hint" of antiaromaticity in 3-lithiocyclopropene and is a small part of the 31.0 kcal/mol energy difference favoring 1-lithiocyclopropene over its 3 isomer⁴⁵ (1-fluorocyclopropene and 3-fluorocyclopropene are almost equienergetic). We also note that preferential bridgehead lithiation of bicyclobutane⁴⁶ is consistent with the calculated result that 1-lithiobicyclobutane is more stable than 2-lithiobicyclobutane (*exo* or *endo*).

The most striking result in the lithium series is the enormous strain reduction (115.4 kcal/mol, Table II) calculated for the idealized, corner-lithiated tetralithiotetrahedrane (**3**)—a result providing some reason for optimism over possible synthesis of C_4Li_4 . In fact, photochemical reaction of dilithioacetylene in liquid ammonia at -45°C produces a new substance which is stable under argon at -20°C .⁴⁷ This material appears to be monomeric C_4Li_4 according to field desorption mass spectrometry. Calculations at the STO-3G and 4-31G levels indicate that face-lithiated C_4Li_4 (**4**) is more stable than the corner-lithiated isomer by 26-27 kcal/mol. In fact, the calculations suggest that **4** completely lacks the classical strain energy of tetrahedrane.⁴⁷



Beryllium Hydride (BeH) Substituent. The substituent BeH is somewhat less of a σ donor than Li but the lowering of the energy of its vacant p orbital relative to that of Li makes it a stronger π acceptor. (Obviously the energy levels of the vinyl π orbitals would be different in the presence of Li or BeH even without explicit π interactions with the substituents because of their different polarization effects; this effect is smaller than the primary effect discussed above and for simplicity we will neglect it.) However, since the dominant effect of BeH is inductive in nature (see discussion of the BH_2 substituent for corroboration), it is less stabilizing than lithium. These qualitative views are in accord with the strain energies in Table I where strain relief (stabilization) in vinylberyllium hydride is less than that in vinyl lithium. The calculations for methylberyllium hydride as well as the vinyl and isopropyl derivatives converged only slowly. Our cyclopropylberyllium hydride calculation did not converge. It is because of these computational difficulties that we did not further investigate BeH derivatives.

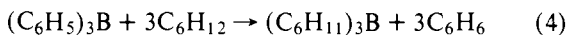
Methylberyllium hydride exists only as the hydrogen-bridged dimer,⁴⁸ while cyclopentadienylberyllium hydride has a pentahapto monomeric⁴⁹ structure like $\text{C}_5\text{H}_5\text{Li}$. However, $(\text{CH}_3)_2\text{Be}$ exists in monomeric form in the gas phase.⁵⁰

Borane (BH_2) and BH_3^- Substituents. The borane (BH_2) substituent is of particular interest because one may calculate planar and perpendicular conformers of, e.g., vinylborane, and reasonably factor out inductive (σ) and resonance (π) effects. This is quite useful since it then allows one to draw the conclusions stated earlier about the relative importance of inductive and resonance effects in Li and BeH derivatives. Similarly, planar and perpendicular conformers of vinyl derivatives (or cyclopropyl, etc.) of trigonal CH_2^+ , CH_2^- , and NH_2 allow one to dissect σ and π effects for these three additional groups which differ greatly in their electronic characteristics. The BH_2 group clearly reduces strain energy (Table I).

Methylborane has been isolated only in dimeric form and

is unstable to disproportionation to B_2H_6 and $B(CH_3)_3$.⁵¹ Calculations suggest that a "classical" CH_3BH_2 structure is favored over a hydrogen-bridged structure.⁵² Although the parents vinylborane and cyclopropylborane have not been characterized, substituted cyclopropylboranes are important intermediates in the hydroboration of cyclopropenes.⁵¹ Uncomplexed monoalkynylorganoboranes, R_2BCCR , are exceedingly rare species.⁵⁵

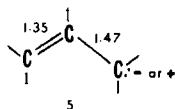
The calculated rotational barrier in vinylborane, 6.6 kcal/mol, is in good agreement with that calculated (8.7 kcal/mol) in another study.⁵⁴ This rotational barrier is significantly smaller than that of the allyl or "3-propenyl" cations (see next section), reflecting the lower π demand of neutral BH_2 compared with CH_2^+ . Furthermore, comparison of the stabilization (strain reduction) in perpendicular vinylborane (6.0 kcal/mol), attributable mostly to inductive effects, with the rotational barrier indicates that σ - and π -stabilizing effects by BH_2 on the vinyl system are about equal in magnitude. This leads one to conclude that the major sources of stabilization in Li and BeH derivatives of strained molecules are in the respective σ frameworks since their vacant p orbitals are progressively higher in energy and thus interact less with filled π orbitals. Further documentation of the stabilizing influence of borane substituents on unsaturated linkages is shown by the following isodesmic reaction:



Experimental calorimetric data show this reaction to be endothermic by 21.1 kcal/mol.

The BH_3^- substituent has the unique feature of being the only strong pure σ donor (i.e., lacking significant π effects) considered in this study. Interestingly enough, the stabilizations calculated for BH_3^- in vinyl, cyclopropyl, and 1-bicyclobutyl derivatives are virtually identical with those calculated for the BH_2 analogues in their most stable conformations. Recalling from the earlier discussion that in such conformations σ and π stabilization afforded by the BH_2 substituent are about equal, one realizes that the inductive stabilization afforded by BH_3^- is about double that afforded by BH_2 . At first glance one might be surprised that the inductive stabilization provided by BH_3^- is not much larger. However, the total charge on the three hydrogen atoms bound to boron is calculated at -0.61 , thus mitigating the group's inductive donation to the carbocyclic network.

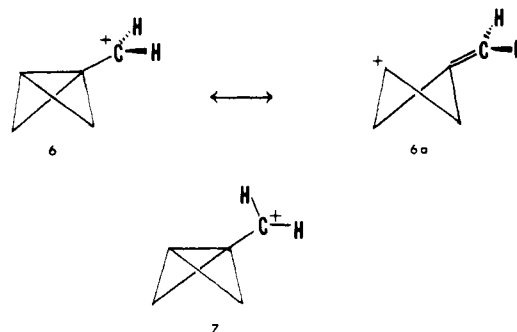
CH_2^+ Substituent. This substituent is a strong σ withdrawer (σ destabilizer) and a very strong π acceptor (π stabilizer). The importance of these two opposing effects is illustrated for the idealized "3-propenyl" cation (**5**, $C_1C_2 = 1.35 \text{ \AA}$; $C_2C_3 = 1.47$



\AA ; i.e., substitute CH_2^+ for H on ethylene) in its planar and (less stable) perpendicular conformations. The value in Table I indicates a rotational barrier of 32.2 kcal/mol for this ion. This can be simply taken as the π stabilization present in the planar conformer of "3-propenyl" cation. Comparison of perpendicular "3-propenyl" cation with isobutyl cation in the manner of Table I indicates a *destabilization* of 7.7 kcal/mol in the former.⁵⁵ This is clearly due to the destabilizing inductive withdrawal of CH_2^+ . This should be contrasted with the result cited earlier for the perpendicular conformer of vinylborane. Perpendicular vinylborane is stabilized owing to the electron-releasing inductive nature of BH_2 . An optimized geometry for (planar) allyl cation ($C_1C_2 = C_2C_3 = 1.385 \text{ \AA}$) is 4.9 kcal/mol lower in energy than the planar "3-propenyl" cation cited above (supplementary Table 1). The optimized STO-3G rotational barrier is calculated at 34.5 kcal/mol. Furthermore,

the stabilization energy is calculated to be destabilized by 4.8 kcal/mol. Thus, we see that stabilizing π interactions between vinyl and trigonal CH_2^+ are about six times as large as destabilizing σ effects. Recall that, for BH_2 (trigonal) attached to vinyl, both σ and π effects are stabilizing and about equal in magnitude.

The σ and π effects are mitigated in cyclopropyl derivatives relative to vinyl derivatives. The stability of the cyclopropylcarbinyl cation and its conformational aspects have been extensively reviewed.^{56,57} The calculated rotational barrier for the methylene group in cyclopropylcarbinyl cation is 26.3 kcal/mol. The lower rotational barrier in cyclopropylcarbinyl cation compared to that in allyl (or "3-propenyl") cation is due to the fact that the π -like (Walsh) orbital in cyclopropane is lower in energy than the π orbital in ethylene.^{17b,c} Thus, the stabilizing π interaction is reduced. An extremely interesting effect having a similar explanation is noted in the comparison between gauche (**6**) and bisected (**7**) conformers of 1-bicyclobutylcarbinyl cation.¹⁵



The calculated barrier to methylene rotation is quite large (31.8 kcal/mol) reflecting mainly the large stabilization in **6** (28.3 kcal/mol) as well as 3.5 kcal/mol destabilization in **7**. This is certainly in large part attributable to the high p character (ca. 96%⁵⁸) and poor overlap in the central bond of bicyclobutane which combine to make this canted π -like orbital localized between C1 and C3 higher in energy than the π orbital of ethylene.^{17b,c} This is mitigated somewhat by overlap with the CH_2^+ substituent's p orbital which is not as good as in a planar allyl or "3-propenyl" structure. Alternatively, we may simply view canonical structure **6a** as an important resonance contributor having considerably reduced strain compared to canonical structure **6**. The stability of **6** may be the explanation for the enhanced reactivity of 1-bicyclobutylcarbinyl *p*-nitrobenzoate, which solvolyzes at least 1000 times more rapidly than cyclopropylcarbinyl *p*-nitrobenzoate.⁵⁹

The stabilization in propargyl cation (10.5 kcal/mol, Table 1) is smaller even than the stabilization in bisected cyclopropylcarbinyl cation and is considerably less than in planar allyl cation. First, the inductive destabilization due to CH_2^+ will be more severe in propargyl cation since the σ framework in acetylene is lower in energy (has more s character) than that in ethylene. Additionally, propargyl cation should evidence less π stabilization since the energy gap between a vacant p orbital on CH_2^+ and the acetylenic π orbital is greater than the gap between the vacant p orbital and an olefinic π orbital. One may cite the adiabatic ionization potentials⁶⁰ of acetylene (11.8 eV) and ethylene (10.5 eV) in support of this view as well as the calculated π orbital energies of acetylene and ethylene.^{17c}

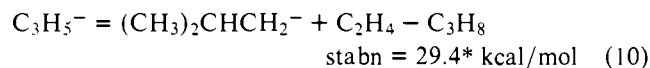
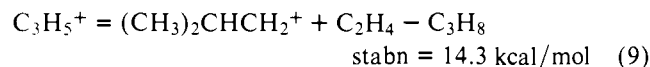
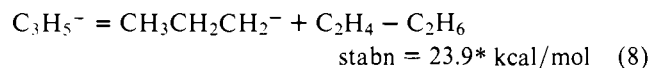
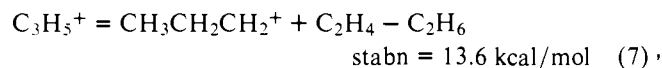
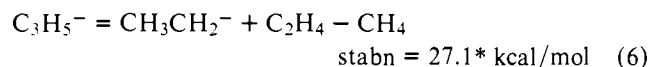
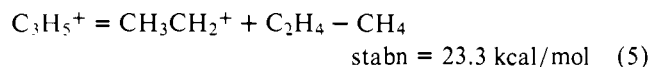
CH_2^- Substituent. The calculations cited in this paper as well as other published work⁶¹ suggest to us that the CH_2^- group, especially in its planar (trigonal) structure, strongly stabilizes unsaturated linkages. The calculated strain reduction in planar allyl anion (67.1 kcal/mol) is the largest value obtained for a substituted ethylene in this study (the stabilization in planar "3-propenyl" anion (**5**), 56.5 kcal/mol, is still quite large). Noting that the rotational barrier in "3-propenyl" anion

(trigonal CH_2^-) is calculated at 40.7 kcal/mol, we conclude that π effects are one and one-half to two times as great as stabilizing σ effects in this system. The predominant source of π stabilization is a strong interaction between the occupied p orbital on CH_2^- and the vinylic π^* orbital. An additional indication of the π stabilization is furnished by comparison of the calculated inversion barriers of isobutyl anion (13.1 kcal/mol, pyramidal CH_2^- most stable), "3-propenyl" anion (2.0 kcal/mol), and allyl anion (ca. 0 kcal/mol).

Although it is true that calculations such as those employed in this study are not very reliable for anions, useful results should be obtained through isodesmic comparisons.⁶² Additional studies of these studies employing the 4-31G basis set are in progress.

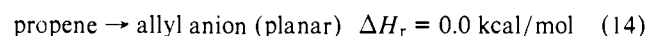
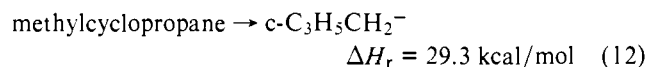
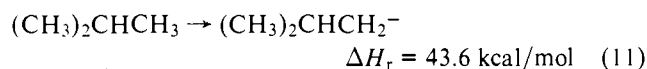
The electron affinity (EA) of methyl radical (CH_3) has been determined recently,⁶³ and its small value (1.8 ± 0.7 kcal/mol) is in rather good quantitative, if not qualitative, agreement with theoretical results calculated with extended basis sets.⁶⁴ These latter studies indicated that CH_3^- is essentially unbound and methyl substitution^{64c} (e.g., C_2H_5^-) does not increase anion stability relative to the radical and an electron. Thus, the enthalpies of formation of CH_3^- , C_2H_5^- , $(\text{CH}_3)_2\text{CHCH}_2^-$, and $(\text{CH}_3)_3\text{CCH}_2^-$ in supplementary Table 1 assume the EAs of the corresponding radicals to be equal to 1.8 kcal/mol. In contrast, the electron affinity of allyl radical has been experimentally determined to be 0.55 eV (12.7 kcal/mol)⁶⁵ and this is employed with ΔH_f° for allyl radical (40.6 kcal/mol) to obtain the enthalpy of formation of C_3H_5^- listed in this table.

We may compare the experimental stabilization energies of allyl cation and allyl anion according to models based upon methyl species, ethyl species, and isobutyl species in the manner of eq 5-10 (an asterisk denotes that ΔH_f° of the radical has been employed with an assumed EA of 1.8 kcal/mol; see above discussion).



In all cases above allyl anion is calculated to be more stabilized than allyl cation. We feel that this is a real effect, although we acknowledge the ambiguity in choosing models which compare anions with cations. Its basis appears to be as follows: (a) π stabilizations in allyl cation and allyl anion are fairly similar; (b) the inductive effect of CH_2^- reinforces π stabilization, while the inductive effect of CH_2^+ is destabilizing and opposes, but is significantly less than, π stabilization in the allyl system. Allyl anion is close to 20 orders of magnitude weaker base in solution than alkyl anions.⁶⁶ Our calculations (best values in supplementary Table 1) suggest an ordering of gas-phase basicities apparent through comparison of the values of ΔH_f for reactions 11-14 shown below. The acidity of the 3 proton of propyne is calculated to be less than the acidity of the allylic proton in propene. This is consistent with the results of Breslow, who finds propargyl anion to be ten orders of magnitude stronger base than allyl anion in solution.⁶⁶ This can also

be explained in the context of this paper. Although the π stabilization should be greater in propargyl anion relative to allyl anion, the π stabilization (the dominant effect) should be less in the former. As the π orbital in acetylene is more bonding than the π orbital in ethylene, the π^* orbital must be more antibonding. Thus, the stabilizing interaction between the π^* orbital of acetylene and the filled p orbital of trigonal CH_2^- should be smaller in propargyl anion than in allyl anion. Although we have assumed trigonal CH_2^- in propargyl anion, a complete study obtaining the optimized structures and energies of propene, propyne, allyl anion, and propargyl anion employing a larger basis set is required in order to derive firmer conclusions on these gas-phase acidities.



Methyl (CH_3) Substituent. The methyl group is strain reducing relative to hydrogen (Table I). There is no evidence in our work for any appreciable hyperconjugative stabilization of neutral strained molecules. One may simply explain the stabilization by methyl in terms of its electron-releasing inductive effect when attached to carbon atoms employing localized external orbitals of increased s character such as the sp^2 orbital aimed at hydrogen in ethylene.⁶⁷ The reductions in strain energies are relatively small (Table I): 6.6 kcal/mol in propene; 2.4 kcal/mol in methylcyclopropane; 9.8 kcal/mol in propyne; 1.5 kcal/mol in 1-methylbicyclobutane.

In many respects we feel that methyl might be employed as the "zero point" in the standardization of other substituent effects, since hydrogen is most unusual from the points of view of its steric requirement and polarizability. In this way we would conclude that perpendicular NH_2 or the CF_3 group destabilizes ethylene relative to methyl since the respective reductions in strain energies in the corresponding olefin (3.9 and 2.5 kcal/mol) are smaller than for propene.

Cyano (CN) Substituent. Cyano substituents were examined in considerable detail because a reasonable amount of thermochemical and structural data exists for unsaturated nitriles. A particular result that attracted our attention is the rather large experimental stabilization (10.6 kcal/mol) claimed for 1-cyanobicyclobutane.⁶⁸ Comparison between calculated (Table 1) and experimental (from data in supplementary Table 1) reductions in strain energies can be made for cyanoethylene (9.3, 0.2 kcal/mol), cyanocyclopropane (5.8, 0.4 kcal/mol), cyanocyclobutane (4.5, 3.5 kcal/mol), and 1-cyanobicyclobutane (5.9, 10.6 kcal/mol). In general, our STO-3G calculations appear to overestimate stabilizations. The noteworthy exception is 1-cyanobicyclobutane and we find ourselves at a loss to explain this discrepancy unless the strain energy was underdetermined experimentally. This could occur if a very small amount of 1-cyanobicyclobutane oligomerized prior to combustion. The cyano group's affinity for π electrons is the basis for the structural changes it induces on a cyclopropane ring: $\text{C}_1\text{-C}_2$ and $\text{C}_1\text{-C}_3$ bonds lengthened, $\text{C}_2\text{-C}_3$ bond shortened.⁶⁹ We employed these experimental ring bond lengths along with normal cyclopropyl C-H bond lengths and angles along with idealized CN parameters²⁵ in one of our calculations of cyanocyclopropane. We found that this "experimental" structure was calculated to be 0.1 kcal/mol less stable than the idealized structure having three equal C-C bond lengths. Although additional optimization of the experimental geometry would undoubtedly produce a structure more

stable than the idealized one, it appears that calculations at the STO-3G level are not sensitive enough to correctly predict small structural changes of this type.

An X-ray crystallographic structure has been published for 1,3-dicyanobicyclobutane which indicates a relatively large dihedral (flap) angle between the two three-membered rings (126° as opposed to 121° in the parent hydrocarbon).⁷⁰ When a calculation of the published geometry was compared to the result for the idealized structure (same geometry as C_4H_6), the latter was found to be more stable by 26.2 kcal/mol. However, experimental uncertainties in the location of hydrogens led to unreasonably short C-H bond lengths in the published structure. When the experimental structure was employed along with C-H bond lengths set at 1.093 Å, the energy improved but this "improved experimental geometry" was still calculated to be 6.8 kcal/mol less stable than the idealized geometry. Either crystal packing is forcing an unnatural structure upon the molecule, or the STO-3G level of approximation simply cannot calculate the most stable geometry.

Trifluoromethyl (CF_3) Substituent. The trifluoromethyl (CF_3) group and other perfluoroalkyl groups have received attention recently for their striking ability to stabilize certain unsaturated linkages and strained species in particular. For example, hexakis(trifluoromethyl)(Dewar benzene) and hexakis(trifluoromethyl)prismane are over 30 kcal/mol more stable relative to the aromatic $(CCF_3)_6$ isomer than hexamethyl(Dewar benzene) and hexamethylprismane are relative to their aromatic $(CCH_3)_6$ isomer.⁷¹ The term "perfluoroalkyl effect" was coined to denote stabilization, assumed to be both thermodynamic and kinetic in origin, conferred on a strained ring system by substituents such as CF_3 .⁷¹ Some of the most spectacular examples include the remarkable stability of hexakis(trifluoromethyl)-3,3'-bicycloprenyl (half-life greater than 2 h at $360^\circ C$),⁷² octakis(trifluoromethyl)cyclooctatetraene (only slight decomposition after 1 h at $400^\circ C$),⁷³ and hexakis(pentafluoroethyl)(Dewar benzene), which is actually more stable than its aromatic isomer at temperatures above $280^\circ C$.⁷⁴ The structural parameters employed in this study for trifluoromethyl derivatives are C- CF_3 1.505 Å, C-F 1.347 Å, C-C-F 112° .⁷⁵

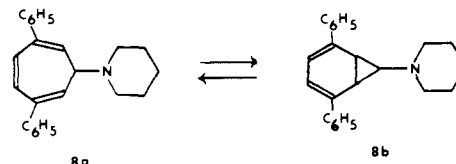
There are very little published thermochemical data for CF_3 derivatives of hydrocarbons. The data in Table I suggest that CF_3 is less stabilizing than CH_3 when attached to vinyl and cyclopropyl groups. This is in accord with the little published thermochemical data and suggests that the enormous stabilizing effects of trifluoromethyl groups are predominantly, if not entirely, manifestations of kinetic stabilization.⁷⁶ We feel that, in an absolute sense, CF_3 is a mildly destabilizing substituent when attached to vinyl and perhaps cyclopropyl. This is explicable if one simply assumes that CF_3 is a σ -withdrawing group having negligible hyperconjugative effects.⁷⁶ For example, the most stable conformation of 3,3,3-trifluoropropene, which we calculate to possess C_s symmetry with a C-F bond eclipsing the olefinic linkage in accord with experiment,⁷⁴ is calculated to be stabilized relative to ethylene by only 2.5 kcal/mol (recall that propene is stabilized by 6.6 kcal/mol). Since a value of 3.2 kcal/mol is an accepted estimate of the "double bond stabilization parameter" of methyl,⁷⁷ then the CF_3 group should be destabilizing by -0.9 kcal/mol ($3.2 - (6.6 - 2.5)$). Thus, the stability of octakis(trifluoromethyl)cyclooctatetraene is surely completely kinetic in character since this molecule may actually be thermodynamically destabilized relative to cyclooctatetraene. The calculated stabilization in trifluoromethylcyclopropane is even smaller than that in 3,3,3-trifluoropropene. The calculated stabilizations afforded 1-trifluoromethylbicyclobutane (8.7) and trifluoromethyltetrahedrane (9.4) are greater in magnitude than those obtained for other species discussed here. We suspect that values of 3-6

kcal/mol are probably more realistic and a significant fraction of this arises from reduced steric repulsions in the strained molecules compared to their acyclic analogues. In any case it appears that any thermodynamic stabilization present in tetrakis(trifluoromethyl)tetrahedrane would be a fairly small fraction of the strain energy of the parent hydrocarbon. Nevertheless, the recently reported isolation of tetra-*tert*-butyltetrahedrane,⁷⁸ which will hopefully be confirmed by direct molecular weight measurements and crystallographic data, provides some optimism for the potential kinetic stability of tetrakis(trifluoromethyl)tetrahedrane.

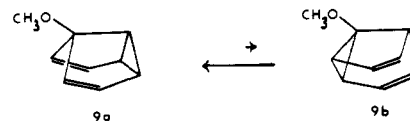
As Lemal and Dunlap have noted,⁷¹ the dramatic decreases in heats of aromatization of isomers of hexakis(trifluoromethyl)benzene are explicable in terms of thermodynamic destabilization of the aromatic isomers rather than reduction in strain of these species.

Amino (NH_2), Methoxy (CH_3O), and Hydroxy (OH) Substituents. The NH_2 , CH_3O , and OH groups are inductive destabilizers and resonance stabilizers and the sum total of their effects upon the stabilities of strained rings and unsaturated linkages is not immediately obvious. The "double-bond stabilization parameter" for CH_3O is 5.2 kcal/mol compared to 3.2 kcal/mol for *n*-alkyl groups such as methyl and 0.0 kcal/mol for hydrogen.⁷⁷ Thus, the stabilizing π effect is dominant. One would expect similar, if lessened, effects for cyclopropanes. The hydroxy group should behave similarly, while one would, at first glance, anticipate greater stabilization by the amino group since it is a weaker σ withdrawer and a stronger π donor.

It has already been noted that the amino-substituted system **8** below is about equally divided between tropyliene and



norcaradiene isomers.¹⁰ This is apparently consistent with the ability of the amino group to stabilize a cyclopropane. However, the semibullvalene equilibrium below is almost completely dominated by the 5 isomer (**9a**)¹² in a manner leading

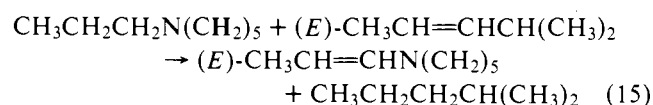


one to assume that CH_3O is a cyclopropane destabilizer. It is tempting to attribute the results above to the increased ability of NH_2 to stabilize a cyclopropane ring which is indicated in the cyclopropyl column of Table I. However, the two systems are quite different and we feel that they may not be quite germane for extrapolation to simple cyclopropanes except where substituent effects are strong. In addition, the cyclopropyl derivatives in Table I have not been uniformly optimized and it would appear that only very precise thermochemical studies will allow conclusions to be drawn on this question.

There are, surprisingly, no experimental calorimetric data for gas-phase enamines. The hypothetical all planar (C_s) aminoethylene (ethenamine) is calculated to be stabilized by 13.4 kcal/mol relative to 2-aminopropane (planar NH_2). Certainly this stabilization is entirely attributable to π interaction and, as expected, is greater than for OH and OCH_3 groups. The data in supplementary Table 1 indicate that the STO-3G calculations, although not completely optimized, predict that the amino group in ethenamine adopts a pyramidal, albeit conjugating, structure (ca. 4 kcal/mol more stable than the planar structure). While the stabilization by a pyramidal, conjugating amino group attached to vinyl is calculated at only 7.8 kcal/mol (compare to 13.4 kcal/mol for tri-

gonal NH₂), the amino inversion barrier is calculated to more than outweigh the additional conjugation in the all-planar structure. However, STO-3G calculations are known to overestimate N inversion barriers,^{79a} and careful optimization with larger basis sets is required for more definitive conclusions. However, a microwave study of ethenamine, while not definitive, indicates pyramidal geometry at nitrogen.^{79b} The stabilization of perpendicular aminoethylene (trigonal NH₂), in which the p orbital on nitrogen is orthogonal to the π system, is calculated at 3.6 kcal/mol. This is 2.3 kcal/mol less than that in propene.

We can partially corroborate our conclusions by considering the following isodesmic reaction:



From calorimetric data on the liquids,¹⁸ we find this reaction to be exothermic by 5.6 kcal/mol. This should be compared with the earlier 8 kcal/mol stabilization predicted for enamines. Strictly speaking, one should consider gas-phase species. However, we note the near equality of ΔH_v° for CH₃CH₂CH₂CH(CH₃)₂ and CH₃CH=CHCH(CH₃)₂ ($\Delta\Delta H_v^\circ = 0.1$ kcal/mol) and of related pairs of non-hydrogen-bonding nitrogen species (e.g., CH₃CH₂CH₂CN and (Z)-CH₃CH=CHCN ($\Delta\Delta H_v^\circ = 0.3$ kcal/mol). As such, we are confident of the qualitative, if not quantitative, aspects of our prediction.

The stabilization in pyramidal aminoethylene is calculated to be 2.0 kcal/mol less than in methyl vinyl ether, while methoxycyclopropane is calculated to be 0.5 kcal/mol less stabilized than cyclopropylamine, for which both structural and calorimetric data exist. The calculated stabilization in methyl vinyl ether is greater than in propene in accord with experimental results (Table I). As in most of our reported results, the magnitudes of stabilizations (strain reductions) have been overestimated. The greater stabilization afforded by NH₂, in a hypothetical planar structure, relative to OCH₃ is understandable in terms of decreased σ destabilization and increased π stabilization afforded by the former substituent. However, the conclusion that the stabilization present in the most stable form of ethenamine is less than that in methyl vinyl ether is, at first glance, surprising. It has to do with the relative magnitudes of resonance interactions and amino inversion barriers calculated at the STO-3G level.

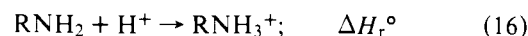
The experimental enthalpy of formation of aminocyclopropane¹⁸ allows one to calculate a thermodynamic stabilization of 2.4 kcal/mol in this molecule. We feel that the excellent agreement between this value and our calculated value (Table I) is somewhat fortuitous. A revised microwave structure has been published for aminocyclopropane.⁸⁰ This structure is not readily explicable through application of Hoffmann's arguments. The results in Table I indicate that CH₃O is less stabilizing than OH. However, we suspect that it is more likely that the most recent study⁸¹ of the small vinyl alcohol molecule has achieved the absolute minimum than studies of methyl vinyl ether, which possesses so many more degrees of freedom. It is apparent that differences in stabilizing abilities between NH₂, OH, and OCH₃ are subtle and may only be settled by finely tuned investigations such as comparison of the tropylidene-norcaradiene equilibrium for all three.

Ammonio (NH₃⁺) Substituent. The ammonio substituent is a particularly interesting group since it is the simplest σ withdrawer lacking significant π effects examined in this study. As such it is anticipated to increase ring strain, or more generally decrease the stability, of unsaturated linkages relative to their saturated analogues. Table I clearly shows this effect

Table IV. Relative Calculated Gas-Phase Basicities of Primary Amines Calculated According to Equation 16, Where the Larger the Positive Value of $\Delta H_f^\circ(\text{rel})$ the Weaker Base, and Relative Calculated Gas-Phase Acidities of Selected Alcohols According to Equation 19 Where More Negative Values of $\Delta H_f^\circ(\text{rel})$ Denote Greater Acid Strength

compd	$\Delta H^\circ(\text{rel})$, kcal/mol
A. RNH ₂	
<i>tert</i> -butylamine	0 (strongest base)
isopropylamine	2.4
cyclopropylamine	8.7
1-bicyclobutylamine	10.5
vinylamine	13.8
ethynylamine	29.9 (weakest base)
B. ROH	
isopropyl alcohol	0 (weakest acid)
<i>tert</i> -butyl alcohol	-3.4
cyclopropanol	-16.4
1-bicyclobutanol	-35.2
vinyl alcohol	-36.2
ethynyl alcohol	-59.6 (strongest acid)

whereby the strain energies of vinylammonium, cyclopropylammonium, ethynylammonium, and 1-bicyclobutylammonium ions are greater than in their saturated analogues. The calculations predict gas-phase basicities (eq 16) shown in Table

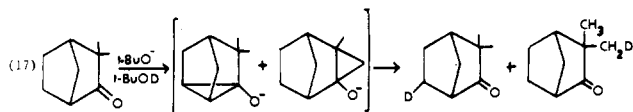


IVA which also support this view. The calculations predict that *tert*-butylamine is a stronger base in the gas phase than isopropylamine, in excellent qualitative and quantitative agreement with experiment.¹⁹ Unfortunately, there are no published data on the gas-phase basicities of the unsaturated amines listed in Table IVA. In further agreement with these calculations are the experimental aqueous basicities of isopropylamine ($\text{p}K_b = 3.33$), cyclobutylamine ($\text{p}K_b = 3.96$), and cyclopropylamine ($\text{p}K_b = 4.90$).⁸² Similarly, 1-bicyclo[1.1.1]pentylamine ($\text{p}K_b = 5.42$)⁸³ is also a weak base compared to its analogue *tert*-butylamine. While the difference in experimental condensed phase basicities of isopropylamine and cyclopropylamine ($\Delta\Delta H^\circ = 2.2$ kcal/mol)⁸² is smaller than the calculated (gas-phase) difference (6.3 kcal/mol, see Table IVA), it is well to remember the role of the solvent, which tends to mitigate this difference. If one assumes that the ammonium salt is solvated more tightly than the amine, it is apparent that "tying back" of the alkyl groups in the manner of cyclopropylamine and 1-bicyclo[1.1.1]pentylamine should increase base strength of these unsaturated species relative to their saturated analogues. Thus, it would appear that solvent effects should mitigate the trends in gas-phase basicities. Finally, we note that a decrease in pH forces the equilibrium of **8** to favor the tropylidene isomer which has now a piperidinium substituent.¹⁰ While this is consistent with our view that ammonium substituents increase strain energies, the effect may also be attributed to the the removal of stabilizing resonance effects. We feel that it is a combination of these two effects.

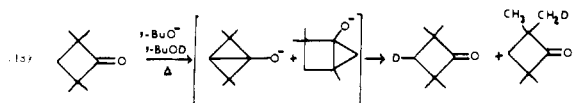
Oxy (O⁻) Substituent. The oxy (O⁻) substituent is a relatively strong σ and π donor and has recently received attention from two other groups of researchers.^{84,85} One can crudely assess the σ effect of O⁻ by comparing the calculated charge on the hydrogen atoms in ethylene (+0.060) with those on vinyloxy (-0.35, -0.055, and -0.061). These stabilizing effects reinforce each other and the reductions in strain energy (Table I) are consistent with this view. The stabilizations are calculated to be quite substantial. It is true that calculations of the present type upon anions often lead to erroneous conclusions, but, as in the case of the carbanions discussed earlier,

one can obtain useful results for alkoxides if isodesmic equations are employed.⁶²

The phenomenon of homoenolization (e.g., eq 17)⁸⁶ is



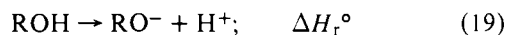
consistent with some stabilization in cyclopropoxy anions. Even more striking is the finding that the C3 protons in 2,2,4,4-tetramethylcyclobutanone are inherently five times as active toward exchange as the methyl protons (eq 18).⁸⁷ Table I il-



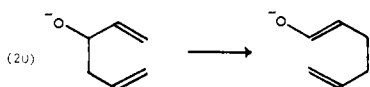
lustrates the extremely stabilizing interaction afforded by O⁻ at the bicyclobutane bridgehead and we feel that this is the reason for preferred exchange of the C3 proton. For further comparison, we calculated the stabilization (strain reduction) O⁻ provides at the bridgehead position of bicyclo[2.1.0]pentane at 7.4 kcal/mol less than at the bridgehead position of bicyclobutane. A direct comparison was attempted between the alkoxide anions in eq 18. The STO-3G calculations find bicyclo[2.1.0]pentane⁸⁸ to be 28.6 kcal/mol more stable than *exo*-2-methylbicyclobutane. Use of Benson's group increment scheme⁴ provides an enthalpy difference of only 8.6 kcal/mol favoring bicyclo[2.1.0]pentane. The inability of the STO-3G basis set to directly compare energies of molecules differing in ring strain is well documented.⁸⁹ (The isodesmic approach which compares substituted molecules with their parent hydrocarbons largely eliminates errors arising from differences in strain energies of different molecular systems.) We calculate 1-bicyclo[2.1.0]pentoxide to be 21.2 kcal/mol more stable than *exo*-2-methyl-1-bicyclobutoxide. If the 20.0 kcal/mol "correction factor" above is applied, 1-bicyclo[2.1.0]pentoxide is still seen to be 1.2 kcal/mol more stable than its isomer.

The calculated stabilization energies (strain reductions) in unsaturated alkoxy anions are quite substantial (Table I). The discrepancy between experimental and calculated heats of formation of ⁻CH₂CHO is quite large (supplementary Table 2). The enthalpy of formation of isopropoxide employed was obtained from the literature.^{20c} The experimental heat of formation of "vinyloxy⁻" is obtained by combining the dissociation energy of H-CH₂CHO (95.1 kcal/mol)⁹⁰ with the electron affinity of CH₂CHO (40.7 kcal/mol),⁹¹ an admittedly poor representation of ⁻CH₂CHO.

The relative gas-phase acidities (eq 19) of some primary alcohols are listed in Table IVB. Unsaturated (strained) alcohols are seen to be stronger acids. Experimental data support the calculated result that *tert*-butyl alcohol is more acidic than isopropyl alcohol.^{20a,b}



Finally, we note that the enormous rate enhancements (10¹⁰-10¹⁷) observed for the oxy-Cope rearrangement (eq 20)⁹² are consistent with our calculated results. The π conju-



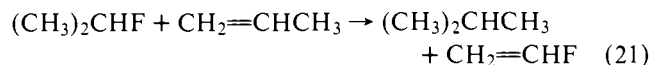
gating effect which accelerates a rearrangement in which carbon is transformed from sp³ to sp² hybridization is expected. However, the sheer magnitude of the effect is, we feel, related to the enormous stabilization calculated for O⁻ attached to unsaturated and strained frameworks which is due to augmentation of the π effect by a large stabilizing σ effect.

Fluorine (F) Substituent. The results in Table I indicate that stabilizations in monofluoro-substituted strained (unsaturated)

Table V

electronic effects	examples	overall effects
π acceptor, σ donor	Li, BeH, BH ₂	stabilization
π acceptor, σ acceptor	conj CH ₂ ⁺ , CN	stabilization if π dominant: CH ₂ ⁺ , CN destabilization if σ dominant
π donor, σ donor	O ⁻ , conj CH ₂ ⁻	stabilization
π donor, σ acceptor	NH ₂ , CH ₃ O, OH, F	stabilization if π dominant: NH ₂ , CH ₃ O, OH, F (in ethylene) destabilization if σ dominant: F (in acetylene)
σ donor	nonconj CH ₂ ⁻ , BH ₃ ⁻ , CH ₃	stabilization
σ acceptor	nonconj CH ₂ ⁺ , CF ₃ , NH ₃ ⁺	destabilization

molecules are small and in some cases destabilizations relative to the parent compounds are indicated. Fluorine is certainly an inductive destabilizer. Its π -stabilizing effect is relatively weak owing to weaker interactions of the low-energy lone-pair fluorine electrons with π^* -type orbitals. The results in Table I suggest that for fluoroethylene the stabilizing π effect is larger than the σ effect, while for fluoroacetylene the destabilizing σ effect dominates. As stated in the introduction, σ effects assume a proportionately larger role in acetylenes than in ethylenes. Somewhat analogous results are found for fluorocyclopropane and 1-fluorobicyclobutane. The results in Table I indicate that F and CH₃ substituents stabilize olefinic linkages equally. This is confirmed by thermochemical data¹⁸ which indicate that the reactants and products of reaction 21 are isoenergetic (use of ethyl rather than isopropyl derivatives does not alter this conclusion). Reaction 21 is a useful approach for calculating substituent effects relative to methyl. If the stabilization effect of the latter is considered to be 3.2 kcal/mol,⁷⁷ then an absolute scale results. This equation is endothermic by 6.6 and 5.5 kcal/mol for Cl and Br substituents, respectively, indicating that they are destabilizing substituents due to decreased π effects. This factor has been discussed by others.⁹³



A molecular structure has been calculated for fluorocyclopropane which exhibits marked alteration of ring bond lengths from those of cyclopropane in accord with experiment.⁹⁴ The study cited employed the double ζ basis set. Our STO-3G calculations indicate that the idealized structure is more stable than the experimental structure by some 0.3 kcal/mol, again indicating the comparative insensitivity of this basis set to small perturbations induced by substituents on the geometries (but not the energies) of these systems.

Conclusions

Our conclusions are summarized in Table V. Although most predictions of thermodynamic stabilization are qualitatively self-evident from this table, some substituents, notably fluorine, provide ambiguities that require more detailed quantitation. While the isodesmic approach provides stabilization energies for substituted strained molecules, attribution among components including ring strain and buildup of exocyclic bond orders is ambiguous. However, substituents such as Li, BH₃⁻, and BH₂ can be said to decrease ring strain. Substituent effects

are sometimes quite substantial and can introduce significant differences in the relative energies of isomeric strained molecules such as the benzene valence isomers.⁹⁵

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Supplementary Material Available: Data used in calculating the strain energies and comparison of experimental and theoretical ΔH_f° values (13 pages). Ordering information is given on any current masthead page.

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Circular Dichroism of Charge Transfer and Magnetic Dipole Forbidden d–d Transitions. Application to Chiral Chelate Complexes

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Abstract: The circular dichroism (CD) of the charge-transfer transitions of chiral metal complexes is discussed. In tris(bidentate) complexes, it is postulated to arise from direct dipole coupling between the charge-transfer and chelate transition moments, leading to a particularly simple expression for the CD which is readily parametrized from normal absorption data. It is shown to be independent of any coupling between the chelates themselves, but depends directly on their stereochemistry. The model is also applied to the CD of magnetic dipole forbidden d–d transitions, which are postulated to gain their CD through their vibronically or spin-orbit induced electric moments coupling with those of the chelates. The implications of the results for the determination of absolute configurations and conversely for the assignment of the transitions are discussed.

Introduction

The circular dichroism (CD) of chiral metal complexes has received much attention in the literature, both as a test of CD models and as a stereochemical probe. Most attention has focused on the d–d transitions (see, e.g., reviews^{1,2} and ref 3) and, in the case of chiral chelate complexes, the coupled chelate bands (e.g., the work of Mason,⁴ Bosnich,⁵ and references collated in Hawkins' book¹). Little direct work on the charge-transfer CD has appeared, and it has usually attracted only passing interest in discussions of the other types of transitions.⁴ This is especially surprising when it is considered that the charge-transfer (CT) transitions are usually electric dipole allowed, and that the CD mechanisms for electric dipole transitions are generally simpler than those of magnetic dipole allowed ones as encountered, for example, in d–d spectra.

The most probable reason for this is that the separable chromophore (independent systems) approach, which is the basis for most general CD models, assumes that the CD arises from the perturbation of an achiral chromophore (A) by another chromophore (B), there being negligible electron exchange (overlap) between the two. CT transitions are delocalized over both the metal ion and part of the ligand system, the latter also being the source of the chiral perturbation. Thus it is not immediately obvious whether a simple CT chromophore can be defined or not. However, as the CT occurs predominantly from the metal ion to the directly ligating atoms (or vice versa), the bulk of the oscillator strength in the normal absorption spectrum must arise from a fairly localized chromophore (metal ion + ligating atoms). With the CT chromophore chosen in such a way, two contributions to the CT CD may be isolated. The first is due to any intrinsic chirality of the

chromophore, and the second, which is present whether the CT chromophore is chiral or achiral, is due to the perturbation by the chiral chelate system of the CT transition moments. These contributions are additive. Only the latter will be discussed in detail in this paper, as it leads to a strong CT CD (especially in tris(chelate) systems) which may be expected to dominate the CD in most complexes.

The other transitions which shall be considered briefly in this paper are the magnetic dipole forbidden d–d transitions, which generally exhibit a far weaker CD than the magnetic dipole allowed ones. The CD of the latter has received copious attention in the literature,^{2,3} but, because of the intrinsic dependence on the magnetic dipole transition moment, is difficult to estimate or empiricize from normal absorption data. The CD of the magnetic dipole forbidden transitions, though weaker, has the distinct advantage that it is readily interpreted in terms of the model presented herein, as well as being readily parametrized from normal absorption data.

Circular Dichroism of Electric Dipole Transitions

There are two predominant mechanisms by which an electric dipole allowed transition of an achiral chromophore A (with transition moment μ_A centered at the origin of A, and corresponding transition energy ϵ_A) can become CD active through perturbation by another chromophore B (characterized by a single transition r , energy ϵ_r , and an electric transition moment μ_B^r if B is intrinsically achiral, or transition moments μ_B^r , m_B^r if B is intrinsically chiral, with m_B^r the magnetic dipole transition moment). These arise from first-order perturbation theory (see, e.g., general expansions in ref 6), so that the CD induced at energy ϵ_A in the electric dipole allowed transition