CHAPTER 3

Carbenes: A Study in Quantitative and Qualitative Theory

Joel F. Liebman

University of Maryland Baltimore County, Catonsville, Maryland

Jack Simons

University of Utah, Salt Lake City, Utah

CONTENTS

MOLECULAR STRUCTURE AND ENERGETICS, Vol. 1

1. INTRODUCTION: WHY WE STUDY CARBENES

In this chapter we discuss the interplay of qualitative and quantitative theory as illustrated by the energetics, structure, and reactivity of carbenes. We have chosen to make carbenes the subject of an entire chapter because these compounds have been of intense interest to experimental and theoretical chemists alike for decades. This interest arises from the fact that despite occasional ambiguity, carbenes contain divalent carbon. These species thus violate the primary tenet of organic chemistry, which asserts the "natural" tetravalence of carbon.

The divalent carbons in carbenes normally result in high reactivity. This divalence allows most of the interesting carbene phenomena to be shown by the 3 atom, 6 valence electron, and 8 all electron level of the parent carbene, CH_2, the second simplest hydrocarbon. (CH narrowly edges out CH_2 for first place.) The archetypal cyclopropane and benzene for the study of strained and aromatic species are rather large: they are composed of 9 and 12 atoms, 18 and 30 valence electrons, and a total of 24 and 42 electrons, respectively.

Part of the interest in carbenes arises from their property of having two generally accessible electronic states, the singlet with all its electrons paired, and the triplet with two unpaired electrons. The former behaves like an electrophile and/or a nucleophile, the latter more like a radical. As such, the singlet and triplet generally have very different, and easily distinguishable, chemical behaviors. For numerous carbenes, each electronic state may be "synthesized" independent of the other, even though direct isolation is rarely achieved. There are few species for which the ground and excited states are of equal interest and accessibility. In addition, carbenes are accessible in the gas phase and in condensed media using the techniques of both thermal and photochemistry. This diversity allows a quite complete picture of the compounds to be formed and subtle effects to be delineated. In the condensed phase, intermolecular interactions of the uncharged carbenes are comparatively weaker than those of many other "reactive intermediates" such as carbonium ions and carbanions, where solvation and ion pairing often play dominant roles.

Carbenes are also interesting because they may be related to numerous other species. Either or both of the two hydrogens of the parent CH_2 may be replaced to form other carbenes, and the resultant substituent effects are usually large. Isoelectronic reasoning allows carbenes to be related to both "reactive intermediates" and classical, stable species. In summary, carbene chemistry is multifaceted and exciting.

2. WHY IS CARBON NORMALLY TETRAVALENT?

We start our discussion of the interplay of structure, energetics, and reactivity in carbenes by discussing why carbon is normally tetravelent. This is a logical place to begin because carbenes violate a primary tenet of organic chemistry by containing a divalent carbon; that is, the dominant Lewis or resonance structure involves two or even occasionally one bonding partner, two bonds, and a total of six electrons around the central carbon. The conventional situation, exemplified in numerous saturated aliphatic and alicyclic hydrocarbons, places four carbon and/or hydrogen neighbors around each carbon, so that there are eight electrons around each carbon. The presence of four bonds is usually explained in the textbook literature in terms of promotion and hybridization of the $1s^22s^22p^2$ (^3P) ground state into an "appropriate state" for the formation of four directed bonds. The energy released by the formation of these bonds is supposed to more than offset the associated promotion energy cost and so stabilize tetravalent carbon. (We note that the two unpaired electrons of the 2p subshell do not require promotion to form the two bonds of the carbenes.) This explanation is qualitatively appealing, but quantitation of the tetravalence phenomenon has generally been ambiguous. We now attempt to provide such a quantification using a comparatively simple model and accompanying numerical estimate of the energies involved.

The reader will note that the "appropriate state" above was *not* identified as sp^3-hybridized carbon. This omission was intentional. Literature theoretical studies have variously indicated that the tetrahedral geometry of the *archetypical* methane with its one tetracoordinate carbon atom (a) is due to the internuclear repulsions of the hydrogens[1] rather than interelectron repulsion or other electronic effects, (b) does not require any s and p admixture at all,[2] suggesting that promotion and hybridization may be totally irrelevant, and (c) is accompanied by $sp^{1.7}$, $sp^{2.2}$, or $sp^{3.4}$ hybridization for the central carbon, where the differing hybridizations were obtained using different calculational and conceptual methods.[3] Thus it should not be surprising that we wish to omit the question of the hybridization of the central carbon atom in carbenes.

Like the textbook models, our model speaks of promotion, hybridization, and the subsequent formation of four bonds. We estimate the energy gained by promoting and hybridizing the carbon atom as equaling the difference in C−C (homolytic) bond energies associated with carbons that are properly geometrically disposed (and thus are "properly" hybridized, if such atoms have any reality as opposed to merely conceptual utility) and those that are associated with atomic carbon, which is unhybridized by definition. As an example of the former, consider the simple case of ethane with its two equivalent carbons. The direct C−C bond homolysis requires 86.6 kcal/mol.[4] However, this number must be corrected by the "tetrahedralization energy" to transform the two resultant CH_3 radicals from their planar geometry as free tetraatomic molecules into species that have the geometry of the CH_3 fragment found in ethane. Quantum chemical calculations[5] of this transformation produce a value of 6.9 kcal/mol for each CH_3. Accordingly, the bond strength corresponding to the first process is $86.6 + 2(6.9) = 100$ kcal/mol.

For the second process, consider the formation of atomic carbon from the formal decomposition of diamond, a species composed solely of tetrahedral carbons. The experimental heats of formation[6] (from graphite) of diamond and of atomic carbon are 0.45 and 171.3 kcal/mol, respectively. Whereas each carbon in diamond has four bonds to adjacent carbons, to prevent the double counting of C−C bonds, each carbon is said to be associated with two bonds. As such, the effective bond strength is $(171.3 - 0.45)/2 = 85$ kcal/mol. The difference of the C−C bond strengths associated with the two processes is thus $100 - 85 = 15$ kcal/mol. We thus take the energy gain due to promotion and hybridization of atomic carbon into the tetrahedral, tetracoordinate carbon form as 15 kcal/mol per C−C bond.

It may be argued that the foregoing comparison may be improved by dealing with two inconsistencies:

1. Solid, and not gaseous, diamond was used—all the other hydrocarbons are taken in their gaseous state at standard temperature and pressure.
2. Diamond is not a typical hydrocarbon—it lacks hydrogen.

With regard to the first difficulty, a correction may be immediately made by adding in the heat of sublimation of diamond. Although this quantity is unknown—and temptingly said to be intrinsically unmeasurable—it may be estimated by two distinct approaches. The first argues that the heat of sublimation is precisely zero: solid diamond is argued to be an ideal gas because there are only intramolecular (ie, no intermolecular) interactions.[7] Alternatively, from the identity

$$\Delta H_{\text{sub}}(\text{s} \rightarrow \text{g}) = \Delta H_{\text{fus}}(\text{s} \rightarrow \text{l}) + \Delta H_{\text{vap}}(\text{l} \rightarrow \text{g}) \tag{3-1}$$

and the observation that ΔH_{fus} is less than ΔH_{vap}, we deduce

$$\Delta H_{\text{vap}} < \Delta H_{\text{sub}} < 2\,\Delta H_{\text{vap}} \tag{3-2}$$

Unfortunately, the heat of vaporization of liquid diamond is a number as unknown, and as experimentally unattainable, as the heat of sublimation of the solid. Nevertheless, unlike heats of sublimation, heats of vaporization are comparatively easy to estimate. In particular, we use rule 2 of Reference 8:

$$\Delta H_{\text{vap}} = 0.3n_{\text{Q}} + 1.1\overline{n}_{\text{C}} + 0.7 \text{ kcal/mol} \tag{3-3}$$

where n_{Q} is the number of quaternary carbons and $\overline{n}_{\text{C}}$ is the number of nonquaternary carbon atoms in the molecule. For diamond, which is composed "solely" of quaternary carbons, n_{Q} effectively is 1 and $\overline{n}_{\text{C}}$ effectively is 0. Thus ΔH_{vap}, per mole of atomic carbon, is 0.3 kcal/mol. Undeniably, ΔH_{sub} is less than twice this value, 0.6 kcal mol^{-1}. This correction is seen to be negligible.

With regard to the second objection, ethane and diamond may be "interpolated" by neopentane, $C(CH_3)_4$, and 2,2,3,3-tetramethylbutane, $C_2(CH_3)_6$.[9,10] Although $(CH_3)_3C$, a radical resulting from suitable C−C bond thermolyses of either hydrocarbon, is in fact pyramidal, the CH_3-C-CH_3 angle[11] is much wider than that found in either of its precursors. As such, the tetrahedralization energy of *t*-butyl radical must also be included. Taking this last number from quantum chemical calculations[12] and the heats of formation of the hydrocarbons and the radicals[13] from experiment, the following processes give the C−C bond energy of interest.

$$C(CH_3)_4 \rightarrow (CH_3)_3C + CH_3;\ E = 101\ \text{kcal/mol} \qquad (3\text{-}4)$$

$$C(CH_3)_4 \rightarrow C + 4CH_3;\ E = 95\ \text{kcal/mol} \qquad (3\text{-}5)$$

$$C(CH_3)_3-C(CH_3)_3 \rightarrow 2[C(CH_3)_3C];\ E = 101\ \text{kcal/mol} \qquad (3\text{-}6)$$

$$C(CH_3)_3-C(CH_3)_3 \rightarrow 2C + 6CH_3;\ E = 95\ \text{kcal/mol} \qquad (3\text{-}7)$$

The range of values found for C−C bond dissociation energies in neopentane and 2,2,3,3-tetramethylbutane is 8 kcal/mol, smaller than that found before using ethane and diamond. However, these two ranges of values are in fact consistent. The values of the bond energies found for the properly geometrically disposed cases, as found for ethane and reactions 3-4 and 3-6 are nearly identical to each other (≃ 100 kcal/mol). The case in which just atomic carbon was produced (ie, diamond) resulted in 85 kcal/mol. In the two remaining cases in reactions (3-3 and 3-5), a typical bond is composed of two carbons that upon dissociation result in one carbon that is properly geometrically disposed and one carbon that is atomic. Their bond energies are nearly identical, about 94 kcal/mol. This value is nearly the average of the all-"properly geometrically disposed" and all-atomic situations. The energy gain associated with electron promotion and hybridization in strainless, aliphatic (or alicyclic) tetrahedral, tetracoordinate carbon is thus about 15 kcal/mol. This energy is large enough that carbon appears unequivocally to "prefer" being tetrahedral and tetracoordinate. Thus we should not be surprised that carbon, if bonded to only two hydrogens, has two unpaired electrons awaiting the formation of two more bonds and that carbenes are generally highly reactive species.

3. THE XCY CARBENE ANGLE AND THE SINGLET–TRIPLET GAP; MODELS, MNEMONICS, AND CORRELATIVES

A. The Inseparability of Singlet–Triplet Gaps and XCY Angles

Many a model for the singlet-triplet gap, E_{ST}, in general carbenes, CXY, are inseparable from those for the XCY angle in the two states. The HCH angle[14] is unconstrained and in singlet CH_2 is about 105°, considerably less than 135° in the triplet. We take these values as "optimal" and associate with them a gap of about 10 kcal/mol favoring the triplet as the ground state.[15] It is not surprising that the singlet–triplet gap for a single species correlates with the distortions of the XCY angle of that species in the two states. It is well established that the XCY angle varies widely in ground and excited states of carbenes. Although this variation is most often due to electronic effects, it sometimes is due to steric effects.

Starting with the latter effects because they are simpler, both quantum chemical calculations and experiment show that di-*t*-butyl carbene to be a ground state triplet.[16] By contrast, direct use of Equation 3-8 (from Reference 17), as well as extrapolations from

$$E_{ST} = 84.5\Sigma\sigma_R^\circ + 43.9 \tag{3-8}$$

other dialkyl carbenes, would have suggested a ground state singlet. It is clear that the two large *t*-butyl groups force the XCY angle to open in both states. Since the triplet angle is significantly larger than that of singlet carbenes, such bulky groups have less of an effect on the triplet than the singlet, and therefore destabilize the triplet less. The triplet drops below the singlet in energy, and so di-*t*-butyl carbene is a ground state triplet. By contrast, we expect cyclopropenylidene to have a severely constricted ($\simeq 60°$ as in cyclopropene) XCY angle in its ground state. Since the constriction arises from the species' nuclear framework, we expect the XCY angle of the triplet state to be of the same order as the singlet. Since the singlet optimal angle is smaller and the assumed distortion is smaller for the singlet, we are not surprised that cyclopropenylidene has a singlet ground state (see Subsection B of Section 8).

B. Gimarc's Qualitative Molecular Orbital Theory

Understanding the origin of the smaller XCY angle of the singlet CH_2 than of the triplet will aid us in the understanding of electronic effects on carbene geometry. Our first model for the XCY angle makes use of Gimarc's "qualitative molecular orbital" theory[18] and Figure 3-1, which shows all the occupied molecular orbitals of CH_2. We now proceed through the relevant rules (ie, omitting rules 4, 6, 7, and 9 of Gimarc's list).

a. "Consider valence electrons only." This means that the effects of the $1a_1$ orbital may be ignored. Certainly a molecular orbital (MO) that is composed almost totally of the C 1s atomic orbital (AO) is expected to have little chemical impact.

b. "Form completely delocalized MOs as linear combinations of valence s and p AOs." The reader will recall that while extensive basis sets were used to calculate chemically accurate numbers, all the qualitative discussion of these results ultimately used the s orbital of hydrogen, and the s and p AOs of carbon and those of affixed nonhydrogenic atoms.

c. "MOs must be either symmetric or antisymmetric with respect to the symmetry operations of the molecule." We remind the reader that designations such as a_1, b_1, and b_2 are symmetry labels and that the shaded and

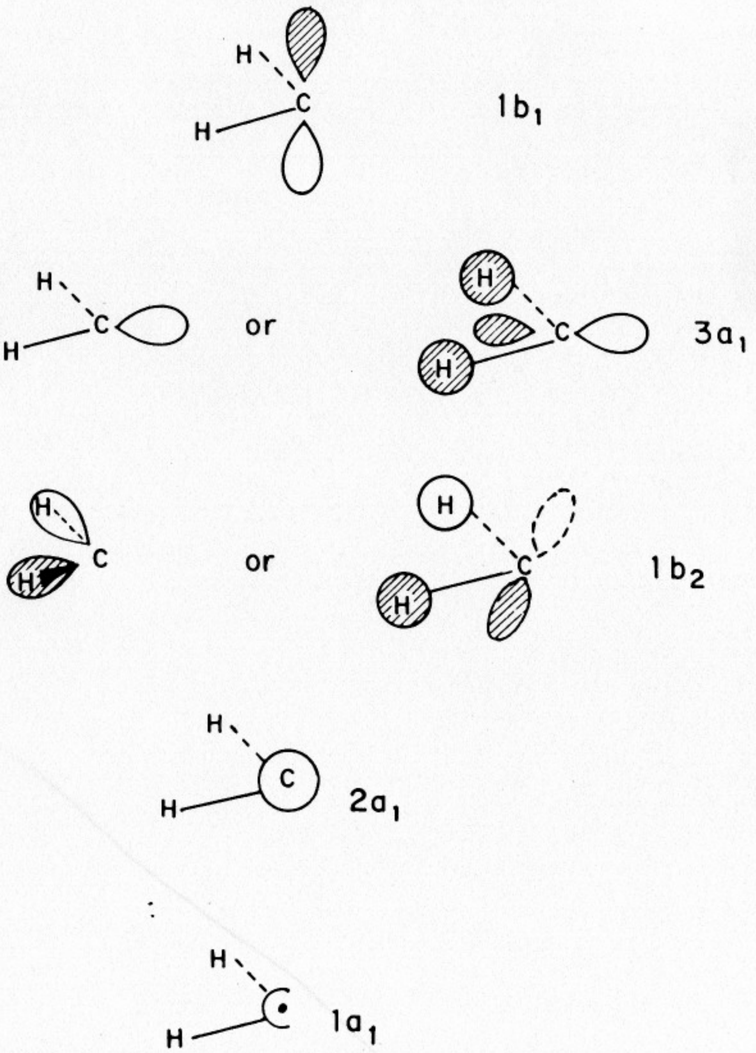

Figure 3-1. The occupied molecular orbitals of singlet and triplet CH_2. By convention, the shaded and unshaded parts of an orbital have opposite signs or phases. Also, in applications of qualitative molecular orbital theory, the bottom-most orbital is ignored and the $2a_1$ and $3a_1$ orbitals are often relabeled $1a_1$ and $2a_1$, respectively.

unshaded parts of the MOs shown are characterized by different phases or signs of the orbital.

d. "The total energy is the sum of the orbital energies of individual energies." As Gimarc himself admits, this rule incorrectly suggests that CH_2 should have all the electrons paired because the $3a_1$ lies lower in energy than the $1b_1$. That error aside, this rule allows us to make comparisons orbital by orbital, whether between a carbene in its singlet state with the same species in the triplet state, or between two altogether different compounds.

e. "The AO coefficients are large in high-energy MOs with many nodes or complicated nodal character." This usually results in the higher energy MOs dominating the observed chemical behavior.

f. "When two orbitals interact, the lower energy orbital is stabilized and the higher energy orbital is destablized. An out-of-phase or antibonding interaction between two orbitals always raises the energy more than the corresponding in-phase or bonding interaction lowers the energy." This rule is often presented in introductory textbooks as "Antibonding is more antibonding than bonding is bonding."

Let us return to CH_2 in the specific and follow from Gimarc himself. The $1b_1$ or 1π orbital is essentially pure carbon 2p because the hydrogens lack the appropriate 2p orbitals. This is true regardless of the HCH angle, and so only the orbitals of σ symmetry need be considered. The highest such orbital, the $3a_1$, is "H−H bonding," whereas the subjacent (the next lower lying) σ orbital, the $1b_2$, is "H−H antibonding." (H−H bonding and antibonding strictly means that the two 1s orbitals of the two hydrogens are respectively in and out of phase. It does not mean that one interaction is simultaneously stabilizing and destabilizing.) Opening the HCH angle decreases the stabilizing effects of the "H−H bonding" interactions in the $3a_1$ MO and also decreases the destabilizing effects of the "H−H antibonding" interactions in the lb_2 orbital. With two electrons in the $3a_1$ orbital (ie, in the singlet state), this orbital "wins out," and so the HCH angle is small. With one electron in the $3a_1$ orbital (ie, in the triplet state), the HCH angle is larger than in the singlet. (It is not, however, increased to 180° as is so often erroneously shown in the textbook literature. This, too, follows from Gimarc's analysis.)

Gimarc has also made related analyses for the HAH angles in the second-row dihydride series BeH_2, BH_2, CH_2, NH_2, H_2O, and for the isoelectronic series CH_2, NH_2^+, SiH_2. By making use of some of his other rules, Gimarc has also studied the angles in mono- and dihalocarbenes and their isoelectronic analogues—interested readers are referred to his studies for more details. We leave qualitative molecular orbital theory with the interesting note that this "H−H bonding and antibonding" logic parallels the relative HNH angles in NH_3 and its radical cation. In the neutral with two electrons in the highest lying a_1 orbital, the angle is 104°, while in the radical cation with only one such electron, the angle is opened to 120°—the species is planar. It will be seen that this relation is not unique—more general carbenes and amines interrelate.

C. Nyholm-Gillespie (or VSEPR) Theory[19]

Another explanation for the relative angles of the singlet and triplet makes use of Nyholm–Gillespie or valence shell–electron pair repulsion (VSEPR) theory. In its simplest form, π electrons do not affect molecular geometry. As such, singlet CH_2 with its lone pair (lp) on carbon will have a larger "lp−C−H" angle and smaller HCH angle than the triplet with its single "free radical" electron and larger HCH angle. This correspondence between angle and electronic state is also seen in SiH_2. It has been additionally argued[20] that there is less H−H repulsion in SiH_2 than in CH_2 and so the smaller HSiH angle is smaller. This results in SiH_2 being a singlet. This difference between the second-row CH_2 and third-row SiH_2 parallels the wider angle in H_2O than in H_2S. The same difference is seen in NH_3 compared to PH_3. Additionally the inversion barrier[21]—the energy needed to increase the HNH and HPH angle to 120°—is markedly less for the former.

Substituted carbene geometries are also compatible with the VSEPR assertion that electronegative substituents are comparatively small: the FCF angles in the singlet and triplet state of CF_2 are smaller than the HCH angles in the two corresponding states of CH_2. Electronegative substituents confine the electrons in the bonds to a smaller region, and so repulsion between them is minimized. This angle dependence on electronegativity parallels the smaller angle in OF_2 than in H_2O, and in NF_3 than in NH_3. (The inversion barriers for the two amines fall in the predicted order: $NH_3 \ll NF_3$). Though less documented, it appears that electropositive substituents occupy a comparatively large volume. Paralleling the experimental linear geometry for Li_2O, it is not surprising that quantum chemical calculations on CLi_2 show a potential energy minimum corresponding to a linear geometry[17,22,23] irrespective of whether the electronic state of the carbene is singlet or triplet. This geometry is compatible with significant contributions from the valence bond resonance structure $^-Li{=}C^+{-}Li$.[24] This may also be suggested for CNa_2, although the literature calculation is only for the triplet.[25] Interestingly, both triplet CLi_2[23] and CNa_2[25] have bent isomers with an MCM angle of about 80–90°. This may be understood in terms of the alternative resonance structure $M_2^+{-}C^-$ wherein there is explicit metal–metal bonding and the component doublet and quartet combine to form the observed triplet. A simple point-charge calculation[25] qualitatively and quantitatively reproduced the energy of binding between the posited M_2^+ and C^- subunits. Qualitative molecular orbital theory documents the importance of this bonding M−M interaction. The unoccupied p orbitals on the metal contribute to metal–metal bonding for both the $1b_1$ and $3a_1$ molecular orbitals with stabilization maximized at small M−C−M angles.[26]

D. Bent's Rule

The findings above are also compatible with simple hybridization logic and Bent's rule:[27] substituents with high electronegativity "prefer" hybrid orbitals with less s character and those with low electronegativity "prefer" hybrids with more s character. Despite our earlier caveats about hybridization, we nonetheless recall the textbook relationships of hybridization and bond angle. From these, one immediately deduces that substituents with low electronegativity would be expected to encourage large XCY angles. This is generally true; for example, HCX is calculated to be linear for X = Li (both singlet and triplet carbenes), BeH (both singlet and triplet carbenes), and BH_2 (just singlet carbene, no doubt because of π effects). It is also true for one "isomer" of triplet CLi_2 and CNa_2.

Yet there is the other "isomer" of these last two species with a very constricted angle. How can the existence of two potential energy minima (ie, two isomers) be understood? The maximum s atomic orbital contribution for carbon is two electrons—whether they be found in an arbitrary covalent compound or in atomic C or C^-. Should the formal presence of C^- in a molecule be suggested anywhere, these CLi_2 and CNa_2 are the most reasonable candidates. Electronegativity logic suggests that a single C−Li or C−Na bond should be rather polar. The C^- ion, as the free species, has a $[^4S]s^2p^3$ electron configuration and electrons and is in addition spherical. Thus the charge transfer from the Li or Na atoms to the C results in electrostatic repulsion between the two partially positive metals. Minimization of this repulsion will result in a linear geometry. Alternatively, maximization of metal–metal bonding, worth about 30 kcal/mol in the current case, requires a bent geometry so that the metals are in close proximity.

Conversely, electronegative substituents are expected to use hybrid orbitals on C rich in p character leaving the remaining orbitals rich in s character. As atomic s orbitals lie lower than the corresponding p orbitals, with increasing substituent electronegativity it is increasingly favorable to leave the two nonbonding electrons in an orbital that maximizes s character. Equivalently, high substituent electronegativity encourages an XCY angle of 90° ("pure" p bonding) and singlet character in carbenes. This is admittedly a σ-electron argument: the additional and important role of the p_π orbitals on carbon and on the substituents has been extensively documented in References 15 and 17 and is discussed elsewhere in this chapter. Arguing in reverse, when the XCY angle is constricted and the X−C and C−Y bonds have mostly p character, the remaining carbon electrons are rich in s character, and so the singlet state of the carbene is preferentially stabilized. The parallel with amines is strong: nitrogen bonded to electron-withdrawing substituents and/or in a small ring is much less basic than the norm; that is, two electrons in the nonbonding nitrogen lone pair are less available for chemical bonding to a proton.

E. Amines and Carbenes

We cross-referenced amines several times in the foregoing discussion of carbenes because there appears to be a parallel between carbene singlet–triplet gaps and amine inversion barriers. For example, the inversion barrier of the amines: NH_2CN (essentially planar), NH_3, NH_2F, and NHF_2 increases in that order and parallels the increasing singlet–triplet gap of CHCN (ground state triplet), CH_2, CHF, and CF_2 (ground state singlet). Even the angle effects, delocalization and aromaticity, and second-row versus third-row comparison hold up: CH_2 is a ground state triplet while c-$(CH_2)_2C$:, c-$(CH)_2C$:, and SiH_2 are ground state singlets; NH_3 has a low inversion barrier, whereas those of c-$(CH_2)_2NH$, c-$(CH)_2NH$, and PH_3 are high. Is this relationship between carbenes, CXY, and amines, HNXY, generally valid? In the absence of comparably accurate data on corresponding (identically substituted) members of both classes of compounds and/or a good explanation for this relation, we do not know. Qualitatively, our answer is a tentative "yes." But, quantitatively, a more muted "not yet confirmed" is required. Is this relationship fundamental, correlative, or "merely" a mnemonic? We do not know.

Admitting that many of the concepts above were qualitative and some even ill defined, we turn for now to a more rigorous theoretical treatment of the chemistry of carbenes and further document the fundamental relationships of the chemistry of carbenes with more "normal" closed-shell species.

4. INTRODUCTION TO THE QUANTITATIVE

Now our emphasis shifts to an understanding of what goes into quantitative theoretical investigations of carbenes. Although much of what is actually done in a state-of-the-art quantum chemical study involves the application of sophisticated computer programming and is often cast in high-tech jargon, the concepts that underlie such studies are easily understood and of substantial chemical importance. We hope to be able to cut through the jargon and focus on the physical essence of how modern quantum chemical tools are stretched to their limits by carbene systems. This necessitates dealing with certain details that must be expressed in mathematical language, but the volume of mathematical equations is kept to a minimum.

To begin our discussion of the theoretical study of carbenes, we need to become familiar with the valence orbitals of the carbenic center. These orbitals, when occupied by zero, one, or two electrons, give rise to the important electronic configurations of carbenes, which are studied in Section 6. Single electronic configurations are not, as we discuss in detail below, accurate descriptions of the true states of carbenes (or of any atom or molecule, for that matter). To describe a carbene's lowest singlet and triplet even reasonably accurately (± 10 kcal/mol in the singlet–triplet splittings, for example!) requires the use of more than one electronic configuration. The conceptual understanding of how and why these configurations must be mixed is treated in Section 7. Several examples of novel electronic states that can arise in carbene systems are analyzed in Section 8.

5. CARBENE ORBITALS

The two valence orbitals on which attention usually focuses when dealing with carbene systems (Figure 3-2) are denoted n and p_π. The n orbital

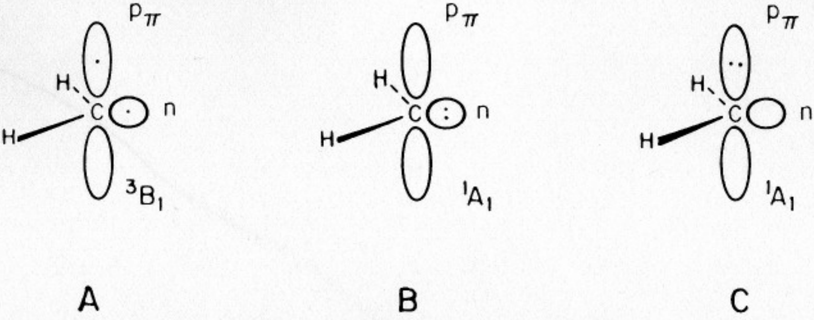

Figure 3-2. The two "important" valence orbitals of carbenes as exemplified by CH_2, in which the n and $3a_1$ MOs are synonymous, as are the p_π and $1b_1$. Triplet ($^3B_1$) CH_2 is thus accurately describable by a $n^1\ p_\pi^1$ configuration (**A**), while the singlet ($^1A_1$) requires admixture of the "conventional" n^2 and the excited p_π^2 configurations (**B** and **C**).

involves both carbon 2s and $2p_\sigma$ atomic orbital character with a relative mixing ratio that can vary from sp hybridization (eg, in vinylidene H_2CC:) through higher p character than in sp^2 hybridization (eg, in singlet methylene where the HCH bond angle[28,29] is 102°).

Although the qualitative shapes of the n and p_π orbitals are familiar to essentially all chemists, their orbital energies and sizes depend on the nature of the groups that are bonded to the carbenic carbon atom. In particular, the electron-accepting and electron-donating characters of both the σ and π components of the attached functional groups play crucial roles in determining the energies and sizes of the n and p_π orbitals.

It would at this time be useful to reflect on the meaning of the energy of an orbital. First it is wise to point out what orbital energies are not; they are not exact measures of atomic or molecular ionization potentials, electron affinities, or excitation energies. They are constructs of the imaginations of chemists. We scientists invented the molecular orbital (MO) model as an idealized concept in terms of which to interpret experimentally observed facts.

Within the conventional MO model,[30] each electron is viewed as moving throughout the molecule (whose nuclear positions are held fixed) "feeling" the Coulombic attractions to all the molecule's nuclei and experiencing some average repulsive potential energy field caused by the *other* electrons in the molecule. Representing the electron's kinetic energy by T, its attractive potential energy to a nucleus of charge $Z_A e$ centered at $\boldsymbol{R}_A$ by $-Z_A e^2|\mathbf{r} - \mathbf{R}_A|^{-1}$, and the average repulsive energy due to the other electrons by $V_{ee}(\mathbf{r})$, the molecular orbital Hamiltonian $h(\mathbf{r})$ for an electron at position $\mathbf{r}$ is:

$$h(\mathbf{r}) = T + V_{ee}(\mathbf{r}) - \sum_{A=1}^{M} Z_A e^2 |\mathbf{r} - \mathbf{R}_A|^{-1} \qquad (3\text{-}9)$$

where the quantum mechanical kinetic energy operator is:

$$T = -\frac{\hbar^2}{2m_e}\nabla_r^2 \qquad (3\text{-}10)$$

Here, m_e is the mass of the electron, and M is the number of nuclei in the molecule. Both the occupied $\{\phi_\mu\}$ and unoccupied $\{\phi_p\}$ MOs are taken to obey the Schrödinger equation of this MO Hamiltonian:

$$h\phi = \epsilon\phi \qquad (3\text{-}11)$$

A central feature of the molecular orbital model[30] is that $V_{ee}(\mathbf{r})\phi(\mathbf{r})$ is computed as the average "Coulombic minus exchange" interaction energy of a so-called test charge or an electron in $\phi(\mathbf{r})$ with a set of electrons that reside in the occupied MOs $\{\phi_\mu\}$:

$$\begin{aligned} V_{ee}(\mathbf{r})\phi(\mathbf{r}) &= \sum_\mu \phi(\mathbf{r}) n_\mu \int |\phi_\mu(\mathbf{r}')|^2 e^2 |\mathbf{r} - \mathbf{r}'|^{-1}\, d\mathbf{r}' \\ &- \sum_\mu n_{\mu,\text{same}} \int \phi_\mu^*(\mathbf{r}')\phi(\mathbf{r}') e^2 |\mathbf{r} - \mathbf{r}'|^{-1}\, d\mathbf{r}'\, \phi_\mu(\mathbf{r}) \end{aligned} \qquad (3\text{-}12)$$

Here n_μ is the number of electrons in MO ϕ_μ (zero, one, or two) and $n_{\mu,\text{same}}$ is the number of electrons (zero or one) in orbital ϕ_μ that have the same magnetic spin quantum number ($m_s = \pm\frac{1}{2}$) as that which occupies ϕ. These two kinds of contribution to $V_{ee}\phi$ are referred to as Coulombic and exchange interactions. The essential facts to be gleaned from this description of the molecular orbital Schrödinger equations are:

1. That an electron in ϕ feels all the molecule's nuclei attracting it.
2. That $V_{ee}\phi$ describes an average (ie, due to the integration over $d\mathbf{r}'$ in Equation 3-12) Coulombic interaction of an electron in ϕ with all the electrons in the occupied MOs ϕ_μ minus an average exchange interaction of ϕ with electrons in all occupied orbitals of the same m_s value as ϕ.
3. That the content of V_{ee}, hence of h itself, depends on what orbitals are defined or chosen to be occupied.

A few implications of these characteristics of V_{ee} should be emphasized. First, V_{ee} and h itself depend on the occupied MOs $\{\phi_\mu\}$, which are supposed to be found by solving the MO Schrödinger equation. This dependence of h on $\{\phi_\mu\}$ gives rise to the use of so called self-consistent field (SCF) iterative methods for solving Equation 3-11. An initial guess (usually taken from knowledge of atomic or fragment orbitals) for the occupied MOs is made, thereby allowing V_{ee} to be evaluated. Then Equation 3-11 is solved to yield new (improved?) orbitals, both occupied $\{\phi_\mu\}$ and excited $\{\phi_p\}$. The new occupied MOs are used to again construct V_{ee} and to then solve Equation 3-11 again for yet better (?) MOs $\{\phi_\mu\}$ and $\{\phi_p\}$. This iteration process is continued until convergence (ie, essentially no change in the $\{\phi_\mu\}$ and $\{\epsilon_\mu\}$ from one iteration to the next) is reached. Convergence, by the way, is not always realized.

The second implication has to do with the physical content of $V_{ee}\phi$ when ϕ is itself one of the occupied MOs, say ϕ_ν. In this case, the so-called self-interaction arising when $\mu = \nu$ partly cancels. That is, the Coulombic interaction terms $n_\mu \int |\phi_\mu|^2 e^2 |\mathbf{r} - \mathbf{r}'|^{-1} \, d\mathbf{r}' \, \phi_\nu$ and the exchange terms $-n_{\mu,\mathrm{same}} \int \phi_\nu^*(\mathbf{r}')\phi_\nu(\mathbf{r}') e^2 |\mathbf{r} - \mathbf{r}'|^{-1} \, d\mathbf{r}' \, \phi_\mu$ involve the same integral (since $\nu = \mu$) multiplying $(n_\mu - n_{\mu,\mathrm{same}})$. If there is only one electron in ϕ_μ, then $n_\mu - n_{\mu,\mathrm{same}} = 0$; if there are two electrons in ϕ_μ then $n_\mu - n_{\mu,\mathrm{same}} = 1$. These observations simply mean that an electron in ϕ_μ feels only a Coulombic interaction (no exchange) with the other electron in ϕ_μ (if there is another electron). If there is only one electron in ϕ_μ, obviously there is no Coulombic or exchange interaction with another electron in ϕ_μ. The bottom line is that $V_{ee}\phi_\nu$ describes the Coulombic and exchange interaction of an electron in ϕ_ν with $N - 1$ *other* electrons in the molecule (where N is the total number of electrons in the system).

In contrast to the case studied above where ϕ was an occupied orbital, the situation in which ϕ is an excited orbital ϕ_p is somewhat confusing at first glance. When ϕ is an occupied orbital ϕ_ν, the specific self-interaction term ($\mu = \nu$) arising in the definition of $V_{ee}\phi$ as given in Equation 3-12 gave rise to cancellation of the Coulombic and exchange interactions. In contrast, when ϕ is unoccupied ϕ_p, $V_{ee}\phi_p$ contains the Coulombic and exchange interactions of ϕ_p with *all* N electrons in the $\{\phi_\mu\}$; no cancellation analogous to the foregoing can occur here. As a result, the unoccupied or so-called virtual orbital solutions of the MO Schrödinger equation (3-11) correspond to solutions in which all N electrons are interacting with the orbital ϕ_p. For this reason, the virtual MOs obtained in conventional MO calculations are usually much less tightly bound (if at all) and much more diffuse (ie, of large radial extent) than one expects. In a sense, they are orbitals that may be more appropriate to utilize in anion studies, since they describe the interaction of ϕ_p with all N of the electrons of the molecules.

With these insights in mind, let us examine the physical content of V_{ee} for the lowest triplet (eg, n ↑ p_π ↑) and singlet (eg, n ↑ n ↓) states of carbenes. It should be clear that the V_{ee} potentials appropriate to these two states are different because the orbitals that are occupied in these two states are different. This in turn means that the n and p_π orbitals (and, in fact, all MOs) of the triplet and singlet states are different. That is, the n orbital of the triplet is *not* equivalent, in energy, hybridization, or size, to the n orbital of the singlet. In the singlet state, the n orbital has a higher (ie, less stable) orbital energy than in the triplet state and a correspondingly larger size (ie, radial extent). These changes are due to the larger Coulombic repulsion that an n electron feels because of the other electron residing in the n orbital in the singlet state.

There is an even larger difference between the p_π orbitals of the triplet and singlet states in the conventional molecular orbital picture. In the triplet state, an electron in the p_π orbital "feels" Coulombic and exchange interactions with all of the $(N - 1)$ other electrons including the single electron residing in the n orbital. In contrast, the p_π orbital of the singlet state is not even occupied! This p_x orbital is a solution to Equation 3-11 that involves interactions with all N electrons of the neutral carbene. Thus, this singlet state p_x orbital is very loosely bound and quite diffuse.

What major points are we trying to make in this description of the properties of carbene orbitals? First, we want to emphasize that the molecular orbital *concept*, although qualitatively clear and chemically very useful, does run into difficulties when viewed closely. In particular, attempts to quantify the concept to permit the numerical calculation of molecular orbitals and their energies are fraught with difficulties. The sources of the difficulty include:

1. The fact that the orbitals themselves define their own potential energy field.
2. The fact that which orbitals are *chosen* as occupied (ie, the configuration one selects) defines the potential V_{ee}, and this potential (hence the resulting MOs) varies from configuration to configuration,
3. The central fact that orbitals are themselves merely constructs of our imagination; thus this *model* has a limit beyond which it cannot be trusted.

Clearly, one way around the limitations and difficulties inherent in the molecular orbital model is to find and utilize a theory that goes beyond (ie, is more exact than) this model. Toward this end, we move on in Section 6 to examine in more detail the nature of the electronic configurations that are of importance in describing electronic motions in carbenes. This investigation is a necessary prerequisite for introducing the method of configuration interaction[31] (CI), which is treated in Section 7.

6. CARBENE ELECTRONIC CONFIGURATIONS

In the jargon of quantum chemistry the word "configuration" means a wave function properly adapted to the spin and spatial symmetry of a specified molecular orbital occupancy. Let's consider a few examples involving the most elementary carbene, methylene (CH_2). Using the coordinate system shown in Figures 3-1 and 3-2, the lowest five molecular orbitals of CH_2 belong to a_1 (1s carbon), a_1 (an even or symmetric combination of two CH-bonding σ orbitals), b_2 (an odd or antisymmetric combination of two CH-bonding σ orbitals), a_1 (the n orbital), and b_1 (the p_x orbital) symmetries. The configuration wave function corresponding to the triplet ($m_s = 1$) $1a_1^2 2a_1^2 1b_2^2 3a_1^1 1b_1^1$ orbital occupancy is given by the following single Slater determinant:

$$\psi(^3B_1, m_s = 1) = |1a_1\alpha 1a_1\beta 2a_1\alpha 2a_1\beta 1b_2 1b_2\beta 3a_1\alpha 1b_1\alpha| \qquad (3\text{-}13)$$

where the individual m_s values of the orbitals are denoted α and β ($m_s = \pm \frac{1}{2}$) and the overall spatial symmetry B_1 of this configuration is obtained as the direct product of the two open-shell orbitals: $3a_1 \otimes 1b_1$. The $^3B_1$ configurational wave functions with $m_s = -1$ and $m_s = 0$ are given by:

$$\psi(^3B_1, m_s = -1) = |\cdots 3a_1\beta 1b_1\beta| \tag{3-14a}$$

$$\psi(^3B_1, m_s = 0) = \frac{1}{\sqrt{2}}[|\cdots 3a_1\alpha 1b_1\beta| + |\cdots 3a_1\beta 1b_1\alpha|] \tag{3-14b}$$

where, in the Slater determinants, the dots denote the $1a_1\alpha 1a_1\beta 2a_1\alpha 2a_1\beta 1b_2\alpha$ $1b_2\beta$ occupancy, which is common to all these determinants. The singlet B_1 wave function belonging to this $3a_1^1 1b_1^1$ orbital occupancy is given as follows:

$$\psi(^1B_1) = \frac{1}{\sqrt{2}}[|\cdots 3a_1\alpha 1b_1\beta| - |\cdots 3a_1\beta 1b_1\alpha|] \tag{3-14c}$$

The other two orbital occupancies that play central roles in all carbene systems are the $3a_1^2$ and $1b_1^2$ occupancies, both of which are singlet and of A_1 spatial symmetry. Their corresponding Slater determinant wave functions are:

$$\psi_{n^2}(^1A_1) = |\cdots 3a_1\alpha 3a_1\beta| \tag{3-14d}$$

and

$$\psi p_\pi^2(^1A_1) = |\cdots 1b_1\alpha 1b_1\beta| \tag{3-14e}$$

The relative energies of the triplet and singlet configurational wave functions shown in Equations 3-14 depend on the relative energies of the n and p_π orbitals and the Coulombic and exchange interaction energies pertinent to each configuration. The energies of the n and p_π orbitals are affected by substituents attached to the carbenic carbon atom. Generally, σ-electron-donating groups tend to destabilize the n orbital relative to the p_π orbital; σ-electron-withdrawing groups do the opposite. Substituents possessing π molecular orbitals that can interact with the p_π orbital of the carbenic carbon can either stabilize or destabilize the p_π orbital relative to the n orbital, depending on whether the π orbital is filled or empty and on whether its energy lies above or below p_π. The energies of the n and p_π orbitals are also geometry dependent. As methylene's HCH bond angle approaches 180°, the n orbital achieves more 2p and less 2s character, and actually evolves into a pure p orbital that is degenerate with the p_π orbital at 180° (ie, linear geometry). Thus the bond angle at the carbenic center influences the 2s–2p hybridization, hence the energy of the n orbital.

The coulombic and exchange energies pertinent to any of the wave functions in Equations 3-14 depend on the size and shape of the orbitals, on the number of electrons that occupy each orbital, and on the m_s values of the electrons. In particular, the n^2 ($^1A_1$) configuration has a rather high Coulomb energy because of the two electrons in the same orbital. In contrast, the $n^1p_\pi^1(^3B_1)$ configuration has relatively lower Coulomb repulsion energy because the two valence electrons are in different orbitals. Hence on the basis of electron repulsion, one would expect the $n^1p_\pi^1$ configuration to lie lower in energy. However, the total energy of a configuration contains more than the electron–electron repulsion energy. It contains the kinetic and electron–nuclear attraction energies also. For the $n^1p_\pi^1$ configuration, the kinetic plus electron–nuclear attraction energy is probably less favorable than it is for the n^2 configuration. Therefore, the relative ordering of the total energies of the n^2 and $n^1p_\pi^1$ configurations is difficult to establish; there is a competition between electron–electron repulsion, which favors $n^1p_\pi^1$ and kinetic, plus electron–nuclear attraction, which favors n^2.

As a result, substituents, which can affect the size of the n and p_π orbitals, can have dramatic effects on the relative energies of the configurations arising from the n^2 and $n^1p_\pi^1$ orbital occupancies. For example, in CH_2 the $^3B_1(n^1p_\pi^1)$ configuration lies considerably ($\simeq$25 kcal/mol) below the $^1A_1(n^2)$ configuration,[32] whereas in CHF the n orbital is stabilized sufficiently that the $^1A_1(n^2)$ configuration lies[33] about 10 kcal/mol below the $^3B_1(n^1p_\pi^1)$ configuration.

Having become familiar with the primary configurations that arise from the n^1, p_π^2, and $n^1p_\pi^1$ orbital occupancies, let us address the relation of these configurations to the actual electronic states of carbenes we observe in nature. We should not lose track of the essential point that configurations are based on the molecular orbital model, so they are not capable of yielding arbitrarily precise descriptions of the true electronic states of carbenes.

The natural question to then ask is, "How do we progress beyond the molecular orbital model and how important is it to do so?". The answer to the first part of this question lies in the method of configuration interaction, which we treat in Section 7.

7. CONFIGURATION INTERACTION IN CARBENES: FUNDAMENTALS

A. The Underlying Principles

In Section 6 we saw that both the n^2 and p_π^2 orbital occupancies of methylene give rise to $^1A_1$ configurational wave functions, whereas $n^1p_\pi^1$ produces $^1B_1$ and $^3B_1$ configurations. In the configuration interaction model of electronic structure[31] we allow (in principle, all) configurations of the same space and spin symmetry to mix (or to combine or interact) to yield a better description of the true electronic states of that symmetry. What is the scientific basis for allowing or invoking this configuration mixing? It has been shown[34] that the set of Slater determinants that can be formed by arranging the N electrons of the atom or molecule among a complete set of orbitals is itself a complete set. That is, if one had available a complete set of molecular orbitals (even MOs that do not necessarily obey any Schrödinger equation such as Equation 3-9) the set of $N \times N$ Slater determinants formed by placing N electrons in all possible choices of MOs consistent with the desired overall space and spin symmetry would be a complete set. This means that any wave function, in particular the exact wave functions of the chosen space and spin symmetry, can be expressed as linear combinations of these Slater determinants. This theorem is the fundamental basis of the CI method in which the correct electronic wave functions Ψ_k are expressed in terms of the Slater determinants $\{\psi_j\}$ as follows:

$$\Psi_k = \sum_j C_{k,j}\psi_j \tag{3-15}$$

The CI expansion coefficient $\{C_{k,j}\}$ appropriate to each state Ψ_k is determined by making use of the variational method,[35] which is an essential ingredient of the conventional CI technique as it is used in practice. In the variational method one combines the philosophy that a linear combination of Slater determinants can, in the complete orbital basis limit, form an arbitrarily accurate description of the exact Ψ_k with the variational theorem stating that the average energy value of any "trial" wave function $\langle\Psi|H|\Psi\rangle$ lies above the lowest true molecular energy of the chosen symmetry E_0:

$$\langle\Psi|H|\Psi\rangle \geq E_0 \tag{3-16}$$

By constructing so-called trial wave functions of the CI form (Equation 3-16) but involving a *limited* set of Slater determinants $\{\Psi_j\}$ constructed from a *limited* set of molecular orbitals $\{\phi_i\}$, one forms a "truncated CI wave function"[31] from a finite orbital basis. This truncated CI function Ψ when substituted into Equation 3-16 will definitely produce an energy higher than the true energy E_0. Therefore the variational method specifies that one should vary the CI expansion coefficients $\{C_j\}$, subject to the constraint that Ψ remain a normalized function, to minimize $\langle\Psi|H|\Psi\rangle$, the idea being that minimizing this quantity brings the energy of Ψ closest to E_0 and supposedly yields the best description of the true wave function attainable in the truncated CI description.

Clearly several lingering questions about this CI method need to be addressed.

1. Although the completeness of Slater determinants and the variational theorem provide a mathematical foundation for the CI technique, what is the chemical significance of the various determinants in the CI function, and how can we intuit the values of the $\{C_j\}$ CI expansion coefficients?
2. How do we go about selecting in a chemically relevant and computationally efficient manner the finite basis of molecular orbitals $\{\phi_j\}$ used to form the Slater determinants, and how do we choose those Slater determinants to be included in the truncated CI expansion?,
3. Is it really necessary to utilize such a formidable looking model to achieve a qualitative understanding of carbenes?

B. Chemical Understanding of Configuration Interaction

The third question raised above has already been answered. We earlier noted that the single electronic configuration picture (ie, the conventional MO model) of the lowest singlet and triplet electronic states is not capable of yielding singlet–triplet energy spacings more accurately than 20 kcal/mol. This, in our opinion, is prima facie evidence that this lowest level model is even qualitatively in error. Thus, it is not only to achieve high accuracy in predicting energies and other properties of electronic states of carbenes that one must resort to the CI model. We believe that at least low-level CI (ie, including few Slater determinants) must be brought to bear if we are to achieve even a proper conceptual understanding of carbenes. This point of view moves us toward the first question posed above.

To clearly understand the chemical significance of configuration mixing, let us return to the specific case of the two ${}^1A_1$ configurations that arise in the most elementary carbene, methylene. Both the n^2 and p_π^2 configurations gave rise to ${}^1A_1$ Slater determinants. Therefore, within the ${}^1A_1$ spin and space symmetry, the lowest level CI wave function that can be postulated is of the form:

$$\Psi = C_1|\cdots n\alpha n\beta| + C_2|\cdots p_\pi\alpha p_\pi\beta| \qquad (3\text{-}17)$$

It is a natural first reaction of a good chemist to wonder why one would ever wish to include the p_π^2 configuration in an attempt to describe the lowest ${}^1A_1$ state of methylene. We will respond to this doubt in two steps. First, we recall that as the HCH bond angle approaches 180°, the n and p_π orbitals become degenerate. Therefore, near 180°, the true wave function might be expected to involve occupancy of both the n and p_π orbitals. Our second answer provides what we feel is a more fundamental insight into CI. It is relatively easy to show (by direct substitution and use of the antisymmetry property of Slater determinants) that the two-term CI wave function of Equation 3-17 is identical to the following two-determinant function:

$$\Psi = C_1[|\cdots \chi_+\alpha\chi_-\beta| + |\cdots \chi_-\alpha\chi_+\beta|] \qquad (3\text{-}18)$$

where the so-called *polarized orbitals*[36] $\chi_\pm$ are defined by

$$\chi_\pm = \frac{1}{\sqrt{2}}[n \pm \sqrt{x}p_\pi] \qquad (3\text{-}19)$$

and

$$X = \frac{-C_2}{C_1} \qquad (3\text{-}20)$$

To appreciate the conceptual significance of rewriting the original CI wave function in terms of the two Slater determinants involving polarized orbitals, let us clarify the meaning of $\chi_\pm$. Clearly χ_+ and χ_- are hybrid or polarized orbitals formed by mixing the n and p_π MOs. Depending on the value

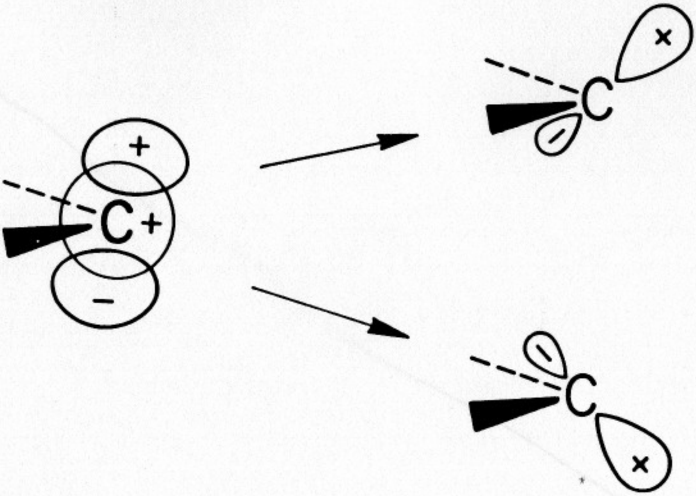

Figure 3-3. The n and p_x orbitals of a carbene and the two polarized orbitals $\chi_\pm = 1/\sqrt{2}\,[n \pm \sqrt{X}\,p_x]$.

of the mixing strength $\sqrt{X}$, which is determined by the ratio of the CI coefficients C_2/C_1, $\chi_\pm$ involves more or less polarization. For $X = 0$, both χ_+ and χ_- collapse to the n orbital; as X increases, the n orbital becomes more and more polarized via its mixing with the p_x orbital. In χ_+ the mixing or polarization occurs in one direction as shown in Figure 3-3, whereas in χ_- the polarization is in the opposite direction.

The content of the two-configuration CI wave function of Equation 3-17, as interpreted through its equivalent form in Equation 3-18, can now be made clear. The determinant $|\cdots\chi_+\alpha\chi_-\beta|$ allows an α electron to reside in χ_+ while the β electron is in χ_-, thereby keeping these two electrons out of each other's way. Alternatively, $|\chi_-\alpha\chi_+\beta|$ allows the α electron to be in χ_- while the β is in χ_+. The fundamental point is that mixing two configurations that differ from each other by *two* electron occupancies (eg, as in the n^2 and p_x^2 configurations) allows the *pair* of electrons to *correlate* their motions in the sense that they remain spatially separated (eg, by one occupying χ_+ while the other is in χ_-), thereby lowering their average Coulombic repulsion energy.

C. Perturbation Theory Estimates of Mixing Coefficients

The strength of CI mixing (ie, C_2/C_1) obviously determines the degree to which the electron pair will correlate its motions via orbital pair polarization. But what determines the degree of CI mixing? In practice the values of C_1 and C_2 are obtained by carrying out a variational CI calculation in which a matrix eigenvalue problem is solved;[31] the eigenvalues are the CI estimates of the electronic energies and the eigenvectors are the CI estimates of the $\{C_j\}$ expansion coefficients. The relative values of the CI expansion coefficients (eg, C_2/C_1 in the two-configuration CI function discussed above) can often be estimated by using perturbation theory.[37] Applied to the methylene example, perturbation theory predicts that the ratio of expansion coefficients is:

$$C_2/C_1 \cong (-2\epsilon_{p_\pi} + 2\epsilon_n)^{-1}\int p_\pi^*(\mathbf{r})n(\mathbf{r})p_\pi^*(r')n(\mathbf{r}')e^2|\mathbf{r} - \mathbf{r}'|^{-1}d\mathbf{r}'\,d\mathbf{r} \qquad (3\text{-}21)$$

The two crucial features to note in this expression are the energy denominator and the electron interaction integral in the numerator. The energy denominator factor tends to produce large C_2/C_1 ratios when the orbital pairs involved in the electron correlation are close in energy and small C_2/C_1 ratios when the orbitals are of vastly differing energies. The interaction integral can be interpreted as involving the Coulombic interaction of two electrons (at **r** and **r**′), each of which resides in a charge distribution given by the orbital product (p_π^*n). Only when the orbital product is substantial will the interaction integral be significant. In particular, if the two orbitals (p_π and n in this example) are localized in different regions of the molecule or otherwise have little or no region of mutual overlap, the interaction integral will be negligibly small and C_2/C_1 will essentially vanish.

In summary, substantial CI mixing is to be expected whenever orbital pairs are close in energy and have substantial regions of spatial overlap. In such cases, strong CI mixing gives rise to strong orbital pair polarization[36] and strong electron pair correlation as described via the polarized orbitals of Equations 3-18–3-20. All carbenes possess at least two molecular orbitals (ie, p_π and n), which fulfill these criteria for strong CI mixing. For this reason, we must utilize at least a two-configuration-level CI model if we are to achieve even a qualitatively proper description of carbenes.

D. Singly Excited Configurations and Orbital Relaxation

Before discussing briefly some specific examples of carbenes that have been examined by CI methods, we should address the roles played by another kind of configuration that is sometimes included in more extensive CI calculations.[31] Although configurations involving the nearly degenerate valence orbitals and differing from one another in how two electrons occupy orbitals (eg, n^2 and p_π^2) are of foremost importance, often other configurations are included in CI calculations to achieve higher accuracy energies.

Configurations that differ from one another in only one orbital occupancy (so-called singly excited configurations) often enter the CI wave function with rather small $\{C_j\}$ coefficients. In the methylene example, the $|\cdots n\alpha n\beta|$ and $[|\cdots n\alpha p_\pi\beta| - |\cdots n\beta p_\pi\alpha|]1/\sqrt{2}$ singlet configurations cannot mix because their spatial symmetries are different, so this pair of configurations does not offer an appropriate example. The $|\cdots n\alpha n\beta|$ and $[|\cdots n\alpha 4a_1\beta| - |\cdots n\beta 4a_1\alpha|]1/\sqrt{2}$ pair of configurations can be used to illustrate the reasons that underlie the role of singly excited configurations. A CI wave function of the form

$$\Psi = C_1|\cdots n\alpha n\beta| + C_2\frac{1}{\sqrt{2}}[|\cdots n\alpha 4a_1\beta| - |\cdots n\beta 4a_1\alpha|] \quad (3\text{-}22a)$$

is identical to

$$\Psi = C_1|\cdots\left(n + \frac{C_2}{\sqrt{2}C_1}4a_1\right)\alpha\left(n + \frac{C_2}{\sqrt{2}C_1}4a_1\right)\beta| - \frac{C_2^2}{2C_1}|\cdots 4a_1\alpha 4a_1\beta| \quad (3\text{-}22b)$$

The first determinant in Equation 3-22b involves a pair of electrons occupying a single orbital given by $n + (C_2/\sqrt{2}C_1)4a_1$; the second determinant is of the doubly excited variety treated earlier. Note that the expression:

$$|\cdots\left(n + \frac{C_2}{\sqrt{2}C_1}4a_1\right)\alpha\left(n + \frac{C_2}{\sqrt{2}C_1}4a_1\right)\beta|$$

is not of the polarized orbital pair form $|\cdots\chi_{\pm}\alpha\chi_{\mp}\beta|$ treated earlier. In the polarized orbital pair, the α and β electrons occupy different orbitals; here they reside in the same orbital: $n + (C_2/\sqrt{2}C_1)4a_1$.

The important point to be inferred from Equations 3-22 is that including singly excited configurations in CI wave functions allows the orbitals to polarize but not in a pair-correlated manner. In the jargon of the quantum chemist, singly excited configurations allow the orbitals to "relax" or adjust their shape. In contrast, doubly excited configurations such as we treated earlier, allow electron pairs to correlate in the sense that each electron in the pair resides in a different orbital. Why do singly excited configurations often enter with very small $\{C_J\}$ coefficients? The reason has to do with how the molecular orbitals are obtained. In particular, if the MOs used to form the Slater determinants in the truncated CI wave function are required to obey an MO-level Schrödinger equation, they are already optimum in the variational energy minimization sense. As a result, a CI wave function can gain no further lowering of the energy by attempting to further modify these orbitals via mixing in singly excited configurations. Therefore, it is quite common to utilize molecular orbitals that do obey Schrödinger equations[11] in quantitative CI calculations, since it is then not essential to allow for singly excited configurations in the truncated-CI wave function.

E. Atomic Orbital Basis Sets

The remarks thus far in Section 7 have focused largely on the concepts of configurations and molecular orbitals. One other aspect of such CI-level treatments must be clarified before we move on to examine a few novel carbene examples. The MOs used to construct CI wave functions are essentially always obtained as linear combinations of so-called atomic orbital (AO) basis functions. These AOs are not exact or even variationally optimized orbitals appropriate for the constituent atoms. They are orbitals whose radial size and shape (ie, l and m_l quantum numbers) are chosen to yield reasonably accurate descriptions of the charge densities of the atoms. These AOs are most frequently of the Slater or Gaussian type,[30] with the Gaussian basis orbitals being preferred for use on polyatomic molecules because they permit more facile evaluation of requisite integrals.

The essential points regarding the construction of a good atomic orbital basis set of either the Slater or Gaussian variety are:

1. The radial sizes of the orbitals depend on, hence reflect, the electronegativity of the atom on which they are located.
2. The angular shape of an atomic orbital is crucial in determining how the AOs can be combined to form MOs.
3. Often we use two (double-zeta) or three (triple-zeta) atomic basis functions of a given l and m_l value but with different radial sizes to permit variational flexibility in describing the true electron density of a molecule.
4. Often we use atomic basis functions having higher l values (polarization functions) than one would expect from considering the valence atomic orbitals of the constituent atom. These polarization functions allow for increased angular or shape flexibility in describing the charge density in the molecule.

In summary, the Slater or Gaussian orbitals used in ab initio quantum chemical calculations on molecules should be viewed not as real orbitals of the atoms but rather as functions of given size and shape or direction, which are located at the atomic centers and allow the MOs to be formed as linear combinations. In the very best quantum calculations, we add more and more basis functions until the results of the calculations do not change within acceptable limits.

8. CONFIGURATION INTERACTION IN CARBENES: ILLUSTRATIVE EXAMPLES

A. Methylene and Halogen-Substituted Methylenes (Halocarbenes)

There is an extensive history of theoretical work on methylene. We will not discuss in detail the realtionship of these theoretical calculations to the long-standing (but recently resolved) experimental and theoretical controversy[39] on the splitting between the $^3B_1$ and $^1A_1$ states of this most elementary carbene. Rather, we will focus on understanding the findings of the theoretical calculations in terms of the CI model described above.

Table 3-1 shows the results of CI calculations of Bauschlicher and coworkers[33] on the lowest energy singlet and triplet states of several halogen-

TABLE 3-1. Singlet–Triplet Energy Splitting in Halocarbenes[a]

Carbene	E_{ST} (kcal/mol)	θ (triplet)	θ (singlet)	C_1	C_2
CH_2	12.8	129.4°	102.8°	0.980	−0.201
CF_2	−46.5	118.2°	104.7°	0.984	−0.177
CCl_2	−13.5	125.5°	109.4°	0.982	−0.189
CHF	−9.2	120.4°	102.2°	0.982	−0.187
CHCl	−1.6	123.3°	102.0°	0.981	−0.192
CHBr	1.1	125.6°	102.6°	0.981	−0.193

[a] According to convention, positive splitting means that the singlet lies above the triplet.

substituted methylenes. The values of C_1 and C_2 pertain to the CI wave function coefficients (see Equation 3-18) of the n^2 and p_π^2 configurations in the singlet state; the triplet state, in all cases included in Table 3-1, is satisfactorily described with a single configuration (ie, it has only one significant CI coefficient).

What observations should we make from Table 3-1? First, we note that the equilibrium bond angles of the triplet and singlet states do not vary widely from carbene to carbene. Likewise, the X ratio of Equation 3-20 ($X = -C_2/C_1$) is relatively constant for all these carbenes. Thus the nature of the polarized orbitals $\chi_\pm$ appropriate to all these carbenes is very much the same as far as their n–p_π mixture is concerned. In contrast, the singlet–triplet energy splitting ranges over nearly 60 kcal/mol and is not always of one sign. The trend in singlet–triplet splitting in the sequence CH_2, CHBr, CHCl, CHF, CCl_2, CF_2 parallels the trend in the expected partial positive charge on the carbenic carbon atom. That is, the more electron-withdrawing power is attached to the carbon center, the more stabilized the singlet state becomes relative to the triplet. This trend is also consistent with the expectation that the n orbital is differentially stabilized relative to the p_π orbital as the partial positive charge on carbon increases. This latter trend in orbital energy splittings is in turn reflected in the slight decrease in $-C_2/C_1$ observed throughout the same sequence of carbenes identified above, which can be interpreted in terms of the n–p_π orbital energy trend through Equation 3-21.

B. π-Cyclic Carbenes[40,41]: c-C_3H_2 and c-C_5H_4

The R$-\ddot{C}-$R functional unit can also occur within a ring possessing π orbitals and electrons that interact (primarily) with the p_π orbital of the carbenic carbon atom. Cyclopropenylidene **(1)**, **(1a)** and cyclopentadienylidene **(2)** are two examples of such carbenes. Banerjee, Simons and Shepard[40] have carried out CI-type calculations on the low-energy singlet and triplet states of both these systems, with quite interesting results.

First, they find the singlet state to be the ground state of c-C_3H_2 (by 50 kcal/mol!), whereas the triplet state is the ground state of c-C_5H_4. This would seem to indicate that the n–p_π orbital energy splitting in much c-C_3H_2 is

TABLE 3-1. Singlet–Triplet Energy Splitting in Halocarbenes[a]

Carbene	E_{ST} (kcal/mol)	θ (triplet)	θ (singlet)	C_1	C_2
CH_2	12.8	129.4°	102.8°	0.980	−0.201
CF_2	−46.5	118.2°	104.7°	0.984	−0.177
CCl_2	−13.5	125.5°	109.4°	0.982	−0.189
CHF	−9.2	120.4°	102.2°	0.982	−0.187
CHCl	−1.6	123.3°	102.0°	0.981	−0.192
CHBr	1.1	125.6°	102.6°	0.981	−0.193

[a] According to convention, positive splitting means that the singlet lies above the triplet.

substituted methylenes. The values of C_1 and C_2 pertain to the CI wave function coefficients (see Equation 3-18) of the n^2 and p_π^2 configurations in the singlet state; the triplet state, in all cases included in Table 3-1, is satisfactorily described with a single configuration (ie, it has only one significant CI coefficient).

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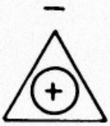


1a

2

larger than it is in c-C_5H_4. Why? Because of the participation of the π orbitals and electrons of the three- and five-membered rings. In c-C_3H_2 we have a three-membered ring involving 3 p_π orbitals (one from the carbenic carbon). As a result of interaction with the olefinic unit's π orbitals, the p_π carbenic orbital is raised in energy. From another point of view, we recall that in all three-membered ring systems we find a low-energy bonding MO and two degenerate (or nearly so) antibonding MOs. Such orbital patterns are well known to lead to stable $(4n + 2)$-electron structures. The triplet state of c-C_3H_2 places an electron in the second π MO of the 3-π-orbital ring system. Electron density in this antibonding orbital is energetically unfavorable (relative to density in an "isolated" p_π orbital of, eg, CH_2). Thus, the triplet state of c-C_3H_2 is destabilized relative to that of CH_2.

In contrast, the carbenic p_π orbital of c-C_5H_4 is *stabilized* by its interaction with the 4 π orbitals of the diene moiety. We recall that the 5 π orbitals of a cyclic system split into one very low energy bonding molecular orbital, a pair of degenerate bonding orbitals, and a pair of degenerate antibonding orbitals. The diene moiety contributes four electrons to the cyclic unit. Therefore, we expect that placing one electron in the carbene p_π orbital will be energetically favorable, since it will enter one of the degenerate bonding π molecular orbitals of the ring. Thus, we expect the triplet state of c-C_5H_4 to be stabilized relative to the triplet state of CH_2.

These findings on c-C_3H_2 and c-C_5H_4 illustrate other interesting effects of the resonance participation of the π orbitals of the unsaturated unit attached to the carbenic center. The X ratio $(-C_2/C_1 \simeq 0.123)$ for the lowest *singlet* state of c-C_3H_2 is smaller than was found in the halogen-substituted methylenes (Table 3-1). This is consistent with the p_π orbital of c-C_3H_2 being destabilized relative to the p_π orbital in CH_2, thereby yielding (see Equation 3-21) a smaller X ratio. We therefore conclude that substituents can even influence the importance of secondary electronic configurations (eg, the p_π^2 configuration here) by affecting the relative stability of the molecular orbitals.

The effects of the π-ring group on the singlet state X ratio is brought to its extreme in the case of c-C_5H_4. Here Shepard and Simons[40b] found that X could range from 0.239 to 15.7 as the C−C bond lengths in the five-membered ring were varied. At bond lengths describing an equal-sided pentagon, the p_π^2 configuration **(3,3a)** is actually more important (ie, $C_2 > C_1$) than the

3

3a

n^2 configuration **(2)**, as a result of which X is larger than unity ($X = 15.7$). That is, the 6-π-electron p_π^2 configuration is more stable than the 4-π-electron n^2 configuration at this geometry. For bond lengths describing two localized π bonds in the diene and an attached carbenic center, the n^2 configuration dominates the p_π^2 configuration ($X = 0.239$). The total electronic energy of the equilateral pentagon geometry lies 33 kcal/mol above the more stable "localized double bonds" geometry, but Shepard and Simons find a 15-kcal/mol barrier, which the former geometry must overcome to rearrange to the more stable geometry. Thus it appears that the lowest energy singlet state of c-C_5H_4 possesses two local minima on its potential energy surface. One structure is stable with respect to rearrangement by 15 kcal/mol and is dominated by the 6-π-electron p_π^2 configuration. The other structure is more stable (by 33 kcal/mol) than the first and is dominated by the 4-π-electron n^2 configuration.

The especially enticing aspect of all these observations is that the electronic nature at the carbenic center can be adjusted by attaching appropriate substituents. That is, one may be able to control the σ and π electrophilicity and nucleophilicity of carbenes via proper substituent choice.

C. Linear Unsaturated Carbenes

The carbenic centers in vinylidene (H_2CC) and higher linear unsaturated carbenes (H_2CCC, H_2CCCC, etc.) are qualitatively different from those in methylene and in the cyclic systems treated above; the former possess sp-hybridized orbitals and a pair of perpendicular p_π orbitals, whereas CH_2 has only one p_π orbital and approximately sp^2 hybridization of the n orbital. Kenney and co-workers[42] have carried out CI and other correlated electronic structure calculations on linear unsaturated carbenes. They predicted the singlet to be the ground state of the first four members of the family $H_2(C)_nC$ ($n = 1, 2, \ldots$), and they obtained singlet–triplet splittings of 51 and 49 kcal/mol for H_2CC and H_2CCC, respectively. The strong stability of the singlet state is largely due to the stabilization of the n orbital caused by its high-2s character (ie, sp hybridization).

By analyzing the CI expension coefficients belonging to the configurations in the optimal wave functions they achieved, these authors found the configurations depicted in Figure 3-4 to be important for the singlet and triplet states of vinylidene. As in all the carbenes discussed above, the triplet state

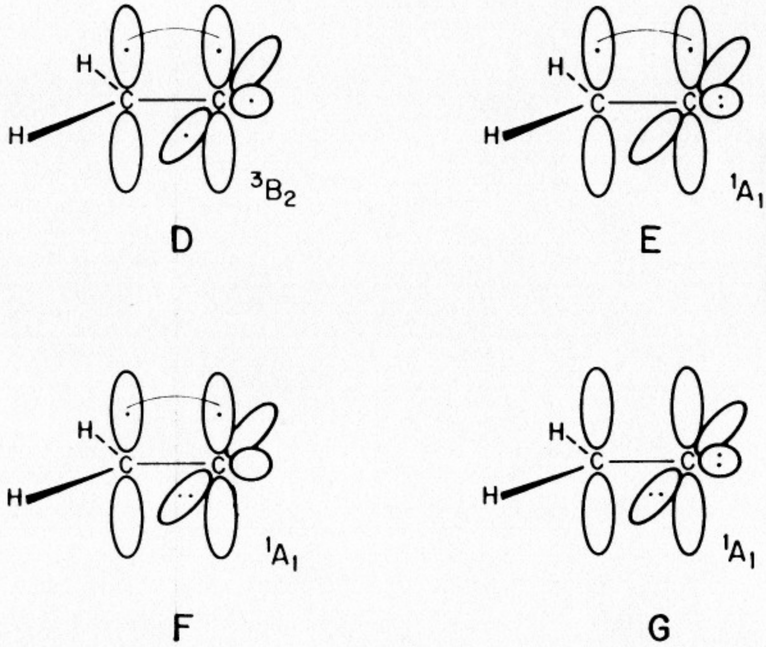


Figure 3-4. Important configurations of vinylidene (CH_2C), where **D** applies to the triplet ($^3B_2$) and **E–G** apply to the singlet ($^1A_1$).

is adequately described by a single configuration of the $n^1p_\pi^1$ form **(D)**. However, the singlet state requires configurations of the n^2 and p_π^2 forms **(E** and **F)** as well as a configuration in which the π^2 orbital occupancy of the double bond is correlated via polarized orbital pair formation involving a $\pi^2n^2-p_\pi^2n^2$ doubly excited determinant **(G)**.

A similar analysis of the most important configurations in H_2CCC indicated that the configurations shown in Figure 3-5 are essential for the lowest triplet and singlet states of this carbene. Configurations **H** and **I** relate to the triplet state: **J–O** pertain to the singlet. Again, we see the characteristic n^2 **(J)** and p_π^2 **(K)** configurations of the singlet, as well as configurations **L** and **M** analogous to the $\pi^2n^2-p_\pi^2n^2$ correlations described above for vinylidene. In this larger carbene, H_2CCC, there are more low-energy π and π^* orbitals available for interaction with the n and p_π orbitals of the carbenic center. As a result, there are more electronic configurations that must be invoked to describe the electron pair correlations (via orbital pair excitations in Slater determinants) that occur in this molecule.

In summary, Kenney and co-workers concluded that these linear unsaturated carbenes have singlet ground states due largely to the large stabilization of the n orbital caused by its sp hybridization. They also concluded that the presence of the π-orbital backbone of the carbene couples strongly

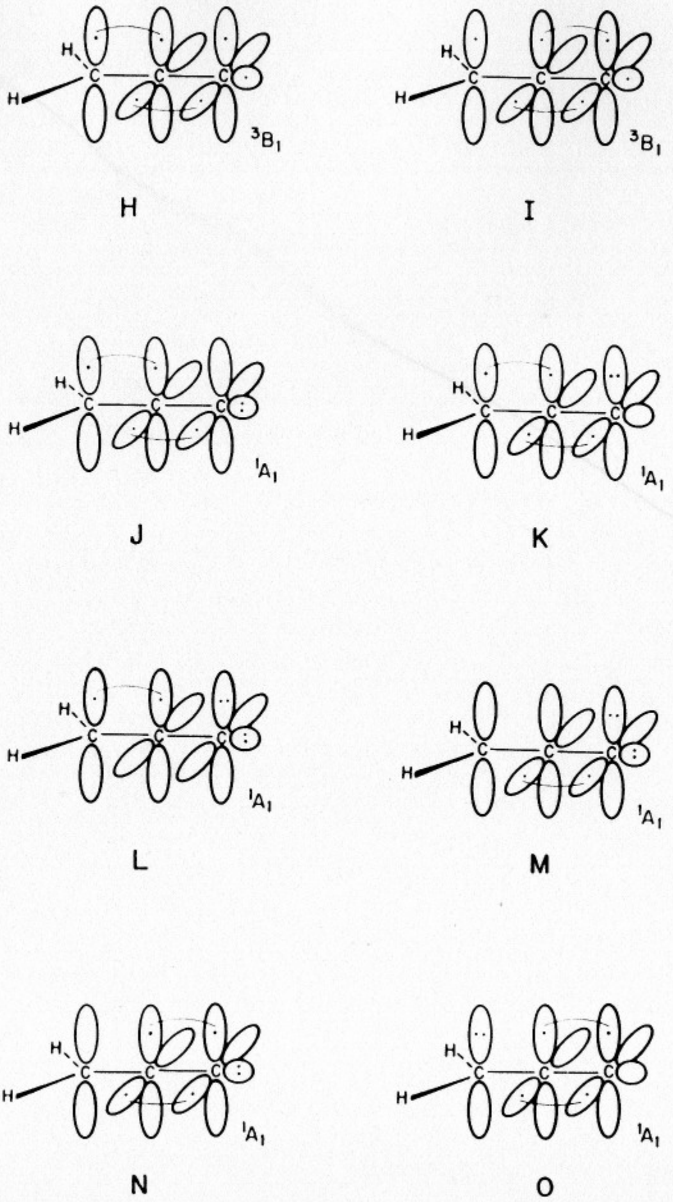


Figure 3-5. Important configurations in H_2CCC, where **H** and **I** apply to the triplet ($^3B_1$) and **J–O** apply to the singlet ($^1A_1$).

to the p_π orbitals of the carbenic center. This coupling allows the π orbitals of the backbone to utilize the carbenic p_π orbitals to form polarized orbital pairs (via $\pi^2n^2–p_\pi^2n^2$ determinants) and to thereby allow for correlation of the π electrons.

9. DICHLOROCARBENE: ADMISSION, ADDITIVITY, AND AFFIRMATION

Let us now return to more qualitative theory by way of dichlorocarbene, CCl_2. High-accuracy quantum chemical calculations[33] and logic based on electronegativity[22,33] and/or π-electron donation[15,17] correctly assert that it is a ground state singlet. For example, in an earlier paper Liebman and coworkers[17] presented simple correlations that related π-electron donation to carbene singlet–triplet gaps, E_{ST}, for a rather wide range of substituents. This was found to be the case whether the substituent donation was described in terms of empirical σ_R° constants (recall Equation 3-8) or the theoretical index $\Sigma\,\Delta q_\pi$ (Equation 3-23).

$$E_{ST} = 84.5\,\Sigma\sigma_R^\circ + 43.9 \tag{3-8}$$

$$E_{ST} = 298.1\Sigma\,\Delta q_\pi + 36.1 \tag{3-23}$$

For most substituents, good agreement was found, although it must be admitted that the atomic orbital calculational level employed (STO-3G) was comparatively poor and known to overstimulate the relative stability of triplets in general.[43] Regardless, the case of X = Y = Cl was clearly out of line (and so ignored in fitting Equations 3-8 and 3-23, though no reason for any idiosyncrasy of dichlorocarbene was offered). The STO-3G calculations also yielded anomalies with CCl_2 when calibration was made with more exact theory:[33] "to convert our [calculated] values of $E(S) - E(T)$ to those obtained by Bauschlicher and coworkers[33] requires subtraction of 27.3, 21.4, 27.0, 23.3 and 1.7 kcal/mol for CH_2, CHF, CHCl, CF_2 and CCl_2, respectively." Again, no explanation was offered. That CHCl fit all the relationships suggested that there was no fundamental deficiency with the basis set for chlorine. That CF_2 fit as well argued against special effects for carbenes with highly electronegative substituents. Reiterating, in the earlier paper, we had no answer to the question of why CCl_2 misbehaved.

Between the publication of our article and the preparation of this chapter, we found that our published value of the singlet–triplet gap for CCl_2 had the wrong sign—we can only surmise that we had been so convinced that dichlorocarbene was a ground state singlet (at any calculational level, not "just" experiment) that the value of −11.8 kcal/mol went unquestioned. What, other than the faith in our equations, eventually convinced us to look again at CCl_2? First of all, the result for CCl_2 fit quite well with our published plots and equations if the alternative sign is used. Second, the discrepancy with the results of Bauschlicher[33] becomes 25.3 kcal/mol when the new sign is employed, and so CCl_2 is more "normal." Finally, implicit in the equations above for E_{ST} is the "macroincrementation reaction" identity:[10]

$$\mathrm{CXY = CAX + CBY - CAB} \tag{3-24}$$

For X = Y, there are also its corollaries:

$$\mathrm{CX_2 = 2CHX - CH_2} \tag{3-25}$$

$$\mathrm{CX_2 = 2CXY - CY_2} \tag{3-26}$$

These relations generally worked,[44] for example, for CF_2 with its singlet–triplet gap from our calculations of −21.2 kcal/mol, one finds: (a) Equation (3-25) gives −15.7 kcal/mol and (b) Equation 3-26 gives −21.3 and −21.1 kcal/mol with X = CN and X = OH, respectively. The "predicted" value is −18 ± 4 kcal/mol, which is acceptably close. However, if X = Cl and our earlier singlet–triplet gap for CCl_2 is used, a disparate value of −3 kcal/mol is found. In contrast, employing the opposite sign would yield a much more acceptable value of −26.6 kcal/mol.

Using the same equations for CCl_2 one finds:

Equation (3-25) gives 10.7 kcal/mol.

Equation (3-26) gives 6.4 kcal/mol.

While a "real" value of +11.8 kcal/mol is compatible with these results, one of −11.8 kcal/mol would be highly dubious. With the more exact calculations of Bauschlicher and associates,[33] the predicted values for CF_2 and CCl_2 would be −31.2 and −16.0 kcal/mol, compared to their "real" results of −44.5 and −13.5 kcal/mol. It would appear that singlet–triplet gap for CCl_2 at the STO-3G level is +11.8 kcal/mol. Employing this number to generate new equations relating substituent π donation and the gap size, one finds:

$$E_{ST} = 83.6\Sigma\sigma_R^\circ + 43.0 \tag{3-27}$$

$$E_{ST} = 296.6\Sigma\, \Delta q_\pi + 35.8 \tag{3-28}$$

CCl_2 is normal. The intercept and slope of Equations 3-27 and 3-28 are nearly identical to those of Equations 3-8 and 3-23 generated before.[45] Our faith in the fundamental simplicity of chemical phenomena is reaffirmed.

10. SPECIFIC FLUORINE SUBSTITUENT EFFECTS

Now that we have discussed CCl_2, what can be said about CF_2? It is well established that fluorine substituent effects are generally large.[46] In this section we briefly discuss some of the relevant effects for carbene chemistry. First and perhaps foremost, difluorocarbene is a highly stabilized, ground state singlet,[15,17,33,47] while bis(trifluoromethyl)carbene, $C(CF_3)_2$, is a ground state triplet. This is due in large part to the role of $-F$ as a powerful π-electron donor, in contrast to $-CF_3$, which π donates negligibly. That is, the resonance structure $^+F{=}C(^-){-}F$ makes a meaningful contribution to the electronic structure of singlet CF_2, but no such structure is important for the triplet CF_2 or to either state of the trifluoromethyl carbene. That F forms a much more stable anion than CF_3 suggests that FC^+F^- will contribute[48] more to singlet CF_2 than any such resonance structure for the triplet or to either state of $C(CF_3)_2$. This again suggests that difluorocarbene will be "more singlet" (a more negative singlet–triplet gap) than bis(trifluoromethyl)carbene. The related comparison of CF_2 and CH_2 likewise suggests that CF_2 will be "more singlet" than CH_2.

This analysis also suggests a second difference between difluorocarbene and bis(trifluoromethyl)carbene: the former will be shown to be more stable, or more precisely, more stabilized than anticipated by comparison with "saturated" or tetravalent carbon-containing species. No thermochemical data are available for the $-CF_3$ species. We may, however, make comparisons with the parent CH_2. Consider the following "macroincrementation"[10] reaction:

$$CF_2 = CH_2F_2 + CH_2 - CH_4 \tag{3-29}$$

Using solely experimental numbers,[49] this reaction is exothermic by 62 kcal/mol for the singlet, suggesting a rather phenomenal stabilization of CF_2. None of the stabilization mechanisms above suggest that the triplet state will be stabilized and no stabilization is found. Using solely experimental numbers except the "preferred"[15] singlet–triplet splits for CH_2 and CF_2, it is found that triplet CF_2 totally lacks the stabilization of the singlet.

Another interesting comparison is between the difluoro- and monofluorocarbenes. The various models for carbene singlet–triplet gaps all correctly predict that the former will be "more singlet." It is not obvious how to predict correctly the relative stabilities of CF_2 and CHF, however. Geminal difluorination generally provides stabilization for compounds containing $>CF_2$ groups. For example, CH_2F_2 is stabilized relative to CH_3F by 10 (± 5) kcal/mol as shown by reaction 3-30.

$$2CH_3F \rightarrow CH_2F_2 + CH_4 \tag{3-30}$$

One would thus expect CF_2 to be stabilized relative to CHF on the basis of the related reaction 3-31.

$$2CHF \rightarrow CF_2 + CH_2 \tag{3-31}$$

However, CF_2 is found experimentally[49] to be considerably less stable than expected: the singlet is stabilized by only 2 (±5) kcal/mol and the triplet is destabilized by 24 kcal/mol!

It would appear that the singlet state of CF_2 has stability beyond that anticipated from our earlier experience in molecular energetics. This is additionally indicated by noting that the quantum chemically determined high-accuracy,[33] singlet–triplet gap of CHCl is nearly the arithmetic average of that of CH_2 and CCl_2 (arithmetical average = -0.4 vs explicitly calculated value for CHCl of -1.6 kcal/mol), as that of CHBr[33] is nearly the average of CH_2 and CBr_2[50] (-2.5 vs 1.1 kcal/mol, respectively). By contrast, the quantum chemical value for CHF is considerably higher than that arithmetically determined (arithmetical average = -16.9 vs directly calculated = -9.2 kcal/mol).

A related indication that the triplet state of CHF and/or the singlet state of CF_2 are anomalously stabilized is from the experimental energy differences[51] of the lowest lying (S_0) and first excited singlet (S_1) for CH_2, CHF, and CF_2: 7100, 17,287, and 37,226 cm^{-1} (where 1 kcal/mol $\simeq$350 cm^{-1}). These energy differences correspond to the energy required to excite to species whose qualitative orbital description (cf Subsection B of Section 3) is the same as the customarily discussed triplet. However, this quantity is far easier to measure spectroscopically than the singlet–triplet gap because it corresponds to an allowed transition, while the latter gap quantity corresponds to a spin-forbidden T_1–S_0 transition. The numerical average for the $S_1 - S_0$ energy difference of CH_2 and CF_2 is about 14 kcal/mol higher than that found for CHF. The stability of the ground state singlet for CF_2 is greater than our expectations. However, none of this precludes the possibility that the excited state triplet (and likewise, the S_1 singlet) is destablized.

To help disentangle this, consider now the "π-fluoro" effect[52] (and the earlier "perfluoro" effect[53] from which it was derived): the ionization energy of a π electron from a planar species is much less affected by the replacement of some (or all) of the hydrogens by fluorine than is the ionization energy of a σ electron. For the series HOH, HOF, FOF, this is readily shown: for π-electron ionization, the values are 12.6, 12.7, and 13.1 eV (where 1 eV $\simeq$ 23.06 kcal/mol), whereas for σ ionization the values are 13.8, 14.5, and 15.7 eV. For the abbreviated, two-member sequence NH_2 and NF_2, the values for π ionization are 12.4 and 11.6 eV, while for σ ionization the values are 12.1 and 14.6 eV. Although they must first be indirectly determined, the corresponding σ and π ionization potentials (IPs) of CH_2 and CF_2 may likewise be compared. Note that singlet and triplet CH_2 ionize to form the identical ion. As such, the experimental (π) IP of triplet CH_2, 10.4 eV, may be combined with the singlet–triplet gap of 0.4 eV to derive a value of 10.0 eV for the singlet's σ IP. Singlet CF_2 with an experimental (σ) IP of 11.4 eV is likewise combined with the singlet–triplet gap of 2.2 eV to derive a value of 9.2 eV for the triplet. Putting all these numbers together, ionization of a π electron from the triplet states of CH_2 and CF_2 costs 10.4 and 9.2 eV, whereas ionization of a σ electron from the singlet states of CH_2 and CF_2 costs 10.0 and 11.4 eV, respectively. That the π IP of triplet CF_2 lies significantly lower than the corresponding value for CH_2, whereas the σ IP of singlet CF_2 lies significantly higher than that for CH_2, suggests that triplet CF_2 is destabilized much as singlet CF_2 is stabilized. From these opposite effects of fluorine substitution, the large singlet–triplet gap of CF_2 arises.

11. ISOELECTRONIC REASONING AND CARBENES

Earlier sections have compared the singlet–triplet gap of CH_2 and SiH_2: the former is a ground state triplet and the latter is a ground state singlet. Both substances are dihydrides, but other than that, how are these two species related? Isoelectronic reasoning provides an answer, and we use this conceptual approach explicitly in this section to compare carbenes (a) with other carbenes, (b) with other electronic-deficient species, and (c) with compounds that are neither a "carbene" nor "electron deficient." The term "isoelectronic" is used here somewhat loosely to indicate that the species so related have the same number of valence electrons and the same number of nonhydrogenic atoms. In that regard, not all the individual species being compared would qualify as isoelectronic by the criteria used in Chapter 2 of this volume. (Note that in Chapter 2 Bent discusses briefly some aspects of the chemistry of carbenes and their analogues: the insertion reactions of CH_2 with those of NH, O, and BH_3. We abstain from repeating this discussion here.)

The first class of compounds to be compared consists of CH_2 and other 6-valence-electron dihydrides formed by varying the central atom. (This process is analogous to that for CH_4 that compares it with SiH_4 and NH_4^+.) We begin by pointing out again that (as discussed more extensively in Chapter 4 of this volume), SiH_2 is a ground state singlet while CH_2 is a ground state triplet. Since the hydrogens lack p orbitals for bonding, it is clear that π-electron factors cannot be invoked to explain this difference. Rather, it is the relative electronegativities[22,55] of the pair of atoms—C and H as compared to those of Si and H—that constitute a major difference between these two dihydrides. That is, 6-electron AH_2 species will tend to be triplet when A is of high electronegativity and singlet when the electronegativity of A is low. As such, one may immediately, and correctly, deduce that NH_2^+ and substituted nitrenium ions will generally be "more triplet" than CH_2 and relatedly substituted carbenes, whereas SiH_2 and its derivatives will be "more singlet."

This can be explained in terms of the relative importance of varying resonance structure. Let E be an arbitrary central atom, and let pro-1 mean that the singlet is preferentially stabilized, and pro-3 likewise for the triplet. In the literature, the following resonance structures have been considered: $(HE)^+ H^-$ (pro-1, Reference 56), $EH^- H^+$ (pro-3, Reference 56), $E^{+2} (H^-)_2$ (pro-1, Reference 22), $E^{-2} (H^+)_2$ (pro-3, Reference 22), $EH(^2\pi)$ H(pro-1, Reference 20) and $EH(^4\Sigma)$ H(pro-3, Reference 20). Regardless of the precise explanation, it would appear that at the very least, σ effects and the difference of the electronegativity of the central atom and those affixed to it provide the chemist with the ability to make general comparisons of the spin states of carbenes and isoelectronic analogues.

Also relatable to electronegativity factors is the seemingly general observation that elements in the third row (and below) have a tendency to "hybridize" less than those in the second row. As such, the HAH angles are expected to be smaller than tetrahedral (ie, classically corresponding to sp^3) and instead to be closer to 90°, corresponding to p^3 and "pure p" bonding. Equivalently, the remaining in-plane, highest lying occupied symmetric (a_1 or n) orbital is "more s," while the highest lying antisymmetric or π orbital (b_1 or p_π) is unaffected because of symmetry. In the simplest approximation, because an s atomic orbital is lower than the corresponding p orbital, putting two electrons in the "a_1^2" or "n^2" singlet state is energetically preferred over the "$a_1^1b_1^1$" or "$n^1p_\pi^1$" triplet state. Interelectron repulsions may drop the triplet below the singlet, but stabilizing the a_1 or n orbital will encourage the 6-valence-electron EH_2 to be a ground state singlet. It is important to note that these arguments can be extended beyond carbenes and other 6-valence-electron species. They relate to why the 8-valence-electron H_2S and H_2Se have considerably smaller HAH angles than H_2O and to why the relative ionization potentials[54] of the three hydrides to form the ^2B and ^2A radical cations (7-valence-electron H_2E species) by loss of a b_1 and a_1 electron, respectively, are: H_2O, 12.6 vs 13.8 eV, $\Delta IP = 1.2$ eV; H_2S, 10.5 vs 12.8 eV, $\Delta IP = 2.3$ eV; H_2Se, 9.9 vs 12.4 eV, $\Delta IP = 2.5$ eV. The second-row element O stands alone; the third- and fourth-row elements S and Se are similar.

The second class of compounds to be compared consists of carbenes in which the atoms affixed to the central carbon are isoelectronically changed by proceeding down a column in the periodic table. (This comparison interrelates such species as the methyl halides, CH_3X, for X = F, Cl, Br, and I.) Surprisingly little systematic carbene chemistry has been reported in this direction except for the cases of X = F, Cl, and Br, and Y = Li and Na. In the case of the mono- and dihalocarbenes, the singlet–triplet gap decreases in the stated order for both the CHX and CX_2 series. This finding is compatible with the importance of both σ and π effects, a conclusion presented in Section 6, where we first discussed these important species (see also Sections 9 and 10). In the case of the alkali metal derivatives of carbenes, the electronic properties of the CHY and CY_2 sets are nearly independent of the metal. The CHY species are ground state linear triplets, while, as noted in Section 3, the CY_2 species consist of ground state triplets with two isomers, one linear and the other markedly bent. None of these organometallic compounds particularly resembles CH_2 any more than do arbitrarily substituted carbenes, and so the general "folklore" rule that asserts that the alkali metals are not "really" isoelectronic to hydrogen is validated.

The third class of isoelectronic molecules to be discussed consists of the substituted derivatives of CHF and the neutral species that may be formally derived from them by "pulling" protons from the fluorine atom. (This sequential process, $-F$, $-OH$, $-NH_2$, $-CH_3$, is well established and is invoked in the comparison of CH_3F with CH_3OH and CH_3NH_2, as well as with F_2 and C_2H_6. In this chapter we emphasize F as a starting point only because the fluorocarbenes are much better understood than their isoelectronic analogues.) In particular, consider first the series CHF, CHOH,

$CHNH_2$, $CHCH_3$. At the STO-3G level, CHF, CHOH, $CHNH_2$, and $CHCH_3$ have singlet–triplet gaps of 12, 1, −3, and 35 kcal/mol. These are to be compared with the 40 kcal/mol calculated for CH_2 at this quantum chemical level. The resulting order of singlet–triplet gaps CH_2, $CHCH_3$, CHF, CHOH, and $CHNH_2$ is inconsistent with the sole importance of σ-electron or electronegativity effects: the values for CHOH and $CHNH_2$ are markedly out of line.

Nearly the same order is found for the singlet–triplet gap of the related series CF_2, $C(OH)_2$, $C(NH_2)_2$, $C(CH_3)_2$: CH_2 (40 kcal/mol), $C(CH_3)_2$ (32), CF_2 (−21), $C(NH_2)_2$ (−26), and $C(OH)_2$ (−26) at the same STO-3G level.[57] It is tempting to ascribe the order solely to π effects. We recall[15,17] that correlations have been made between the carbene singlet–triplet gap and "theoretical and empirical measures of π donation by substituents."[58] However, as shown elsewhere in this series (Chapter 5, Volume 3; Chapters 6, 8, and 9, Volume 4), considerable care must be used in any such analysis.

For example, we may consider the stabilization of substituted benzenes as an archetype for substituent effects on general hydrocarbons, and therefore on CH_2. To do so, consider the following macroincrementation reaction:

$$C_6H_5X = C_6H_6 + (CH_3)_2CHX - C_3H_8 \tag{3-32}$$

The stabilization is in the order $X = NH_2 > OH \backsim F > CH_3$ and so roughly corresponds to the foregoing order of carbene singlet–triplet gaps. It also corresponds to intuitive ideas of π interaction by substituents. However, using solely experimental values, the stabilization energies are only about 4, 3, 3, and 1 kcal/mol! Perhaps benzene is not electron deficient enough to achieve the desired degree of substituent effects. Consider, then, the following reaction for studying substituent effects of acetyl derivatives:

$$CH_3COX = CH_3CHO + (CH_3)_2CHX - C_3H_8 \tag{3-33}$$

Here more significant stabilization energies are found; for example, for $X = CH_3$ the value is 7 kcal/mol. The values for NH_2, OH, and F are all much larger and in the order $OH > NH_2 > F$, with three nearly identical numbers: 26, 25, and 24 kcal/mol. As noted above, it really is not obvious with which other system it is best to compare the effect of π donation on carbene singlet–triplet gaps.

Nonetheless, it is clear there is a statistically meaningful, and chemically useful, correlation between substituent constants. An example of this utility is found in the series HCCN, FCCN, HOCCN, H_2NCCN, CH_3CCN. Knowing that the singlet–triplet gap decreases in the order CH_2, $CHCH_3$, CHF, CHOH, $CHNH_2$ suggests that for the cyanocarbenes, the gap should decrease in the order HCCN, CH_3CCN, FCCN, HOCCN, H_2NCCN. The four values available in the literature (STO-3G calculations) are HCCN (59 kcal/mol), FCCN (29), HOCCN (19), and H_2NCCN (16), in complete agreement. Since apparently no calculations have been reported on CH_3CCN, we decided to study this carbene. The newly calculated STO-3G singlet–triplet gap[59] is 55.9 kcal/mol, in complete agreement with the order above. Even reliable quantitation is achievable, using the macroincrementation reaction:

$$\mathrm{XCCN} = \mathrm{CHX} + \mathrm{HCCN} - \mathrm{CH_2} \tag{3-34}$$

the arithmetically "predicted"[44] STO-3G gaps are 54, 30, 20, 16 kcal/mol, while those quantum chemically calculated are 56, 29, 19, and 16 kcal/mol. (Even $C(CN)_2$, manifestly *not* isoelectronic to any of the carbenes above and a "trouble-maker" for the earlier correlation, works out well here, since the "predicted" value is 77 kcal/mol and the calculated value is 79 kcal/mol.)

Yet another isoelectronic argument compares two molecules differing only in that the nuclear charges of at least one of the component atoms in a substituent has been varied. (Such a comparison may be made between $CH_3-{}^-BH_3$ and $CH_3-{}^+NH_3$. In that ethane is equivalent to "methylmethane," CH_3-CH_3 is also logically included in this grouping.) For carbenes, the following sets of substituents have been so compared: set 1 = $-{}^+FH$, $-OH$, and $-{}^-NH$, and set 2 = $-{}^+NH_3$, $-CH_3$, and $-{}^-BH_3$. In the former set the singlet–triplet gaps for the monosubstituted carbenes precipitously decline in the order given. (At the STO-3G level, the gaps are 30, −1, and −17 kcal/mol.) The same trend is also found for the first two members in the disubstituted case, no data being available for $C({}^-NH)_2$.[60] This result is opposite to the predictions of the σ-orbital, electronegativity-based model. Thus this latter picture is mostly relegated to predicting the effects of varying the central atom. By contrast, the π-donation explanation is compatible with the data. It may be tempting to speak of $HC-{}^-NH$ as C-deprotonated formaldimine, $HC^-=NH$, and no longer consider it even as a carbene, but we forewarn the reader of the carbene character of the isoelectronic vinyl anion, $HC^-=CH_2$ (see Section 12). For the latter set of three carbenes, the singlet–triplet gap is nearly the same (34, 35, and 36 kcal/mol), as befits substituents with but rather minor π interactions.

We now talk about isoelectronic species related by protonation or deprotonation of a substituent. (Such comparison may be made between $CH_3-{}^-NH$, CH_3NH_2, and $CH_3-{}^+NH_3$, ie, deprotonated, parent, and protonated methylamine.) The following comparisons are made: $-F$ vs $-{}^+FH$, $-OH$ vs $-{}^+OH_2$, and $-{}^+NH_3$ and $-NH_2$ vs $-{}^-NH$. All these so-derivatized carbenes are understandably "more singlet" than the parent CH_2. However in each set, the species with the most positive, hence electronegative substituent, is the "most triplet" and the least positive species, the "most singlet." The realization that π effects are more important than σ effects for understanding the singlet–triplet gap of carbenes when we are not considering any variation of the central atom still does not explain why $HC-{}^+FH$ is "so triplet." Our only thought is that while the double-bonded resonance structure $HC^-={}^{+2}FH$ is quite bizarre, the nonbonded resonance structure, HC^+ FH, appears sensible. The latter would certainly strongly "encourage" $(HCFH)^+$ to be a singlet. [Admittedly, at the STO-3G level,

CH^+ is a ground state triplet[59] but by only 1 kcal/mol. In that triplets are greatly and falsely stabilized at this level, cf the result for CH_2, there is neither really any contradiction with the experimental $^1\Sigma$ ground state for CH^+ nor our assertion about $(HCFH)^+$.]

C-Protonated species are also isoelectronic to the parent carbenes—the term "carbenium ion" for this class of carbocations speaks to this. The reader may recall the discussion of the cyclic carbenes c-C_3H_2 and c-C_5H_4 in Section 6 and note now how this parallels that of the molecular structure and energetics of the aromatic (2-π, c-$C_3H_3^+$) and antiaromatic (4-π, c-$C_5H_5^+$).[61] This protonation relation is not only a conceptual tool. The gas phase syntheses of suitable carbenes[49,62,63] via proton transfer:

$$CHXY^+ + BH \rightarrow CXY + BH^+ \tag{3-35}$$

makes use of the often-surprising fact that electron-deficient species, at least in the gas phase, are also bases with rather significant proton affinities.[64] Without going into experimental details here of the synthesis of gas phase ions or of the actual measurements, we merely record the following proton affinities (kcal/mol): CH_2 (singlet), 207; CHF, 193; CF_2, 173; CFCl, 186; CHCl, 207; CCl_2, 193; CHOH, 229. These numbers show that CH_2 is of comparable basicity to NH_3; CCl_2 is comparable to benzene; and CHOH is more basic than most amines.

The remaining use we will make of isoelectronic reasoning compares carbenes to other species that are not normally viewed as related to carbenes at all. The first example contrasts HCF to other 2-heavy-atom, 12-valence-electron species. As the C is transformed into the isoelectronic, but more electron-deficient, species, N^+, and the F into the isoelectronic, but more electron-rich, species O^-, one expects the degree of π bonding to increase—and so it does, to form the closed-shell[65] HNO, H–N=O. Conceptually moving the proton of the bonding hydrogen onto either the N or O nucleus is accompanied by formation of a triplet, regardless of whether O_2 or NF is formed. By contrast, removal of a proton from either the N or O nucleus results in formation of a singlet, whether it be H_2CO, HCOH, H_2NN, or HNNH.[15]

Analogously, by conceptually transferring protons from the affixed fluorines to the central atom, the 3-heavy-atom, 16-valence-electron singlet CF_2 is transformed into another singlet O_3. If CF_2 is a tamed 1,1-diradical (ie, if the two unpaired electrons on the central atom are paired to form a singlet), O_3 is a tamed 1,3-diradical.[66] Consistent with this are computational findings that HNO_2 (Reference 67) and H_2CO_2 (Reference 66) are nearly triplets. Singlet CCl_2 is much more saturated than either singlet or triplet CH_2, and so we are not surprised that the reaction

$$(CH_3)_2CCl_2 + CH_2 \rightarrow (CH_3)_2CH_2 + CCl_2 \tag{3-36}$$

is exothermic by 60 kcal/mol for the all-singlet reaction and by 53 kcal/mol for all the species in the ground state. By contrast, the triplet states of CCl_2

and CH_2 are more comparably unsaturated, although there is clearly some stabilization of the dichlorocarbene due to the $\mathrm{Cl-(\cdot)\dot{C}-Cl{:}}$ and $\mathrm{Cl-(:)\dot{C}-\dot{Cl}}$ resonance structures. As such, the reaction (3-36) for the all-triplet case is exothermic by only 37 kcal/mol. For the SO_2 case, consider the reaction for all ground state species:

$$(CH_3)_2SO_2 + S \rightarrow (CH_3)_2S + SO_2 \qquad (3\text{-}37)$$

which is exothermic by 52 kcal/mol. This suggests that CCl_2 and SO_2 have comparable "carbene" character. Likewise consider the noncarbene carbene CO and the reaction for all ground state species,

$$(CH_3)_2CO + CH_2 \rightarrow (CH_3)_2CH_2 + CO, \qquad (3\text{-}38)$$

which is exothermic by 138 kcal/mol. CO is hardly unsaturated, but it is also unambiguously an example of divalent carbon.

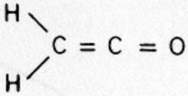
12. AN EPILOGUE: HIDDEN CARBENES AND THE DICHOTOMY OF DICOORDINATE VERSUS DIVALENT CARBON

We began by comparing divalent carbon with carbon that is tetracoordinate and tetravalent. We also equated species with divalent carbon with carbenes. Now we discuss species whose carbene character is a matter of ambiguity. In this chapter, we focused our attention on compounds with dicoordinate carbon and so omitted discussion of:

1. CO, a highly stable species that is an unequivocal example of divalent carbon.
2. Isocyanides (RNC), a relatively reactive and unstable class of species for which there may be disagreement over whether they are examples of divalent carbon. The reader, however, should recall our discussion of vinylidene (H_2CC:) and other linear unsaturated carbenes (H_2CCC:, H_2CCCC:, . . .) in Section 6. There is little question that these species qualify as carbenes and CO, HNC, and H_2CC are isoelectronic. But this isoelectronic relationship is not the desired link with which to conclude that isocyanides and CO are carbenes, because the normal, tetravalent, organic compound HCCH is isoelectronic as well.
3. "Carbenoids," a term casually used to describe a loosely bound complex of a carbene and some other, generally metal-containing, species.
4. "Metallocarbenes," a somewhat ambiguous[68] term for metal–carbene complexes that are formally analogous either to (a) nonmetal ylids but with a central metal atom in a formally high oxidation state or (b) "normal" transition metal complexes with low oxidation state metals and a carbene ligand.

It is important to emphasize that we talked about compounds containing dicoordinate carbon—it is also necessary to assert that these contain divalent carbon. To say that a species has a dicoordinate carbon says that it has two bond partners and thus discusses its "connectedness" and geometric structure; to say that carbon is divalent says that it forms two bonds and so speaks to the more subtle question of its electronic structure. To illustrate this problem, recall Hine's closing discussion[69] in the first monograph on carbenes. He posited a singlet carbene with one electron-accepting substituent and one electron-donating substituent, which we therefore schematically draw as $A-\ddot{C}-D$. Because of the acceptor substituent, the additional, simple, resonance structure $^-A=C^+-D$ contributes to the description of the carbene regardless of the nature of the substituent D. Likewise, one may draw the corresponding structure with the donor substituent, $A-C^-=D^+$, regardless of the nature of the substituent A. Some 30 years of theoretically motivated experimental carbene chemistry[70] (and nearly 20 years of experimentally motivated theory[71]) have shown that substituents with energetically low-lying pairs of electrons adjacent to the carbene center provide stabilization by such $-\ddot{C}-D \leftrightarrow -C^-=D^+$ resonance. Push-pull stabilization logic naturally results in the final resonance structure, $^-A=C=D^+$. Hine then singled out the strong, and so presumably highly stabilizing, acceptor group $-CH_2^+$, and the strong, and presumably highly stabilizing, donor group $-O^-$. The resultant species, which is immediately recognized as ketene, is in fact stable enough to be isolable. In agreement with Hine, few would want to consider ketene to be a carbene—the formal Lewis structure $CH_2=C=O$ argues that this species contains a central tetravalent carbon.

However, let us take ketene (**4**) and bend the heavy atom C#C#O framework, where the symbol " // " is a "hedge" with respect to whether we view the bonds as single or as double. There are two limiting geometric cases for the bending—one in which all five atoms in the ketene remain in the same plane and the other in which the H–C–H plane is perpendicular to the planar, heavy-atom framework. Consider the former. The resultant species is recognizable as acetyl-2-yl, $(\cdot)CH_2-C(\cdot)=O$, **5.** This is hardly recognizable as a carbene, but is instead rather accurately described as a low-lying excited state of ketene. Consider the latter limiting case (sequentially **4a, 6, 7**). Eventually the bending is severe enough that the terminal carbon and oxygen are within bonding range and the carbene oxiranylidene (**7**) is "synthesized." Is oxiranylidene isolable? No one has succeeded yet. Is it bound? That is, does it correspond to a potential energy minimum, or does it rearrange effortlessly (without energy of activation) back into ketene? We do not know. However, quantum chemical calculations[72] at the 4–31G level show that it is 80 kcal/mol higher in energy than ketene. This 80 kcal/mol is enough energy to break apart the molecule into singlet CH_2 + CO. Of the species above, we would not consider ketene or its excited state to be carbenes, but the cyclic oxiranylidene and the fragment CH_2 would definitely be so labeled. It would thus appear that singlet carbenes are closer to "normalcy" than one thinks. Equivalently, it is inherently ambiguous what constitutes singlet carbenes.



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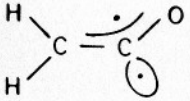

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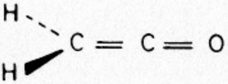

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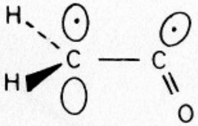

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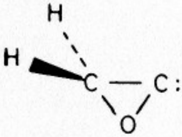

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What about the triplets? Paralleling Hine's discussion, consider a triplet carbene center with its two substituents, $X-\dot{C}(\cdot)-Y$. How can it be stabilized? Imagine X and Y as substituents having one unpaired electron apiece. The carbene may then have 4, 2, or 0 unpaired electrons, and it may be a quintet, triplet, or singlet. If the unpaired electrons formally of the X and Y groups are in perpendicular planes, then each electron can interact with one of the two unpaired electrons on the carbene carbon. This results in two double bonds. Choosing two O atoms for X and Y yields such a stabilized species, the singlet, carbon dioxide, **8.** Again, this is clearly a case of tetravalent carbon, and indeed, $O=C=O$ is the simplest Lewis structure for CO_2. However, one can also place the two unpaired electrons of the two oxygens in the same plane. This results in a bent species, **9,** and roughly corresponds to $O=C(\cdot)-O(\cdot)$, the lowest lying excited triplet of CO_2. One can even put the two unpaired "oxygen" and the two "carbene" electrons in the plane of the $O-C-O$ framework as it bends. This results in dioxiranylidene, **10.** This species is clearly strained and unstable relative to ring opening to carbon dioxide. At the 4-31G level,[72] it lies more than 160 kcal/mol higher in energy than "normal" CO_2. In accord with the general finding that this level of quantum chemical calculation is inadequate for three-membered rings, much more rigorous recent quantum chemical calculations[73] reduce this value to "merely" 110 kcal/mol. It is thus intrinsically stable relative to dissociation to CO + O, and indeed, the same studies suggest that this cyclic isomer of CO_2 sits in a potential well. Eventual isolation cannot thus be precluded.

$O=C=O$

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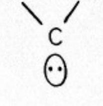

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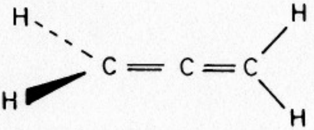
Analogous considerations apply to the species formed by distorting the isoelectronically related linear species with $X = Y = CH_2$, allene (**11**). So doing produces the biradical allyl-2-yl (**12**) and the carbene cyclopropylidene (c-$(CH_2)_2C$:, **13**). Although allene is a stable species, neither of the distorted $X = Y = CH_2$ cases has been isolated. However, unlike either of the earlier two examples, allene and its distorted counterparts may be functionalized to modify the relative stability of the three different forms. Chapter 3 of Volume 3 offers a general discussion of functionalized distorted allenes; for now it suffices to note that the 6-π, and the presumably aromatically stabilized carbene cycloheptatrienylidene (**14**), have been experimentally shown to be less stable than 1, 2, 4, 6-cycloheptatetraene (**15**) with its twisted allene skeleton. By contrast, the analogously stabilized cyclopropenylidene (**1**), with 2 π electrons appears to be a better description of c-C_3H_4 than is 1,2-cyclopropadiene (**16**). This logic should sound familiar: Section 6 of this chapter discusses the latter and c-C_5H_4 from the vantage point of aromaticity.

Moving on to more explicitly ambiguous cases of carbene nature, consider first C_2HN.[74] Is this tetraatomic molecule cyanocarbene, $H-\ddot{C}-C\equiv N$? Or is it keteniminyl-1-yl, $H-\dot{C}=C=\dot{N}$, or perchance, ethynylnitrene, $H-C\equiv$



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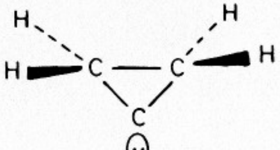

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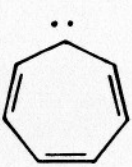

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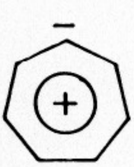

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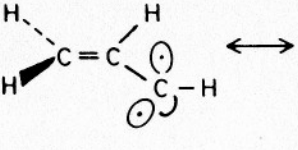
$C-\dot{N}\cdot$? The nonobvious answer is that the second description is the best for the ground state triplet species, and the first is best for the singlet. Regrettably, it is necessary to use CI calculations to show this. HCCN, so obviously a carbene, seemingly is a 1,3-diradical. What about HCNO? Is it nitrosocarbene ($H-\ddot{C}-N=O$), formaldoximinyl-1-yl ($H-\dot{C}=N-\dot{O}$), or formonitrile oxide, also known as fulminic acid ($H-C\equiv N-O$)? Is this species a singlet or a triplet? In fact, HCNO is a closed-shell, ground state singlet with complete octets for all the "heavy" atoms: the nitrile oxide formulation is the most accurate.[75] Yet, the isoelectronic nitrilimines and nitrile ylids (with the general formulae RCNNR′ and RCNCR′R″)[76] undergo 1,1-cycloaddition reactions[77] and so suggest carbenelike behavior. It seems hardly obvious when carbenelike behavior will be manifested.

Vinylcarbenes[78] such as $CH_2=CH-CH$: (**17**) enjoy similar ambiguity because they may also be formulated as derivatives of allyl-1,3-diyl, $\cdot CH_2-CH=CH\cdot$ (**17a**). In this case one may rotate the 3-carbon and its two pendant groups and remove the allylic conjugation, **18.** This loss of conjugation would be energetically costly were it not for the compensation of 1,3-bonding. Forming a complete 1,3-bond results in a species recognized as a cyclopropene (**19**), with a highly strained C−C bond. Although cyclopropenes are, in fact, more stable than vinylcarbenes, much of the thermal rearrangement chemistry of the former is derived from the reactions of the latter.[79] Conceptually replacing the saturated carbon by oxygen results in a related class of species where the relative stabilities are even more comparable. The 4-π oxirenes are antiaromatic, whereas cyclopropenes are nonaromatic. Furthermore, the new C=O bonds in the ketocarbenes derived from the oxirenes are stronger than the new C=C bonds in the vinylcarbenes derived



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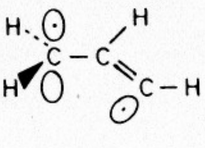

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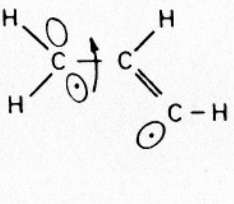

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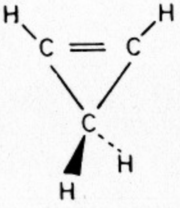

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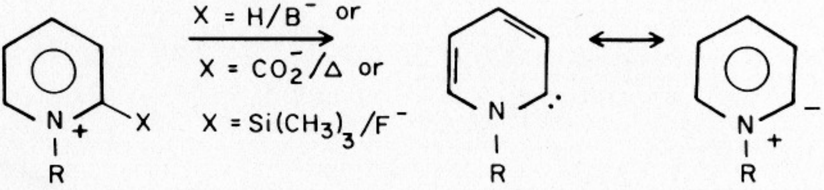
from the cyclopropenes. The presence of a divalent carbon in ketocarbenes is thus energetically competitive with solely tetravalent carbon in the oxirene.

Other species are on the borderline of carbene–noncarbene behavior because singlet carbenes are inherently electron deficient. As noted numerous times in this chapter, substituents with energetically low-lying pairs of electrons adjacent to the carbene center will thus provide stabilization. As such, amino-, alkoxy-, and thio-substituted carbenes are much more stable than the singlet state of the parent CH_2. This is documented[80] by the simple reversible thermolysis of suitably substituted tetraaminoethylenes into the "monomeric" diaminocarbenes via reaction 3-35.

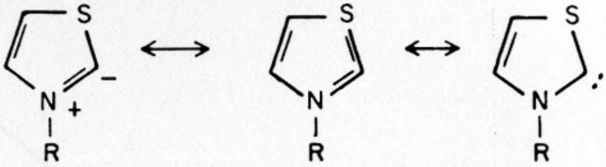
$$(R_2N)_2C=C(NR_2)_2 \rightleftharpoons 2\ (R_2N)_2C \qquad (3\text{-}35)$$

By loss of a proton, loss of a silyl group, or loss of CO_2 from suitable pyridine derivatives (**20**), the cyclic carbenes, the *N*-substituted 1,2-dihydropyridine-2-ylidenes (**21**), are readily formed.[81] However, these carbenes are more realistically described as highly stable zwitterions or ylids and so pictorialized as pyridinium-2-ylides (**21a**).



20 **21** **21a**

Analogously, when $-CH_2^-$, a stronger electron pair donor than even $-NH_2$, substitutes for one hydrogen, singlet CH_2 is even more stabilized. The resulting product, $(CHCH_2)^-$, may appear not to be a carbene at all because it is customarily named vinyl anion and rewritten in the "inverted" form, $CH_2=CH^-$. Yet quantum chemical calculations[82,83] have shown there is more negative charge on the β carbon than on the α, suggesting a meaningful contribution from the resonance structure $:CH-CH_2^-$. This result is corroborated by gas phase solvation studies on vinyl anion and a collection of other negative ions.[82,83] These studies also included ethynyl and cyanide anions, and carbenelike behavior was found. That is, the atomic charges are consistent with significant contributions from $:C=C^-H$ and $:C=N^-$. Indeed we note with some amazement that more than 25 years have passed since Breslow[84] related the carbenelike behavior of these two anions with that of the neutral species, carbon monoxide, isonitriles, the stabilized pyridinium (**21** and **21a**) and thiazolium ylids (**22, 22a** and **22b**) to derive what is now the textbook mechanism of in vivo reactions catalyzed by thiamine (vitamin B_1).



22 **22a** **22b**

It would appear that carbenes are more ubiquitous than is usually assumed. Equivalently, the distinction between carbenes and noncarbenes is often at best rather blurry. Paraphrasing our statement in the introductory section, carbene chemistry is multifaceted, interesting, and important.

ACKNOWLEDGMENTS

The authors would like to thank Drs. K. N. Houk, N. G. Rondan, and D. Van Vechten for numerous discussions, incisive questions, and clarifying remarks, and F. Baldwin, T. Ford, P. Gagné, and A. Mahoney for assistance in the preparation of this manuscript.

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9. All data on these two compounds, and on any species for which no alternative, explicit citation is given, come from J.B. Pedley and J. Rylance, "Sussex–N.P.L. Computer-Analysed Thermochemical Data: Organic and Organometallic Compounds" (University of Sussex, Brighton, UK, 1977). These two compounds also provide us with the opportunity to show an example of the validity of our assumptions. In the particular, we use Equation (3-3) to estimate the heat of vaporization for neopentane and the heat of sublimation of 2,2,3,3-tetramethylbutane. For the former, the "predicted" value is 5.4 kcal/mol, identical

to the experimental value. For the latter, the "predicted" heat of vaporization is 7.9 kcal/mol, and so the heat of sublimation lies between 7.9 and 15.8 kcal/mol. The experimental value is 10.4 kcal/mol, completely within the predicted bounds. Converting these numbers to the more meaningful kilocalories per mole of carbon basis, the bounds are 0.99 and 1.98, while the experimental number is 1.30.

10. For Equations (3-5) and (3-7), we must employ "strainless" 2,2,3,3-tetramethylbutane (ie, one lacking methyl–methyl repulsions). This hypothetical species is derived by adding two molecules of 2,2-dimethylbutane and subtracting one of *n*-butane. Arithmetically combining the various heats of formation shows the "real" compound to be strained by 4.8 kcal/mol. (This approach of adding and subtracting experimental data on whole molecules to obtain thermochemical information has been formally named "macroincrementation" and is reviewed in Chapter 6 of Volume 3 of this series.)
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14. All experimental molecular geometries (eg, interatomic angles) given in this chapter are taken from the text and/or tables of B.M. Gimarc, "Molecular Structures and Bonding: The Qualitative Molecular Orbital Approach" (Academic Press: New York, 1979), unless otherwise said. Other slightly different angles have been reported in the experimental literature. Some high-quality, theoretically derived values for the HCH angle are given in the references accompanying Section 5. It is interesting to note many textbooks refer to linear triplet CH_2, an error presumably arising from an early and incorrect structural assignment in the experimental research literature.
15. For a thorough, chronological listing and discussion of the singlet–triplet gap in CH_2, see E.R. Davidson, in "Biradicals" (W.T. Borden, Ed.; Wiley–Interscience: New York, 1982). Some selected more recent references are presented in Section 7 of this chapter. Davidson also presents an essentially complete collection of singlet–triplet gaps for other carbenes and related species and various models for the qualitative understanding of these numbers. Without meaning to "prejudice" the reader, we note that Davidson prefers a π-donation model, which was first theoretically discussed at length by R. Hoffmann, G.D. Zeiss, and G.W. Van Dine (*J. Am. Chem. Soc.* **1968,** *90,* 1485) and R. Gleiter and R. Hoffmann (ibid, **1968,** *90,* 5457).
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18. See B.M. Gimarc (Reference 14), from which our discussion is adapted, and an earlier, less extensive treatment by Gimarc (*Acc. Chem. Res.* **1974,** *7,* 384).
19. Discussions of this method are usually relegated to the pedagogical literature: eg, R.J. Gillespie (*J. Chem. Educ.* **1970,** *47,* 18) and "Molecular Geometry" (Van Nostrand: London, 1972). More recently, however, theoretical inquiries into why VSEPR works so well have begun to appear. See, eg, L.S. Bartell and Y.Z. Barshad (*J. Am. Chem. Soc.* **1984,** *106,* 7700).
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56. See Liebman, Politzer and Sanders, op. cit., Reference 21.
57. Perhaps we should not be so apprehensive about using STO-3G values for the singlet–triplet gap. Of all the carbenes with π-donating substituents mentioned so far, Davidson (Reference 15) gives "probably reliable estimates" for seven. Comparing his selected values with those from STO-3G calculations (Reference 17), one finds:

	Singlet–triplet gap values (kcal/mol)		
Carbene	Davidson[15]	STO-3G calculations[17]	ΔE_{ST}
CHF	-9	12	21
CHOH	-21	1	22
CHCl	-2	25	27
CF_2	-50	-21	29
$C(OH)_2$	-46	-26	20
$C(NH_2)_2$	-50	-26	24
CCl_2	-12	12[a]	24
CH_2[b]	10	40	30

[a] See Section 9.

[b] Values for methylene given for completeness.

It is seen that the difference between the two sets of numbers is a comparatively constant 25 (± 5) kcal/mol, where the "expected error [of Davidson's numbers] is less than 5 kcal/mol" (Reference 15, page 80, footnote a).

58. See Reference 17, page 5049.
59. Rondan, N.G.; Houk, K.N. Unpublished calculations.
60. See Reference 55 where high-accuracy quantum chemical calculations on $C(OH)_2$ and $C(-{}^{+}FH)_2)$ were reported. These authors also argued that "*increasing* the electronegativity of the substituents should *preferentially stabilize the triplet* when the substituents are π donors" (their italics).
61. $C_5H_5^+$ and its substituted derivatives enjoy the same spin and structural diversity as C_5H_4. Note, however, we know of no form of C_5H_4 corresponding to the "pyramidal carbocations." (For a review of $C_5H_5^+$, its substituted derivatives, and pyramidal carbocations, see A. Greenberg and J.F. Liebman, "Strained Organic Molecules" (Academic Press: New York, 1978, pp. 379–385. For general studies of largely generally boron-containing unsubstituted pyramidal species, see Chapter 6 of this volume.)
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79. This oxirene–ketocarbene interconversion is reviewed by E.G. Lewars (*Chem. Rev.* **1983,** *83,* 519), while related interconversion reactions of oxirenes, thiirenes and azirenes, is reviewed by Greenberg and Liebman in "Strained Organic Molecules" (op cit, pp. 313–317).

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