Organic and Biological Chemistry

On Stabilizing a Singlet Methylene

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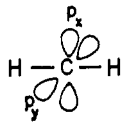
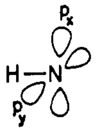
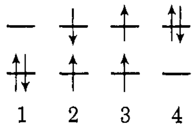
Abstract: Three ways to break effectively the degeneracy of the nonbonding p orbitals of a linear methylene and thus possibly to stabilize a singlet ground state are discussed: (1) by reducing the RCR angle from 180°, (2) by approaching or connecting the methylene to a system with low-lying unoccupied levels, (3) similarly attaching a component with high-energy occupied levels. A particular case of the latter type is the "foiled-reaction" methylene —the result of beginning an intramolecular addition whose culmination is sterically impossible. Among the likely candidates for singlet ground states are cyclopropenylidene, the 4-carbene of 2,5-diazacyclopent-1-ene, vinylidene, the 7-carbenes of norbornadiene, and the 8-carbene of tricyclo[3.2.1.$0^{2,4}$]octene. σ^2 methylenes attached to a π system should be nucleophilic while p^2 methylenes should be electrophilic.

In a linear methylene or a nitrene the energy levels for the p_x and p_y orbitals are degenerate. Population of these levels by two electrons inevitably leads to a triplet ground state of the molecule.[1] We have for some time been interested in the electronic structure of methylenes and in the theoretical criteria for obtaining a singlet ground state.[2]





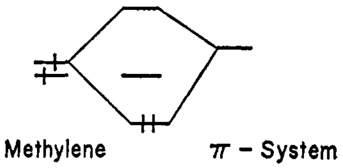
It is clear that the degeneracy of the p_x and p_y orbitals must be destroyed in order to provide the opportunity for a stabilized singlet. Trivial destruction of the degeneracy is insufficient. The effect must be a major one. Consider the four possible configurations resulting from the placing of two electrons in two energy levels of approximately equal energy. We will call configuration 1 the normal or ground configuration, 2 and 3 singly excited, and 4 doubly excited. Electron interaction will place the singlet 2 at higher energy than the triplet 3, and configuration interaction will mix the like symmetry configurations 1 and 4. The magnitude of the level splitting is crucial. If it is small (less than about 1.5 eV,[2] then it is most likely that the ground state of the system will be represented by the stabilized triplet 3. If the splitting is large (more than about 2 eV) than the singlet 1, with an admixture of configuration 4, will be the ground state.



The following are different ways of breaking the degeneracy of p_x and p_y. Most were anticipated qualitatively by others[3,4] and some we have explored previously.[2]

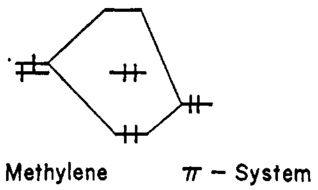
1. The degeneracy of p_x and p_y can be broken by bending, *i.e.*, reducing the RCR angle from 180°. This leaves one p orbital, the one perpendicular to the plane of bending, essentially unaffected. The p orbital in the bending plane is stabilized, acquires s character, and will be referred to as σ in the ensuing discussion.

2. It can be broken by approaching or connecting the methylene to a system with low-lying unoccupied levels. The approach or connection must be such that the empty orbitals (usually π^*) interact selectively with one and not the other of the two methylene p orbitals.



The methylene is expected to transfer some charge to the acceptor π system, to become more electron deficient. Our previous work has analyzed several cases of this type, *e.g.*, formyl methylene.

3. It can be broken by approaching or connecting the methylene to a system with high-lying occupied levels. Again the interaction must be selective with one of the methylene p levels.



The approaching level may be a π level or a lone pair. We have analyzed the intermolecular lone pair interaction carefully in a discussion of electron-rich

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[1] R. S. Mulliken, *Rev. Mod. Phys*, **4**, 1 (1932); G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1950, p 369.

[2] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

[3] H. W. Wanzlick, *Angew. Chem.*, **74**, 129 (1962).

[4] W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **89**, 3069 (1967).

three-center bonding.[5] A combination of intramolecular lone-pair interaction and an enhanced bending effect is probably responsible for the ground-state properties of the only *bona fide* singlet methylenes identified to date—CF_2, CHF, CHCl.[6] The methylenes in this category are expected to gain some electron density from the donors.

A novel special case of this category is the "foiled-reaction" or "nonclassical" methylene. This is a system in which an artificial energy minimum is created as a result of initial stabilization due to the inception of a typical facile methylene reaction (such as addition to a double bond) which is foiled by the impossibility of attaining the final product geometry. We will illustrate this interesting case in detail below.

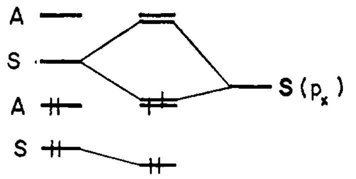
Mixing. We first analyze the case of one carbene p orbital incorporated into a cyclic π-electron system. The geometry is illustrated in Figure 1. There are two cases depending on the number of electrons, $4n$ or $4n + 2$, in the polyene.

The analysis can be simplified to deciding whether the highest occupied or the lowest vacant orbital of the polyene has the correct symmetry to allow interaction with the methylene p. A complete analysis would involve evaluation of the second-order perturbation sum

$$\Delta E = \sum_{\substack{\text{polyene}\\ \text{orbitals}}} \frac{|H_{0i}|^2}{E_0 - E_i}$$

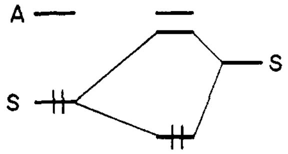
but we estimate the denominator is dominant and so levels close in energy to the methylene p_x will be decisive.

I. 4*n*. An interaction diagram for $n = 1$ is given. Here the lowest unoccupied (but not the highest occupied) orbital of the diene has the correct symmetry for interaction with the methylene p_x. This will be true for all polyenes with $4n$ π electrons.



Unfortunately not much differentiation is achieved for cyclopentadienylidine itself. This is because the p_y orbital has also been stabilized by the bending necessary at the carbene center. In an extended Hückel calculation it emerges 0.13 eV *below* the delocalized p_x.[7]

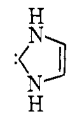
II. 4*n* + 2. Here the highest occupied polyene orbital is always symmetric and the lowest vacant orbital antisymmetric. p_x is destabilized by the mixing and the splitting of the methylene degeneracy is reinforced by a stabilization of σ by bending. The optimum case should be cyclopropenylidene, for which the interaction diagram is given.



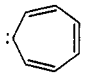
The splitting of σ and p amounts to 3.17 eV here from an extended Hückel calculation. We are thus led to the prediction of a singlet ground state for this molecule.

More generally there appears the possibility of stabilizing a singlet methylene when the methylene interacts with a polyene having already the aromatic grouping of $4n + 2$ π electrons. σ–p splittings for some of the molecules we tried are shown.

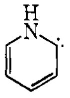
I, 3.17 eV



II, 3.45 eV



III, 1.00 eV



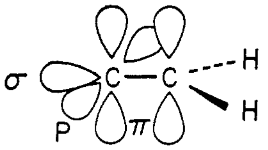
IV, 1.77 eV

Derivatives of the molecules I–IV have been prepared recently.[4,8–10] In all cases the methylenes exhibit nucleophilic properties (see below), but nothing is known about their electronic states. The di- and tribenzoderivatives of III were found to be triplet ground states,[11] in accordance with the moderate splitting calculated. We found that large splittings were preserved in molecules isoelectronic with II in which O or S were substituted for one or both of the NH groups. Sizable splittings were also preserved in species isomeric and isoelectronic with IV.

Bending. In Figure 2 we reproduce the energy surface for bending in the ground and excited configurations of dimethylmethylene. The maximum energy gap is 0.65 eV at a C–C–C angle of 120°. The one-electron energy splitting increases to smaller angles as well, and the total energy of the σ^2 configuration rises at angles below 120° only as a consequence of steric interference of the methyl groups. This suggests that if the steric influence is removed further stabilization might occur. The simplest case that comes to mind is cyclopropylidene. Here we calculate a splitting of 1.13 eV, which is in the anticipated direction but not very large.

Carrying the bending idea to its literal extreme we arrive at the methylene derived from ethylene–vinylidine. Our calculation was carried out on a fragment of an ethylene, with C=C 1.34 Å.

The electronic structure of this molecule is of some interest. The important energy levels are at the following energies: π 13.22, σ 12.73, p 10.81, π* 8.24 eV. The σ and p levels are of course somewhat more delocalized than the above picture indicates. The



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[5] R. Gleiter and R. Hoffmann, *Tetrahedron*, in press.

[6] C. W. Mathews, *J. Chem. Phys.*, **45**, 1068 (1966), and references therein; J. Duchesne and L. Burnelle, *ibid.*, **21**, 2005 (1953); A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 525, 1541 (1966).

[7] The method of calculation is described in R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers. The parameters we use are given in ref 2.

[8] H. Quast and S. Hünig, *Angew. Chem.*, **76**, 989 (1964).

[9] H. Quast and E. Frankenfeld, *ibid.*, **77**, 680 (1965).

[10] W. M. Jones and J. M. Denham, *J. Amer. Chem. Soc.*, **86**, 944 (1964).

[11] I. Moritani, S.-I. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh, and N. Mataga, *ibid.*, **89**, 1259 (1967).

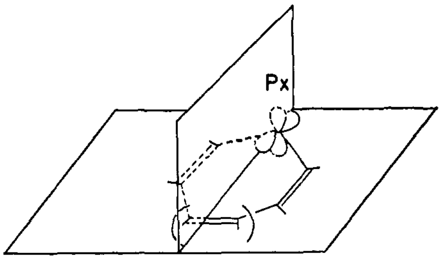


Figure 1. A methylene center incorporated into a cyclic π electron system.

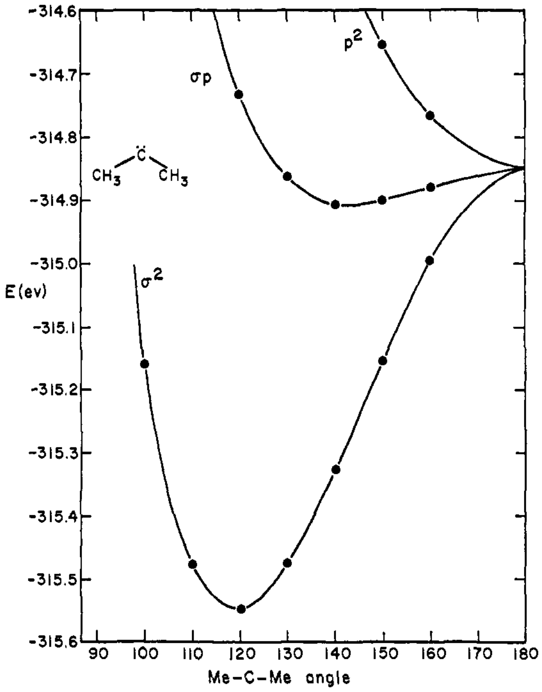
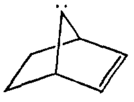
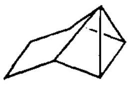


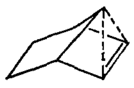
Figure 2. Potential energy curves for dimethylmethylene in a conformation in which both methyl groups are staggered.

σ–p splitting of 1.92 eV is quite large and the molecule may in fact possess a singlet ground state.

Foiled Reaction. The approach of a methylene to an ethylene leads usually to addition, forming a cyclopropane. From our calculations such an approach is a facile process requiring no energy of activation.[12] Now it is interesting to construct a system in which the culmination of the addition process is impossible, and so to create an artificial equilibrium geometry part way between the initial unreacted conformation and the very strained adduct. The idea is best illustrated on the example of the 7-methylene of norbornene (V).


V


VI


VII

Intramolecular addition would give VI, a molecule which has at one carbon all four bonds on one side of a plane. This molecule should be terribly strained, and so the system may choose an intermediate geometry, VII, in which the 7 bridge is bent partway over. This situation is analogous to formation of a nonclassical carbonium ion, since there is an obvious analogy between the electronic structure of a carbonium ion and a singlet methylene.

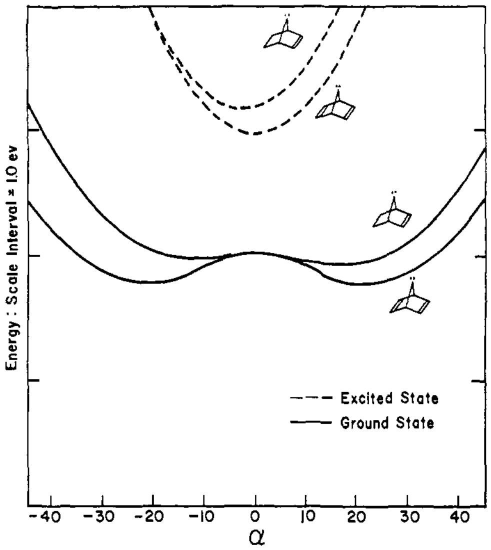


Figure 3. Potential energy curves for the σ^2 and σ_p configurations of the methylene formed by removing the two 7 hydrogens of norbornadiene and norbornene. In the bending motion C_7 is moved in such a way as to keep the C_1–C_7 and C_4–C_7 distances constant. The angle α measures the angle of bending of the C_1–C_7–C_4 plane away from its symmetrical position. In the case of norbornene positive α corresponds to bending toward the double bond.

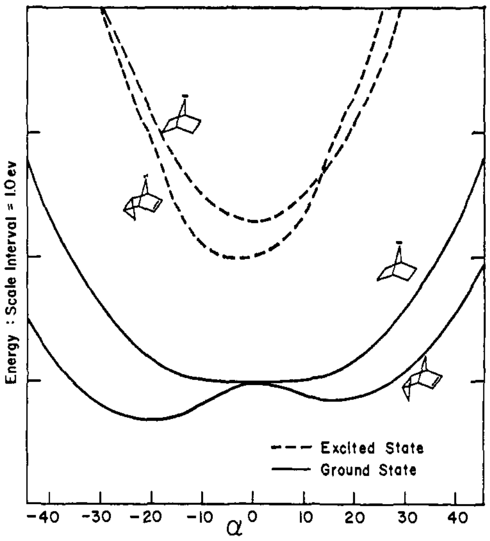
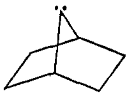
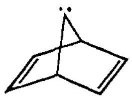
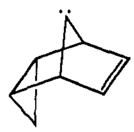


Figure 4. Potential energy curves for the bending motions of molecules VIII and X. The constraints on the motion are similar to those described for molecules V and IX. In the case of X positive α corresponds to bending the bridge toward the double bond.

Extended Hückel calculations were performed for V and the methylenes VIII, IX, and X.


VIII


IX


X

In these calculations the 7 atom was moved by an angle α out of the originally vertical 1,4,7 plane and in the plane bisecting the 2,3 and 5,6 bonds. The ground and excited configuration energy curves are displayed in Figures 3 and 4.

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(12) R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).

The results are as anticipated: nonclassical minima in the ground configuration, none in the excited. Moreover the general shape of the curves parallels that which our group has previously found for carbonium ions.[13] Even here interaction with a cyclopropane in X yields a deeper minimum than interaction with a double bond. The nonclassical methylene minima are much shallower than those for a carbonium ion. The σ–p splitting is quite large for all of these molecules: for IX it is 2.28 at the equilibrium geometry of the ground configuration.

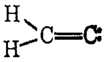
Thus there exists the definite probability of a singlet, stabilized, nonclassical methylene. Chemical stability is of course another question, since it depends on the ease of *all* possible reaction pathways from the compound in question. Should the species not possess any chemical stability then we do not really know how its nonclassical structure can be extracted. One experiment which might provide a very indirect clue to the geometry of V would be the stereochemistry of its addition to RX or isobutene. The weak argument is that if the methylene is bent over toward the double bond, then the sterically bulky substituents on the addend should prefer the side *anti* to the double bond. In another line of reasoning the methylene V is nucleophilic (see below) and so one can envisage the addition of RX as being initiated by a nucleophilic displacement on R by the methylene group of V. This would result in the R group entering *syn* to the double bond. Stereospecificity was observed in a reaction which could be interpreted as involving the addition of CH_3Br to V,[14] but the resulting product had the opposite stereochemistry to that expected from our argument.

Nucleophilic and Electrophilic Methylenes. Suppression of the normal proclivity of methylenes for addition to double bonds has been identified in the literature as a consequence of increased nucleophilic character of π-delocalized methylenes.[3,4,10] We believe we can make somewhat clearer the relationship between the nucleophilicity and the electronic structure of a given singlet methylene.

We chose to examine the total charge on methylene carbon. For CH_2 itself we obtain the net charges given in Table I. While p remains localized at the central carbon, σ is increasingly delocalized. We would thus expect a σ^2 methylene to be less negative than a p^2 methylene, provided no conjugating groups are attached. The actual variation in charge for σ^2 methylenes is slight.

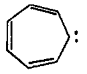
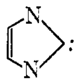
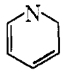
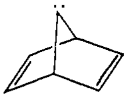
Table I. Net Charges as a Function of HCH Angle

	Angle of bending, deg				
	180	160	140	120	100
σ^2	−0.30	−0.28	−0.23	−0.18	−0.17
p^2	−0.30	−0.30	−0.31	−0.33	−0.38

$CH_3-\ddot{C}H$ (120°)	−0.23
$CH_3-\ddot{C}CH_3$ (120°)	−0.23
	−0.21
 $H_2C{=}C\colon$	−0.21

When a π-electron system is attached to a methylene, drastic changes occur. Two cases must be distinguished.

1. σ^2 **Lower Than** p^2. Here the p orbital of the methylene, unoccupied in CH_2, now has obtained some electron density from the π system. The methylene carbon becomes more negative, nucleophilic. Some examples are shown. The effect is particularly striking in molecule II, when it is realized that it is overcoming the natural electronegativity difference between C and N. In the saturated molecule corresponding to II (3,5-diazacyclopentene) the central carbon carries a charge of +0.50.

$CH_2{=}\ddot{C}H-CH$ (120°)	−0.50
$C_6H_5-\ddot{C}H$ (120°)	−0.56
 I	−0.68
 III	−0.86
 II	−0.43
 IV	−0.65
 IX (bent 20°)	−0.43

2. p^2 **at Lower Energy Than** σ^2. Here the methylene center loses electron density. The p orbital, localized in CH_2, is now delocalized over the entire π system. The methylene should be more electrophilic. Two examples follow: $H\ddot{C}-CHO$ ("linear") +0.33, $H\ddot{C}-NO_2$ (130°) +0.41.

Acknowledgment. We are most grateful to the Deutsche Forschungsgemeinschaft for a fellowship to R. G. and to the Sloan and Chevron Foundations, the National Institutes of Health, and the National Science Foundation for financial support.

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[13] R. Hoffmann, *J. Amer. Chem. Soc.*, **86**, 1259 (1964).

[14] L. Skattebøl, *Tetrahedron*, **23**, 1107 (1967).