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# Chemical Implications of $\sigma$ Conjugation

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**Abstract:** Although it has been known for many years that resonance integrals between hybrid AOs of a given atom do not vanish, the chemical significance of this has only recently been appreciated. Here the role of such *σ-conjugative* interactions is considered in detail, with special reference to bond localization and aromaticity, the structures of radicals and biradicals, triplet carbenes, stabilities of conformers including the gauche and anomeric effects, and chelotropic reactions.

Organic chemists over the years have developed a qualitative molecular model that has proved extremely effective as a guide in their chemical thinking, in devising syntheses and exploring reaction mechanisms. According to this model, bonds are normally formed by pairs of electrons shared between pairs of nuclei, the electrons forming such a bond being correspondingly localized. Localization breaks down in certain clearly defined situations, in particular in cyclic conjugated molecules and transition states. The correspondingly delocalized electrons then have to be treated in terms either of resonance theory[1] or, better, in terms of PMO theory.[2,3] We will describe this as the *current molecular model* (CMM).

It has become apparent in recent years that electrons in saturated molecules are delocalized in certain situations, for example, where unshared pairs of electrons interact with one another via intervening $\sigma$ bonds.[4] Their photoelectron spectra also clearly indicate delocalization. Increasing use has therefore been made of complete MO descriptions of molecules, the interactions between different parts (*R*,*S*) of a molecule (*RS*) being treated in terms of second-order perturbation theory, using MOs of the parts (*R*,*S*) as the zeroth-order approximation. This approach has been made the more appealing by the photoelectron studies, which have seemed to provide evidence for the postulated interactions, and by a feeling that a description of molecules in terms of MO theory is "truer" than one in terms of localized bonds.

This kind of approach needs detailed information concerning the MOs in molecules, obtainable only by calculations using a computer. The corresponding model cannot therefore be used as a basis for chemical thinking. Second-order perturbation theory was used in the original PMO theory when necessary, but only in connections where a detailed knowledge of MOs was not needed.[3] A clear distinction was moreover drawn between *collective* properties of molecules, i.e., properties which depend on all the electrons taken together, and *one-electron* properties which depend, in the MO formulation, on the electron(s) occupying individual MOs. Heats of formation, geometries, and dipole moments are typical collective properties; light absorption and ionization energies are one electron ones. Only collective properties can be treated in terms of localized bonds.

There are, however, a number of phenomena that have eluded description in terms of the CMM and have indeed been largely ignored for this reason. The fact that cyclopropane and cyclobutane have similar strain energies, the pyramidal structure of *tert*-butyl radical, and the bent structure of triplet carbene ($CH_2$) are typical examples. There are also various phenomena that have been difficult to explain in terms of the CMM and which have consequently been taken as evidence for its inadequacy. My purpose here is to draw attention to a feature of the CMM which accounts in a simple manner for many of the apparent anomalies indicated above, i.e., the fact that resonance integrals between hybrid AOs of a given atom do not vanish. While this has been known for a long time, while a HMO type model based on it has been used from time to time in calculations of the ionization energies of paraffins, and while Herndon[4] has recently shown that a PMO version accounts well for the strengths of the bonds in them, its full implications have not been recognized. A preliminary account of the ideas developed here has appeared[5] in print. Here they are discussed in more detail and applied to some other phenomena that have been difficult to explain in terms of the CMM.

## $\sigma$ Conjugation

The current treatment of bond localization was originally developed in terms of resonance theory,[1] which suggested a qualitative distinction between the delocalized systems of $\pi$ electrons in conjugated molecules and the supposedly localized two center bonds present elsewhere. The analysis was based on the directional properties of hybrid AOs combined with the assumption that orbitals which are mutually orthogonal do not interact with one another. Thus, in a compound $CR_4$, where the bonds are formed by interactions between four $sp^3$ hybrid AOs of carbon ($\phi_i$, $i = 1 - 4$) and four AOs of the ligands ($\psi_i$) (see Figure 1a), each AO ($\phi_i$) overlaps only with the corresponding ligand AO, $\psi_i$, while the carbon AOs are mutually orthogonal. The molecule should then be properly represented by a wave function corresponding to pairs of electrons localized in two-center bonds because there are no significant interactions between the AOs forming one bond and those forming the others. The situation in a conjugated polyene is clearly different (Figure 1b) because the 2p AOs forming adjacent $\pi$ bonds *do* overlap with one another. Such a molecule cannot then be properly represented in terms of localized C—C and C=C bonds. The two-center $\pi$ MOs coalesce into a "resonating" system over which the $\pi$ electrons are delocalized. The fact that the lengths of the C=C and C—C bonds in a conjugated polyene differ from those in paraffins and olefins seems to support these conclusions, particularly since the bonds in a polyene are more nearly equal, as would be expected if there is in fact a resonance interaction between them.

While this argument is given in nearly all current chemical text books, it is nevertheless fallacious. It is true that the resonance integral between any hydrogen like (s, p, d, etc.) AO of a given atom and any other AO vanishes if the AOs are orthogonal, even if the latter is of hybrid type. However, the resonance integral between two mutually orthogonal hybrid AOs of a given atom does *not* vanish. It would do so if the component hydrogen-like AOs had similar energies, but this is not the case. Consider for example two sp hybrid AOs, $\phi^+$ and $\phi^-$, of a carbon atom given by

$$\phi^+ = (1/\sqrt{2})(s + p)$$
$$\phi^- = (1/\sqrt{2})(s - p) \tag{1}$$

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(1) See: Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955.

(2) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341, 3345, 3350, 3353, 3355, 3357; *Sci. Prog.* (*Oxford*) **1952**, *40*, 604.

(3) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1975.

(4) Herndon, W. C. *J. Chem. Ed.* **1979**, *56*, 448; *Tetrahedron Lett.* **1979**, 3801.

(5) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1980**, *88*, 957.

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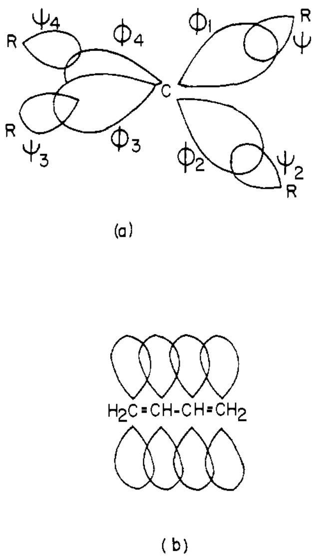

**Figure 1.** (a) Conventional description of $CR_4$ in terms of hybrid AOs. (b) Conventional $\sigma\pi$ description of butadiene.

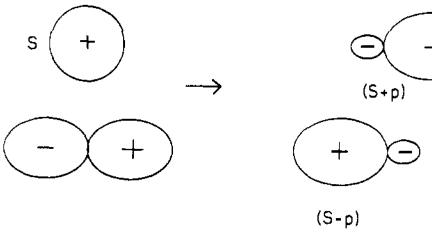

**Figure 2.** Formation of sp hybrid AOs from an s AO and a p AO.

where s and p are the contributing 2s and 2p AOs; see Figure 2. The resonance integral between them, $\beta$(sp,sp), is given by

$$\beta(\mathrm{sp,sp}) = (1/2)\int \phi^+ \mathbf{H}\phi^- \, d\tau = (1/2)\int (\mathrm{s} + \mathrm{p})\mathbf{H}(\mathrm{s} - \mathrm{p})d\tau = (1/2)\left(\int \mathrm{sHs}d\tau - \int \mathrm{pHp}d\tau\right) = (1/2)(I(\mathrm{s}) - I(\mathrm{p})) \quad (2)$$

where $I$(s) and $I$(p) are the valence state ionization energies of the 2s and 2p AOs, respectively. If $I$(s) and $I$(p) were equal, $\beta$(sp,sp) would vanish—but they are *not* equal. Indeed, $I$(s) is greater than $I$(p) by 10 eV, i.e., 230 kcal/mol.[6] Hence:

$$\beta(\mathrm{sp,sp}) = 5\ \mathrm{eV} = 115\ \mathrm{kcal/mol} \quad (3)$$

So far from vanishing, the resonance integral is about *five times* greater than that between adjacent 2p AOs in a conjugated hydrocarbon! The values of the resonance integrals between other types of hybrid can be found[5] in a similar manner:

$$\beta(\mathrm{sp^2,sp^3}) = 3.3\ \mathrm{eV} = 77\ \mathrm{kcal/mol};\ \beta(\mathrm{sp^3,sp^3}) = 2.5\ \mathrm{eV} = 58\ \mathrm{kcal/mol} \quad (4)$$

While smaller than $\beta$(sp,sp), they are still much greater than the $\pi$ resonance integral between adjacent 2p AOs in a polyene.

It has been known for many years that such integrals do not vanish and MO treatments of paraffins have indeed been reported[7,8] in which the corresponding interactions were taken into account. Most of these have, however, been concerned with ionization energies of molecules where the differences between MOs composed mainly of 2s AOs or of 2p AOs are manifest. The possible implications of such interactions in other connections have not been realized. The success of the localized bond model has moreover given the impression that even if such interactions exist, they cannot be of much significance. The simple interpretation in terms of localized electrons also has obvious pedagogical advantages. The results in eq 3 and 4, however, make nonsense of this interpretation. Since the interactions between neighboring CC $\sigma$ bonds in a paraffin are *greater* than those between neighboring CC $\pi$ bonds in a conjugated polyene, the current distinction between conjugated and nonconjugated systems is inconsistent with the simple HMO-type theory on which the current model is based.

The concept of bond localization was originally introduced to explain why the length of a given kind of bond is the same in any nonconjugated molecule and why the heats of atomization of such molecules can be expressed as sums of bond energies, the bond energy of a given bond always having the same value. The lengths of the C—C and C═C bonds in conjugated hydrocarbons, however, differ from those in paraffins or olefins, and the heats of atomization of conjugated hydrocarbons are greater than a sum of the corresponding bond energies. This seemed to indicate that there is a basic difference between conjugated molecules and nonconjugated ones, an idea supported by the well-known effects of conjugation on chemical reactivity and light absorption and by the existence of aromatic conjugated molecules for which there seemed to be no nonconjugated counterparts. Furthermore, Lennard-Jones[8] had shown that the MO wave function for a paraffin or olefin can be transformed into an equivalent representation in terms of *equivalent orbitals* (EO), each EO being composed almost entirely of the two AOs forming a two center bond. Similar transformations can be carried out for other nonconjugated molecules but not for conjugated ones. Any orbital description of the latter has to be based on $\pi$ orbitals derived from 2p AOs of more than two carbon atoms. This result seemed to account for the apparent localization of bonds in saturated molecules and their apparent delocalization in conjugated ones, providing a further argument in support of the conventional distinction between conjugated and nonconjugated systems.

However, as Dewar and Schmeising[9] pointed out 25 years ago, the properties of a localized bond linking two atoms would be expected to vary with the hybridization of the AOs used to form it. The differences between the C–C single bonds in paraffins and polyenes could be due simply to the different hybridization of the carbon atoms forming them. Indeed, if allowance is made for this, the bonds in *all* classical[10] molecules appear to be localized, their lengths being constant and their heats of formation being expressable as additive sums of appropriate bond energies. Additivity breaks down only in nonclassical[10] molecules where the bonds can be written as either single or double and cannot therefore be characterized as either. Indeed, subsequent work[11] has shown that essential[10] single or double bonds always make the same constant contributions to the heats of formation of molecules of all kinds, even nonclassical molecules where some or all of the other bonds are genuinely delocalized. The central bond in biphenyl (Ph–Ph) is a typical example, its length, and its contribution to the heat of formation, being the same as that of a "polyene single" bond in a classical polyene.

Additivity also breaks down in the case of certain other properties of polyenes, in particular light absorption and ionization energies. The same, however, is true for paraffins. "Bond localization" holds to the same extent in *all* classical molecules,

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(6) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.

(7) (a) Hall, G. G. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 541; *Trans. Faraday Soc.* **1953**, *49*, 113. (b) Brailsford, D. F.; Ford, B. *Mol. Phys.* **1970**, *18*, 621. (c) Murrell, J. N.; Schmidt, W. *Trans. Faraday Soc.* **1972**, *68*, 1709. (d) Herndon, W. C. *Chem. Phys. Lett.* **1971**, *10*, 460. (e) Bieri, G.; Dill, J. D.; Heilbronner, E.; Schmeltzer, A. *Helv. Chim. Acta* **1977**, *60*, 2234.

(8) Lennard-Jones, J. E.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1950**, *210*, 190. Lennard-Jones, J. E.; Hall, G. G. *Trans. Faraday Soc.* **1952**, *48*, 581.

(9) (a) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166; **1960**, *1*, 96. (b) Dewar, M. J. S. "Hyperconjugation"; Ronald Press: New York, 1962.

(10) A classical molecule is one for which only a single classical ("unexcited resonance") structure can be written, as opposed to nonclassical molecules for which there are two or more such structures. An essential single (double) bond is one which is single (double) in all possible classical structures.

(11) (a) de Llano, C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1969**, *91*, 789. (b) Dewar, M. J. S.; Harget, A. J. *Proc. R. Soc. London, Ser. A.* **1970**, *315*, 443, 457. (c) de Llano, C. Ph.D. Dissertation, The University of Texas at Austin, 1969.

conjugated and nonconjugated alike. The EO transformation is no more than a red herring in this connection because the resonance integrals between EOs do not vanish. Bond localization is not a real phenomenon and attempts to relate it to any kind of localization of electrons are mistaken in principle.

### The Localized Bond Model: Hybridization

The term "bond localization" does not therefore refer to any real property of a molecule. It implies only that in certain respects the molecule behaves *as if* the bonds in it were localized. Consequently we can represent the behavior of such molecules in terms of a simple model (the localized bond model) that is easy to visualize and is therefore very useful as a practical aid to chemists in thinking about molecules. When the localized bond model fails, the corresponding "delocalized bonds" are treated in terms of the current HMO-based model. This procedure seemed logical when bond localization was thought to be a direct consequence of this model. Since this is not in fact the case, we must try to find some other basis for it, if only to know when to expect it to fail.

In the PMO model[2,3] delocalization of electrons is treated in terms of perturbation theory, the interaction between parts of a larger system being treated as perturbations. The problem of bond localization can clearly be treated in this way, starting with a model where the electrons in a molecule are localized in bonds and treating the interactions between the localized "bond eigenfunctions" as the perturbation. This approach was applied to conjugated polyenes in the original papers[2] introducing PMO theory, leading to a simple explanation of bond localization in them.[3,12] The effect on the total energy of a polyene was found to be due only to second-order perturbative interactions between the bonds, even though the bond functions for bonds of the same kind (C–C, C–H, etc.) are identical and therefore degenerate. While the corresponding first-order perturbations are large, they cancel when summed over all the electrons. The second-order perturbations between pairs of $\pi$ bonds lead to an overall stabilization, the contribution to it by each such interaction being the same. Since each interaction involves a pair of carbon atoms that are initially linked by a single (C–C) bond, the total interaction energy is proportional to the number of conjugated C–C bonds. If a corresponding correction is added to the C–C bond energy, the heat of atomization of a polyene will then be equal to a sum of fixed ("polyene") C=C, C—C, and C—H bond energies. The lengths of the C—C and C=C bonds also have constant values because the $\pi$ interactions involved are constant. Conjugated polyenes are therefore expected to show bond localization, in the phenomenological sense indicated above, even though the electrons in them are delocalized. It was also shown[2,3] that the interaction energy across any essential single bond in a conjugated molecule, e.g., between the phenyl groups in biphenyl (Ph–Ph), also has the same value so the properties of such bonds are the same as those of "polyene single bonds".

This argument depends, however, on the cancellation of the first-order perturbations when summed over all of the $\pi$ electrons. The apparent localization of bonds therefore applies only to *collective* properties of conjugated molecules, i.e., properties that depend collectively on all the $\pi$ electrons in them. While the first-order perturbations between localized CC $\pi$ bonds do not lead to any net change in the collective properties of a polyene, they do greatly affect the individual orbitals and orbital energies. *One-electron* properties, i.e., properties that depend on individual MOs (e.g., light absorption, ionization energies, or the distribution of unpaired spin in radicals), cannot therefore be interpreted in terms of localized bonds. Failure to appreciate this distinction has caused much confusion, leading to the misapprehension that bond localization is a real phenomenon that should apply to all molecular properties.[12]

If the interactions between different hybrid AOs of an atom are taken into account, each two-orbital $CH_2$ unit in a *n*-paraffin is seen to play the same role as a two orbital =CH—CH= unit in a linear conjugated polyene (Figure 3). The relevant resonance integrals moreover alternate in magnitude in both cases. In a conjugated polyene, the resonance integrals for the single bonds are smaller than those for the double bonds. In a paraffin, the resonance integral for the intraatomic interaction between two $sp^3$ hybrid AOs of a given carbon atom is smaller than that for the interatomic interaction between the AOs forming a CC $\sigma$ bond.[4] The interaction between two adjacent $CH_2$ units in a paraffin, like that between two adjacent =CH—CH= units in a conjugated polyene, is thus greater than the interaction between the two AOs inside a given unit. The conjugated chain is terminated in each case by a one-orbital group; $CH_3$– in the case of a paraffin and $CH_2$= in the case of a polyene (Figure 3). The two systems are thus isoconjugate, any interactions between AOs in one being exactly parallelled by corresponding interactions between AOs in the other. The $\sigma$ bonds in paraffins should therefore be localized for the same reasons that the $\pi$ bonds in conjugated polyenes are localized. Similar comments naturally also apply to the $\sigma$ bonds in the latter, these forming $\sigma$-conjugated systems that differ from those in paraffins only in that the corresponding intraatomic resonance integrals are different (eq 4).

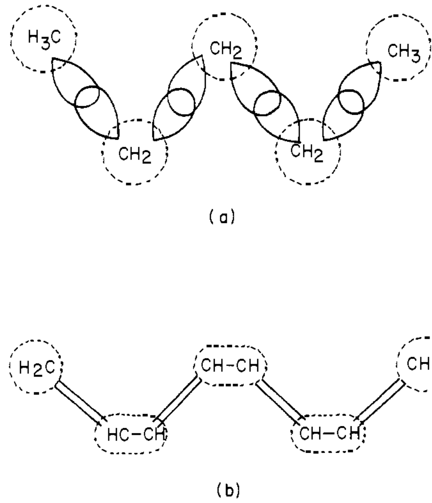

**Figure 3.** (a) The $\sigma$-conjugated system of $\sigma$ bonds in a *n*-paraffin. (b) The $\pi$-conjugated system of $\pi$ bonds in a linear polyene.

So far we have neglected the contributions of CH bonds, which must also be involved in $\sigma$-conjugative interactions both with each other and with the CC bonds. Let us then consider a paraffin molecule in more detail, starting with localized two-center CC and CH bonds and using second-order perturbation theory[2,4] to estimate the interactions between them. The interactions are of three types, involving two CC bonds (C–C–C), a CC and a CH bond (C–C–H), or two CH bonds (H–C–H). Denoting the three corresponding second-order perturbations ($P$) by

$$P(\mathrm{CC,CC}) = a \qquad P(\mathrm{CC,CH}) = b \qquad P(\mathrm{CH,CH}) = c \quad (5)$$

and the unperturbed CC and CH bond energies by $E°_{\mathrm{CC}}$ and $E°_{\mathrm{CH}}$, respectively, the heats of atomization ($\Delta H$) of the first five paraffins are easily seen[21] to be:

$$\begin{aligned} &\mathrm{CH_4},\ \Delta H = 4E°_{\mathrm{CH}} + 6c \\ &\mathrm{C_2H_6},\ \Delta H = E°_{\mathrm{CC}} + 6E°_{\mathrm{CH}} + 6b + 6c \\ &\mathrm{C_3H_8},\ \Delta H = 2E°_{\mathrm{CC}} + 8E°_{\mathrm{CH}} + a + 10b + 7c \\ &n\text{-}\mathrm{C_4H_{10}},\ \Delta H = 3E°_{\mathrm{CC}} + 10E°_{\mathrm{CH}} + 2a + 14b + 8c \\ &i\text{-}\mathrm{C_4H_{10}},\ \Delta H = 3E°_{\mathrm{CC}} + 10E°_{\mathrm{CH}} + 3a + 12b + 9c \quad (6) \end{aligned}$$

Note that the increments in $\Delta H$ per $CH_2$ group, between ethane and propane, and between propane and n-butane, are the same, being given by

$$\Delta H(\mathrm{CH_2}) = E°_{\mathrm{CC}} + 2E°_{\mathrm{CH}} + (a + 4b + c) \quad (7)$$

It is easily shown[14] that the $CH_2$ increment in all *n*-paraffins, from

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[12] (a) Dewar, M. J. S. *Chem. Eng. News* **1965**, *43*, 86. (b) *Tetrahedron Suppl.* **1966**, *8*, 75; "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

[13] Dewar, M. J. S. *Chem. Eng. News* **1965**, *43*, 86.

ethane onwards, has this value. Their heats of formation should then be a linear function of the number of carbon atoms in them, as indeed is well-known[15] to be the case. The PMO values can moreover be written in the form:

$$\Delta H(C_mH_{2m+2}) = (m - 1)E_{CC} + (2m + 2)E_{CH} \tag{8}$$

where

$$E_{CC} = E^\circ{}_{CC} + (1.5a + 3b - 1.5c)$$
$$E_{CH} = E^\circ{}_{CH} + 0.25(2b + 5c - a) \tag{9}$$

Equation 8 corresponds to the value expected for localized bonds with bond energies given by eq 9. The $\sigma$-conjugative interactions between the bonds in a paraffin can thus be taken into account by using appropriate values for the CC and CH bond energies, just as the piconjugative interactions in conjugated polyenes can be allowed for by using appropriate bond energies for "polyene" C—C and C=C bonds.

Methane, however, does not follow eq 8. As the results in eq 6 show, the difference in $\Delta H$ between it and ethane differs from the value predicted by eq 7 by an amount $D$, given by

$$D = (2b - a - c) \tag{10}$$

Methane is indeed observed[15] to deviate from the linear relation followed by the other *n*-paraffins, being less stable than predicted by 2 kcal/mol, this then being the value of $D$.

This deviation is easily understood in terms of the CMM. If $D$ were zero, the interaction energy between a CC bond and a CH bond would be the average of the interactions between two CC bonds, and between two CH bonds. $D$ is a measure of the deviation from the mean. A similar situation arises in two-center $\sigma$ bonds, the bond energy of a A–B bond being generally greater than the mean of the A–A and B–B bond energies. This difference, which forms the basis of Pauling's[16] electronegativity scale, is easily explained[3] in terms of PMO theory. Since the $\sigma$-conjugative interaction between bonds has a stabilizing effect, $a$, $b$, and $c$ are negative. The value of $D$ (+2 kcal/mol) then indicates that the stabilization due to an interaction between two dissimilar bonds (CC, CH) is *less* than the mean of the corresponding interactions between pairs of similar bonds.

The $CH_2$ increment between propane and isobutane also differs from the value given by eq 7 but this time in the opposite direction, i.e., by $-D$. Isobutane should therefore be *more* stable than *n*-butane by 2 kcal/mol. The reason for this difference is the same as that for the opposite deviation in methane. Although the increase in the *number* of bond interactions is always the same (i.e., six) for each addition of a $CH_2$ group, the effect on the energy depends on the types of bond that interact. It is easily seen[14] that the same difference should appear generally in branched paraffins, these being more stable than the *n*-isomers by 2 kcal/mol per branch. Thermochemical data[15] show that this is indeed the case, apart from steric effects when branching leads to overcrowding.

Insertion of $CH_2$ into the methine hydrogen of isobutane to form neopentane ($C(CH_3)_4$) leads,[14] however, to a change in $\Delta H$ that differs from eq 7 by $-2D$, rather than $-D$, so neopentane is more stable than *n*-pentane by $(D + 2D)$, i.e., $3D$. The double branch in neopentane is thus predicted to have as great a stabilizing effect as *three* single branches. This conclusion is also consistent with the thermochemical data.[15] While the observed difference in $\Delta H$ (5.2 kcal/mol) between *n*-pentane and neopentane is a little less than predicted, this is not surprising in view of the steric crowding due to the double branch.

This general scheme, involving bond energies and vicinal interaction energies, was first suggested on a phenomenological basis by Zahn[17] in 1934. His work has been largely overlooked, partly because it appeared at a time when accurate thermochemical data were scanty and partly as a result of the hiatus due to World War II. Its formulation in terms of PMO theory by Dewar and Pettit,[14] twenty years later, also escaped attention because the postulated $\sigma$-conjugative interactions were thought at the time to be negligible, only hyperconjugative interactions being recognized. The magnitudes of the resonance integrals involved in $\sigma$-conjugation now make it clear that it must in fact be much more important than hyperconjugation, vindicating the treatment[14] of paraffins in terms of it. This treatment can of course be extended to other classical molecules.

Hybridization was originally introduced to explain the phenomenon of bond localization. As our analysis shows, it succeeds in doing this, but not in the way originally intended. While electrons are not in fact localized in bonds, as the original interpretation assumed, a model based on the assumption that they are so localized nevertheless reproduces much of the behavior of molecules very closely. Since this "localized bond model" is also very simple, it has proved of major practical value to chemists. It should, however, be clearly recognized that it is a *model*. A model is a simple mechanism that reproduces certain properties of a more complex one well enough to be of value in predicting the behavior of the latter, the more complex system being too complicated for its behavior to be predicted directly. The value of a model is further increased if it is simple enough to be clearly comprehended by those using it. In this sense the localized bond model of molecules is a very successful model, reproducing the collective properties of molecules very effectively and at the same time simple enough to serve as a basis for chemical thinking.

No model can be perfect. When a model fails in some way, failure may be avoided by modifying it. One must, however, be careful not to destroy its usefulness by making numerous ad hoc modifications. The pleasing aspect of the modification suggested here is that it overcomes a number of very different failings of the localized bond model by one small and simple addition.

Our PMO treatment of localization starts with a zeroth approximation in which the electrons are localized in sets of identical CC and CH bond orbitals. The large first-order perturbations between these orbitals scramble them together and lead to large changes in the corresponding orbital energies. The changes cancel, however, in calculating the total energy of the molecule or any of its other collective properties. These are affected only by second-order perturbations which are not only much smaller but also have constant values. They can therefore be taken into account by using appropriate values for bond properties; see eq 9. This is why bonds in classical molecules appear to be localized. The representation of a molecule in terms of localized bonds is clearly much simpler than the MO one because it avoids the need to treat each molecule individually. Even the small deviations from additivity are accounted for by the PMO treatment.

This simplification is, however, possible only in discussions of the collective properties of molecules. In the case of one-electron properties the MO model has to be used. Does this then imply that the picture of molecules given by the localized bond model is less "real" than the MO one? By no means! MO theory is not a description of reality. It is only the embodiment of another molecular model, the MO model.[18] MOs are no more "real" than "localized bonds". The MO model in turn fails in cases where correlation effects are unusually important, e.g., ref 19. An even more elaborate model must then be used. We do not know, and probably never will know, what molecules are "really" like. Our understanding of them is based on models that reproduce their properties well enough to be useful. The localized bond model reproduces very effectively certain properties of molecules that happen to be of special importance to chemists. Indeed, it reproduces them better than does the MO model. The observed additivity of bond properties in saturated molecules is better than

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(14) Dewar, M. J. S.; Pettit, R. *J. Chem. Soc.* **1954**, 1625.

(15) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

(16) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(17) Zahn, C. T. *J. Chem. Phys.* **1934**, *2*, 671.

(18) For "model" one can read "theory". A model is simply the embodiment of a theory.

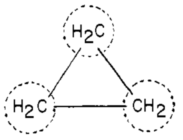
(19) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431.

would be expected from even the most sophisticated MO calculations. Properties of molecules that are reproduced at once by the MO model are also often obscured in more elaborate treatments. The only criterion of a model is its usefulness, not its "truth".

As this discussion emphasizes, hybridization is not a real phenomenon. It is a constituent part of the localized bond model. Estimates of the hybridization of carbon atoms are meaningful only within the confines of this model, insofar as they can be related to experiment. Attempts to deduce the hybridization of AOs from MO calculations are wrong in principle because hybridization has no place in the MO model. For example, C–H NMR coupling constants have been used, apparently successfully, as a criterion of the hybridization of carbon atoms in the localized bond model. They have also been calculated theoretically, using MO theory. Attempts to use these calculated values to estimate hybridization are, however, as mistaken as would be attempts to explain in terms of MO theory why space-filling molecular models are usually made out of plastic.

**σ Aromaticity**

Localization of bonds breaks down in cyclic polyenes because of the nonadditivity of second-order perturbations.[2,3,13] The original PMO papers[2] presented a method for treating this problem using first-order perturbation theory which accounted for the deviations from additivity embodied in Huckel's rules and which has proved an effective basis for the interpretation of aromaticity in all its aspects.[3,13] The analogy between paraffins and polyenes suggests that similar deviations should manifest themselves in cycloparaffins. In particular, cyclopropane (**1**) should be isoconjugate with benzene (**2**) and hence *σ aromatic.*



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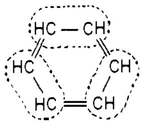

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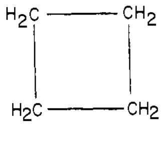

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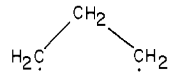

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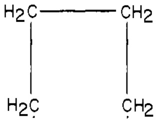
The properties of **1** present anomalies that have usually been ignored for lack of an explanation:

(a) The strain energy of **1**, as conventionally[15] defined (*conventional strain energy*, CSE), is 27.5 kcal/mol.[15] The strain energy calculated, using the CCC bending force constant (1.08 mdyne/Å) estimated[20] from the vibrational spectra of paraffins, is 104 kcal/mol. Anharmonicity in bending would be expected to *increase* the strain energy, certainly not to reduce it by 75%. This is a monstrous anomaly. The problem moreover arises *only* in the case of compounds containing three-membered rings. Thus, the strain energy calculated in the same way for cyclobutane (**3**), 21.6 kcal/mol, is *less* than its CSE (26.5 kcal/mol[15]), the difference being attributable to eclipsing strain. It is difficult to see on any basis how the CSE of **1** and **3** could be almost the same, given that the angle strain at each carbon atom in **1** (49.5°) is two-and-one-half times that in **3** (19.5°).

(b) Besides, if the strain energies of **1** and **3** are really much the same, as their CSEs imply, why is **1** so very much more reactive than **3**? **1** undergoes reactions, e.g., electrophilic addition leading to ring opening, which are not observed at all in the case of **3** or indeed in any cycloparaffin that does not contain a cyclopropane ring.

(c) Yet, if the strain energies of **1** and **3** are really different, why is the energy (61 kcal/mol)[21] required to convert **1** to the trimethylene biradical (**4**), almost the same as that (62.5 kcal/mol)[22] required to convert **3** to the corresponding biradical (**5**)?



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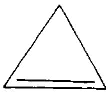

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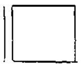

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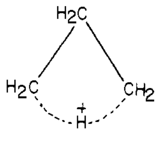

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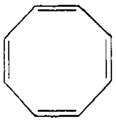

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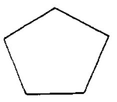

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(d) Ring strain should weaken bonds and make them correspondingly longer. The lengths of the CC bonds in **3** (1.55 Å)[23] are indeed greater than those in paraffins (1.53 Å). Those in **1** are, however, *shorter* (1.51 Å).[24]

(e) According to current ideas, the CH bonds in **1** are formed by carbon AOs with unusually high s character. This, for example, seems to be indicated by the size of the corresponding CH NMR coupling constant.[25] Since the binding energy of a carbon $sp^2$ hybrid AO is greater than that of a corresponding $sp^3$ hybrid AO, the proton NMR signal for **1** would therefore be expected to appear downfield relative to those for $CH_2$ groups in paraffins. In fact, it appears *upfield* by 1 ppm.[26]

(f) Problems also arise in the case of cyclopropene (**6**) and cyclobutene (**7**). The fractional increase in angle strain on passing from **1** to **6** (14%) is less than that on passing from **3** to **7** (25%). Yet, while the CSE of **7** (30 kcal/mol)[15] is little greater than that of **3**, that of **6** (54 kcal/mol)[15] is nearly double that of **1**.

All these problems resolve themselves if **1** is indeed σ aromatic.

(a) If **1** is σ aromatic, its CSE is the difference between its real strain energy (RSE) and the stabilization due to aromaticity (σ aromatic energy; SAE). The latter is expected to be larger than that of benzene (20 kcal/mol[11]) because the resonance integrals between AOs in a paraffin are larger than those between adjacent 2p AOs in a conjugated hydrocarbon. The RSE of **1** must therefore be much larger than its SCE, as indeed appears to be the case.

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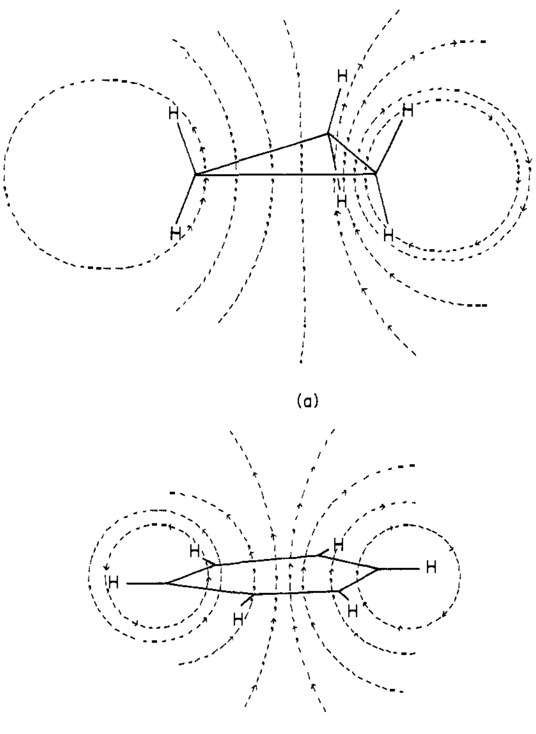

**Figure 4.** Magnetic lines of force in (a) cyclopropane and (b) benzene.

(b) In the reactions of **1** that differ so markedly from those of other paraffins, the three-membered ring survives more or less intact. The rate-determining step in electrophilic addition, for example, involves the formation of a nonclassical ion,[27] either "edge-protonated cyclopropane" (**8**) or a $\pi$ complex[28] ($\|\!\rightarrow CH_3^+$). Such a structure will retain at least a large part of the aromatic stabilization of **1**. The increase in one CC internuclear distance will, on the other hand, lead to a significant fractional decrease in the *real* strain energy (RSE). Since the RSE of **1** is very large and since the decrease in it is not offset by a corresponding decrease in the SAE, the net decrease in energy should be very large and act as a strong driving force for the addition.

(c) Opening of the ring in **1** will reduce the RSE to zero but it will also nullify its SAE. The driving force for ring opening is then the difference between them, i.e., the CSE of **1**, which is almost the same as that of **3**.

(d) The shortness of the CC bonds in **1** is easily understood if they are strengthened by $\sigma$ aromatic stabilization. The lengthening of the CC bonds in **3** may likewise be due, at least in part, to the fact that **3** is isoconjugate with cyclooctatetraene (**9**) and hence *$\sigma$ antiaromatic*.

(e) The upfield NMR shift can be understood in terms of diamagnetic shielding due to an aromatic ring current[29] in the cyclopropane ring. In benzene (**2**), the ring current leads to a downfield shift because the protons lie in the region where the magnetic lines of force have turned round and consequently reinforce the applied field (Figure 4a). In **1**, they are expected to lie in the shielded region (Figure 4b). Similar reversals have been observed in a number of $\pi$ aromatic systems for protons lying above the ring; see, e.g., ref 30.

(f) If the RSE of **1** is in fact several times greater than that of **3**, a small increase in the angle strain of **1** should lead to a much larger increase in the strain energy than the increase brought about by a larger increase in the angle strain of **3**. Note that the greater angle strain of **6** is not compensated by any increase in the $\sigma$-aromatic energy because the $\sigma$-aromatic systems in **1** and **6** are similar.

While **3** should in principle be $\sigma$ antiaromatic, analogy with **9** suggests that the corresponding antiaromatic energy is probably quite small. The antiaromatic energy of planar **9**, neglecting ring strain, is 2.6 kcal/mol,[11] much less than the aromatic energy of benzene (20 kcal/mol[11]). The aromaticity of benzene is admittedly enhanced by the equivalence of the CC bonds in it. In **9** the bond lengths alternate. However, a similar difference may be expected between **9** and **3**. The extreme angle strain in **1** should reduce the overlap between the AOs forming the CC bonds in it, thus reducing the alternation of CC resonance integrals normally present in paraffins.

An attempt was made in the earlier paper[5] to estimate the SAE and RSE of **1**. The values obtained (55.1 and 77.4 kcal/mol, respectively) were only rough approximations, neglecting in particular the effects of anharmonicity and eclipsing strain. Nevertheless it seems clear that the SAE of **1** must be large and that molecular mechanics schemes might benefit if a specific empirical allowance were made for it.

The aromatic/antiaromatic energy of a conjugated ring is expected[2,3,13] to fall off rapidly with increasing ring size if the bonds in it alternate, i.e., if the corresponding resonance integrals alternate. The bond lengths in a cyclic [4*n* + 2]annulene therefore tend to be equal in order to maximize its aromatic stabilization. A further factor favoring the equalization of bond lengths, important in the case of larger rings, is a tendency of electrons of opposite spin to segregate themselves in alternate bonds.[18] The bond lengths in aromatic annulenes therefore tend to be approximately equal. In a cycloparaffin, however, the resonance integrals cannot normally be equalized by any change in geometry because the resonance integrals are of different types, corresponding to interactions of different kinds. The only possible exception is cyclopropane (**1**) where, as noted above, the poor overlap of the AOs forming the CC bonds must reduce the corresponding resonance integrals and so make them closer to the intraatomic ones. $\sigma$ aromaticity is therefore likely to be largely confined to molecules with three-membered rings.

Some residual effects of $\sigma$ aromaticity might, however, be expected in the next higher potentially $\sigma$ aromatic cycloparaffin, i.e., cyclopentane (**10**), which is isoconjugate with [10]annulene. The observed heat of formation of **10** seems at first to refute this idea because it is more *positive* than expected from the $CH_2$ increment in paraffins by 6.2 kcal/mol.[15] However, while the bond angles (108°) in a regular pentagon are close to the tetrahedral value (109.5°), planar **10** contains five eclipsed CC bonds, which should together lead to a much larger destabilization (15 kcal/mol). The observed heat of formation of **10** is therefore more *negative* by 9 kcal/mol than would be expected if it were planar. While **10** is in fact puckered, leading to a decrease in eclipsing strain, it is not clear that the whole of the difference can be accounted for in this way. Part of it may well be due to $\sigma$ aromaticity.

While this discussion has been limited to cyclic hydrocarbons, the same principles should naturally apply to analogous compounds of other elements. Other species with three-membered rings (e.g., oxirane, thiirane) do indeed resemble cyclopropane in exhibiting unexpected stability combined with unusual chemical behavior. The remarkable stability of cyclopropenium $(C_3H_3)^+$ can also be explained nicely in terms of $\sigma$ conjugation. Although the angle strain in it is very much greater than in **1**,[31] so also should be its $\sigma$-aromatic energy, the resonance integral between two $sp^2$ AOs of a carbon atom being much larger than that between two $sp^3$ AOs (eq 4). The increase in $\sigma$ aromaticity combines with the $\pi$

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[27] (a) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432. (b) Lischka, H.; Kohler, H.-J. *Ibid.* **1978**, *100*, 5297. (c) Bischof, P. K.; Dewar, M. J. S. *Ibid.* **1975**, *97*, 2278.

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[29] The possibility that the upfield shift might be due to a ring current has been suggested previously but only in terms of hyperconjugative ($\pi$-type) interactions between the $CH_2$ groups. See: (a) Bley, W. R. *Mol. Phys.* **1971**, *20*, 491. (b) Benson, R. C.; Flygare, W. H. *J. Chem. Phys.* **1973**, *58*, 2651.

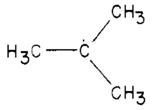
[30] A striking example is provided by the huge upfield shift of the inner protons in bridged [18]annulenes; see: DuVernet, R. B.; Otsubo, T.; Lawson, J. A.; Boekelheide, V. *J. Am. Chem. Soc.* **1975**, *97*, 1629.

[31] Using thermochemical data from ref 15, the RSE of cyclopropenium ion is estimated to be 114 kcal/mol.

aromaticity to make cyclopropenium a very stable carbocation.

## σ Conjugation in Radicals

The structure of the *tert*-butyl radical (**11**) presents a curious problem.



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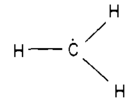

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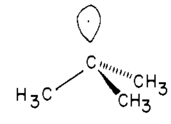

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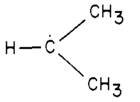

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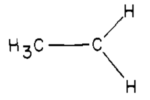

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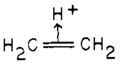


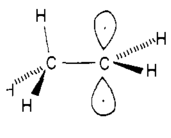
$H_2C \overset{H^+}{\overset{\uparrow}{=}} CH_2$

16

Methyl radical **12** is not only planar but also resists distortion from planarity quite strongly, judging by the frequency (607 cm$^{-1}$)[32] of the out-of-plane bending vibration. Since the repulsions between the methyl groups in **11** should be greater than those between the hydrogen atoms in **12** and since hyperconjugation between the methyl groups and the radical center in **11** should be greatest when the carbon atoms in it are coplanar, it was formerly taken for granted that **11** must also be planar. Recent studies of **11** by ESR[33] and ultraviolet photoelectron[34] (UPE) spectroscopy seem, however, to have provided very strong evidence that it is in fact pyramidal, having the structure indicated in **13**. This surprising result is moreover supported by theoretical calculations[35,36] which indeed predict *all* alkyl radicals, other than methyl (**12**), to be pyramidal. The resemblance between the UPE spectra[34] of *tert*-butyl (**11**) and isopropyl (**14**) radicals certainly suggests that **14**, like **11**, has a pyramidal equilibrium geometry. While the ESR spectrum[37] of ethyl (**15**) and isopropyl (**14**) radicals indicate that the methyl groups in them rotate freely, this could be due to the barrier separating the pyramidal isomers being very low. The UPE data for **15** provide no information concerning its geometry because the resulting cation is thought[38] to have the π complex structure (**16**). The reported out-of-plane CH bending frequencies for **12** (607 cm$^{-1}$),[32] **15** (541 cm$^{-1}$),[39] and **14** (375 cm$^{-1}$)[39] would also be difficult to explain if all three radicals were planar, given that the frequencies of the corresponding CH bending vibrations in olefins vary much less.[40] Lower frequencies would be expected in **14** and **15** if the bending potential function has indeed a double minimum.

While, as noted above, theoretical calculations predict **11** to be pyramidal, they do not explain why it is pyramidal. Any acceptable explanation of any chemical phenomenon must be phrased in terms either of the CMM or of some new principle of sufficient usefulness or generality to justify its incorporation in the CMM. Quantitative calculations do not in themselves provide such explanations.

Paddon-Row and Houk[35] have attributed the nonplanarity of **11** to hyperconjugative interactions between the unpaired electron and CH bonds of adjacent methyl groups, which are maximized when one of the CH bond orbitals is parallel to that occupied by the odd electron (see **17**). If the radical center is planar, the methyl group(s) will then be unsymmetrically oriented with respect to the nodal plane of the 2p AO occupied by the unpaired electron (see **17**). Paddon-Row and Houk assume that the unbalanced repulsions between the hydrogen atoms distort the radical center from planarity and that the resulting pyramidal structure is further favored by an increase in the hyperconjugative interactions when the unpaired electron consequently occupies a hybrid AO.



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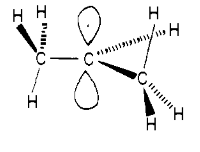

18

This mechanism for pyramidalization is, however, open to criticism. The postulated conformational interactions cannot alone be responsible because the need for having a CH bond of each methyl group parallel to the singly occupied AO can be met equally well in the case of **14** by the structure **18** where the repulsions between the hydrogen atoms are the same on both sides of the nodal plane. One is therefore forced to rely on the assumption that pyramidalization favors the hyperconjugative interactions, an assumption contrary to current ideas and with no obvious basis. Explanations of this kind are convincing only when one can see that the phenomena in question could have been predicted if anyone had thought of the explanation in advance. That is clearly not so here. It is also difficult to see how the ideas advanced could be of value in any other connection.

The pyramidal structure of **11** can, however, be explained simply and convincingly in terms of σ conjugation.

Consider the ethyl radical (**15**). If the radical center in it is pyramidal (**19**), the three carbon AOs used to form the C–C bond and to house the unpaired electron form a three-orbital system analogous to the three-orbital π system in the allyl radical; cf. **19** (**15**) with **20** (**21**). **15** should therefore be stabilized by σ conjugation, just as **21** is by conjugation. The stabilization of **15** vanishes, however, if the radical center is planar, because the unpaired electron then occupies a 2p AO so that the resonance integral between it and the hybrid AO used to form the adjacent CC σ bond vanishes. σ conjugation therefore favors a pyramidal geometry for the radical center in **15**. The tendency to pyramidalize should naturally increase along the series **15** < **14** < **11** because of the increasing number of methyl groups that can σ conjugate with the radical center if the latter is pyramidal. The calculations[35,36] show this trend.

This argument, however, neglects σ conjugation by CH bonds, which should also tend to pyramidalize radicals. Yet methyl radical (**12**) is planar. There are two reasonable explanations for this.

(a) Replacement of a terminal carbon atom in **21** by a heteroatom reduces the stabilization energy. Radicals of this kind are most stable when they are symmetrical. σ conjugative stabilization of a carbon radical by adjacent CC bonds should

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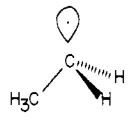

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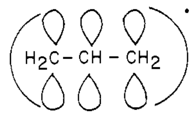

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$H_2C{=}CH{-}\dot{C}H_2$

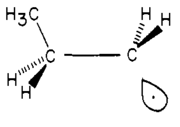
21

$CH_3CH_2CH_2{}^{\cdot}$

22

$H_2C{=}CH{-}CH{=}CH{-}\dot{C}H_2$

23



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therefore be more effective than stabilization by CH bonds.

(b) The repulsions between the three pairs of electrons in the CH bonds of **12** tend to make it planar. The repulsions are reduced if the CH bonds are replaced by CC bonds because the latter are longer and the electrons forming them correspondingly further apart (see[41]).

Whatever the explanation, CC $\sigma$ conjugation clearly stabilizes radicals much more effectively than does CH $\sigma$ conjugation. As we have already noted, methyl radical is not only planar but also resists deformation from planarity quite strongly. On the other hand the frequency of the corresponding CH bending vibration (607 $cm^{-1}$) is much less than the frequencies of analogous CH bending vibrations in olefinic methylene groups ($\sim$900 $cm^{-1}$), a difference which implies significant $\sigma$-conjugative stabilization of nonplanar structures. The effects of CH $\sigma$ conjugation are therefore by no means negligible.

Since $\sigma$ conjugation involves interactions only between different hybrid AOs of a given atom and since sp$^n$ hybrid AOs have axial symmetry, $\sigma$-conjugative interactions should be unaffected by rotation about $\sigma$ bonds formed by such AOs. However, while hyperconjugation is not as important as $\sigma$ conjugation, it may nevertheless serve to distinguish between structures which are equivalent so far as $\sigma$ conjugation is concerned, in particular between different rotamers of a pyramidal radical.

Consider, for example, the geometry of the *n*-propyl radical (**22**), which is the $\sigma$-conjugated analogue of the pentadienyl radical, **23**. In discussing the electronic properties of conjugated molecules, it is usual to assume that the phases of the AOs are chosen in such a way as to make all the overlap integrals between them positive and all the resonance integrals negative. It is easily seen that the corresponding condition in a $\sigma$-conjugated system is that the phases of all the larger lobes of the hybrid AOs have the same sign, which we take to be positive (see Figure 5a). It can be shown[2,3] that the bond orders between positions in a neutral AH separated by $(4n + 2)$ carbon atoms are positive while those between positions separated by $(4n - 2)$ carbon atoms are negative. The same should also be true for positions in a paraffin separated by the corresponding number of hybrid AOs. Now hyperconjugation in a paraffin involves, in this sense, a 1,4 interaction (Figure 5b) so the corresponding bond order should be negative.[2,3] The interaction will then be antibonding if the corresponding 1,4 resonance integral is, as usual, negative. The radical will therefore be more stable, the less negative (or more positive) the 1,4 resonance integral.

The situation can be seen clearly from a standard PMO analysis of the effect of the additional interaction on the pentadienyl radical, **23**. The NBMO coefficients[2,3] are shown in Figure 5c, calculated assuming the resonance integrals to be equal. The additional interaction, corresponding to the hyperconjugative interaction in **22**, converts **23** to cyclobutadienylmethyl radical, the NBMO coefficients of which are shown in Figure 5d, the resonance integrals again being assumed equal. If, on the other hand, the resonance integral for the extra interaction is similar in magnitude to the others but opposite in sign, corresponding to a negative overlap integral between the AOs,[13] the coefficients are as indicated in Figure 5e.[3,13] The cyclic interaction in Hückel[13] cyclopentadienylmethyl (Figure 5d) thus has a destabilizing effect, converting the five-atom conjugated system in **23** into a three-atom

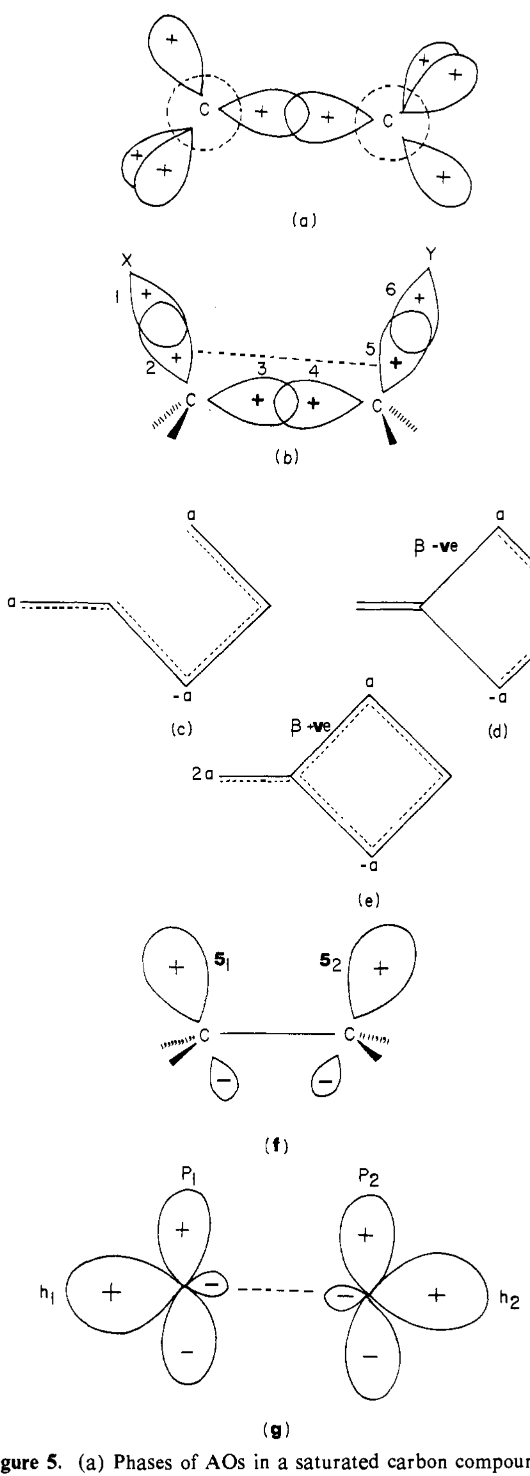

**Figure 5.** (a) Phases of AOs in a saturated carbon compound. (b) $\sigma$ conjugation and hyperconjugation. NBMO coefficients in (c) Hückel pentadienyl, (d) Hückel cyclobutadienylmethyl, and (e) anti-Hückel cyclobutadienylmethyl. (f)(g) Dissection of hybrid AOs in b into $\sigma$ and $\pi$ components.

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[41] The effects of repulsions between vicinal bonds, and the decrease in them brought about by increasing bond length, probably play a larger role in chemistry than has usually been realized. For example, the fact that compounds of silicon are far more reactive than those of carbon to $S_N2$-type reactions is probably due primarily to the smaller covalent radius of silicon. See: Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

one, whereas in the anti-Hückel[13] isomer (Figure 5e) it enhances the interaction with the exocyclic methylene. The Hückel-type ring is therefore antiaromatic while the anti-Hückel one is aromatic.[13]

Consider now the resonance integral between two hybrid AOs, $\phi_1$ and $\phi_2$, at the ends of a C–C bond (see Figure 5f). Each can be written (Figure 5f,g) as a combination of a hybrid AO ($h_1$ or $h_2$) pointing along the bond and a 2p AO ($p_1$ or $p_2$) at right angles to it. Since the resonance integrals between $h_1$ or $h_2$ and $p_1$ or $p_2$ vanish because they differ in symmetry, only the resonance integrals between $h_1$ and $h_2$ ($\beta(h_1h_2)$), and between $p_1$ and $p_2$ ($\beta(p_1p_2)$) contribute to that $\beta(\phi_1\phi_2)$ between $\phi_1$ and $\phi_2$. The former remains unchanged by rotation about the intervening $\sigma$ bond while the latter is proportional to the cosine of the dihedral angle ($\theta$) between the positive lobes of $p_1$ and $p_2$. Hence:

$$\beta(\phi_1\phi_2) = R\beta(h_1h_2) + S\beta(p_1p_2)\cos\theta = A + B\cos\theta \qquad (11)$$

where $A$ ($=R\beta(h_1h_2)$) and $B$ ($=S\beta(p_1p_2)$) are independent of $\theta$ and negative. Thus, the resonance integral between the hybrid AOs, $\phi_1$ and $\phi_2$, is most negative (or least positive) when $\theta = 0°$ and least negative (or most positive) when $\theta = 180°$. The combined effects of $\sigma$ conjugation and hyperconjugation should therefore stabilize **22** most effectively when the methyl group is trans to the AO occupied by the unpaired electron (see **24**).

This argument ignores analogous hyperconjugative interactions involving CH bonds in **22**. These should again be greatest when one or the other CH bond is trans to the singly occupied AO, corresponding to a staggered conformation for the methyl group. However, since the stabilization due to any kind of conjugative interaction involving a CCC bond should be greater than that involving a CH bond, the most stable configuration of **22** should be that indicated in **24**. No relevant calculations for **22** have as yet been reported, its geometry having been assumed, probably incorrectly,[35,36] to be planar.

Note that this argument does not depend on the values of $A$ and $B$ or on the sign of $A$. If $\beta(\phi_1\phi_2)$ is calculated using Slater orbitals $A$ and $B$ are both negative with $A < B$. Thus, $\beta(\phi_1\phi_2)$ is negative when $\theta = 0°$ and positive when $\theta = 180°$.

This discussion applies only to radicals that are not stabilized by electromeric substituents able to conjugate with the radical center. While hyperconjugation is much less effective than $\sigma$ conjugation, the same is not necessarily true of conjugation.

Consider for example the allyl radical (**21**). The mesomeric stabilization of such a species is greatest when it is symmetrical, the resonance integrals of the two bonds being equal. This can be achieved in the case of **21** by equalizing the CC bond lengths. In the isoconjugate ethyl radical (**15**), however, the corresponding resonance integrals are intrinsically different and this difference limits the stabilization that $\sigma$ conjugation can bring about. Conjugation evidently wins out in **21** because it is undoubtedly planar.

To avoid possible misunderstanding, it should be emphasized that $\sigma$ conjugation is not expected to lead to extensive delocalization of electron spin, as does $\pi$ conjugation in $\pi$ radicals like **21**. The alternation of resonance integrals in saturated systems inhibits delocalization. The resonance integral between the singly occupied AO and the adjacent AO should moreover be unusually small because the carbon atom at the radical center will not be $sp^3$ hybridized, the deviation from planarity due to $\sigma$ conjugation being limited by the opposing effects of steric repulsions and hyperconjugation involving the adjacent groups. Ab initio calculations[35] indeed indicate this to be the case.

## Biradicals

The role of biradicals as intermediates in reactions has become a topic of major interest in recent years, the term "biradical" being used here in its usual chemical sense, i.e., to denote a singlet species in which two electrons appear to be more or less uncoupled, not a triplet in which decoupling is enforced. In the cases of major interest the "unpaired" electrons still interact with one another to a significant extent, giving rise to a semiclosed-shell species now commonly called a *biradicaloid*. Here we will use the term "biradical" to denote any singlet species with "biradical character", without any implication concerning the degree of coupling between the "unpaired" electrons.

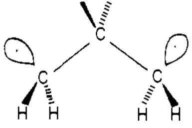
The arguments given in the previous section suggest that the radical centers in biradicals should be pyramidal, like those in simple radicals. Here again we will be concerned only with saturated radicals where $\sigma$ conjugation is dominant and where the radical centers are expected to be correspondingly pyramidal. Such a biradical will be isoconjugate with a $\pi$ biradical in which two electrons are localized in 2p AOs of a conjugated system. Thus the trimethylene biradical (**4**) is isoconjugate with the $\pi$ biradical (**25**). Now **25** is not a biradical because the unpaired electrons in it can couple, giving rise to a normal polyene, **26**. A similar coupling would then be expected between the radical centers in **4**, by $\sigma$ conjugation through the intervening $\pi$ bonds. Here, however, a basic difference between $\sigma$ conjugated and $\pi$ conjugated systems again shows itself. Conversion of **25** to **26** is assisted by a reorganization of the resonance integrals by interchange of C—C and C═C bonds to match the changing CC bond orders. This is impossible in the case of **12** because the resonance integrals in it cannot vary. The interaction between the radical centers in **4** thus corresponds to conversion of **25** to a hexatriene (**27**) in which there has been no change in bond lengths, so that the C═C bonds are still long and the C—C bonds short. Clearly the difference in energy between **25** and **27** will be much less than that between **25** and **26** and the stabilization of **12** should be correspondingly small. However, since the coupling between the radical centers in **4** is possible only if they are pyramidal, the $\sigma$-conjugative interaction between them should reinforce their nonplanarity. While the geometry of **4** has not been determined by experiment, calculations[42,43] by fairly sophisticated ab initio methods have indicated that the radical centers in it are nonplanar. No satisfactory explanation for this has, however, yet been given in terms of current qualitative theory.[43]

$$H_2\dot{C}{-}CH{=}CH{-}CH{=}CH{-}\dot{C}H_2 \qquad H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

25 26

$$H_2C{=\!=\!=}CH{-}CH{=\!=\!=}CH{-}CH{=\!=}CH_2$$

27



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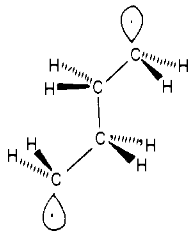

29

The discussion in the previous section leads to the further prediction that **4** should have the specific conformation indicated in **28**, the AOs housing the unpaired electrons being in each case trans to the adjacent CC bonds. This prediction is also in agreement with the ab initio calculations.[42,43]

So far we have considered only "through-bond" interactions between the radical centers in **4**, involving $\sigma$ conjugation or hyperconjugation. However, there is also the possibility of a direct interaction between them, by overlapping of the "singly occupied" AOs. If such overlap is between the larger lobes of the AOs, or between their smaller lobes, the corresponding overlap integral will be positive and the corresponding resonance integral negative. The direct interaction will then be bonding if the bond order between the terminal AOs in **4** is positive and antibonding if it is negative.[2,3] The parallel between **4** and **26** shows that the bond order is in fact positive, corresponding to a 1,6 interaction in an

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(42) Doubleday, Jr., C.; McIver, Jr., J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533.

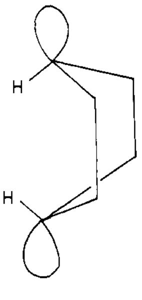
(43) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 638.

AH.[2,3] The conformation **28** of **4** should therefore be further stabilized by the through-space interaction between the small lobes of the "singly occupied" AOs.

The through space interaction is presumably responsible for the fact that thermal isomerization of substituted cyclopropanes seems[44] to take place preferentially by simultaneous inversion of the configurations of *two* carbon atoms, by disrotation in the biradical (**4**) formed by breaking the bond between them. It is easily seen that disrotation retains in-phase overlap of the AOs involved in the breaking/reforming bond.

The possibility of through-bond interactions between AOs was first suggested by Hoffmann et al.[45] in terms of a MO treatment. The present discussion, in terms of the localized bond model, leads to similar conclusions in a simpler manner. It has the further advantage of explaining simply and convincingly why the radical centers in biradicals are pyramidal and it also explains why certain configurations in radicals and biradicals are preferred.

Calculations for a number of other biradical intermediates in reactions have led to conclusions consistent with the analysis given above. Thus the tetramethylene biradical (**5**) is predicted[46] to have the staggered geometry indicated in **29**, the terminal carbon atoms being pyramidal with the unpaired electrons trans to the adjacent CC bonds. Here the bond order between the "singly occupied" AOs is expected to be negative, corresponding to a 1,8 interaction in a conjugated polyene, so any through-space interaction between the radical centers should be antibonding. Cyclization to cyclobutane consequently involves a HOMO/LUMO crossing.[47] A similar situation arises in the intermediates in the boat and chair intermediates in the Cope rearrangement of 1,5-hexadiene, which are predicted[48] to have the structures indicated in **30** and **31**, respectively, and similar intermediates are predicted[49] in Claisen rearrangements. The double electrocyclic ring opening of bicyclobutane (**32**) to butadiene (**33**) is another example, being predicted[50] to take place via the biradical **34** where both the radical centers are pyramidal.



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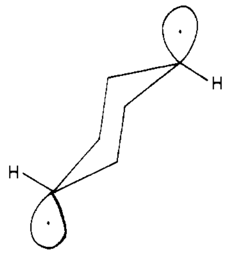


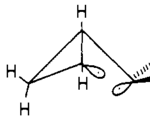
31

32

33

## Conformational Analysis

The arguments given above concerning the configurations of radicals should apply equally to hydrocarbons in general. A hyperconjugative interaction in a paraffin again involves an interaction between AOs that are 1,4 to one another, the bond order between being consequently negative. The hyperconjugative interaction will then be bonding if the resonance integral between the two AOs is positive and antibonding if it is negative. The interaction will therefore be most strongly bonding when the relevant AOs are trans to one another and most strongly antibonding when they are cis.



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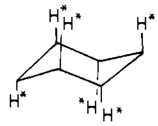

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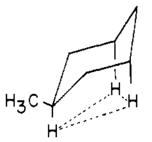

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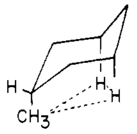

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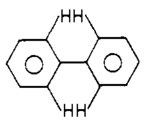

38

$CH_3-CH_2^-$

39

As we have seen (eq 11), the resonance integral between such a pair of AOs, $\phi_1$ and $\phi_2$, can be expressed as a sum of two terms, one independent of the dihedral angle ($\theta$) between $\phi_1$ and $\phi_2$ while the other, $\beta(p_1p_2)$, is proportional to cos$\theta$. Consider the hyperconjugative interactions in $CH_3X$ between the three CH bonds and the CX bond. If one CH bond is trans to CX, so that the corresponding dihedral angle is 180°, the dihedral angles for the other two are +60° and −60°. This values of cos$\theta$ for the three CH bonds are then 1, $^1/_2$, and $^1/_2$, respectively, so according to eq 11 the three interactions should sum to zero. This, however, would be true only if the relevant $\pi$ type AOs, $p_1$ and $p_2$, were pure hydrogen-like p AOs. So they would be if the relevant potential function had $C_\infty$ symmetry, but the symmetry here is $C_3$ (corresponding to the threefold symmetry of the $CH_3$ group). The AOs, $p_1$ and $p_2$, will then differ from hydrogen-like AOs by being more concentrated along the CH bonds, in order to make the bonds as strong as possible, and the same will be true of the carbon AO forming the CX bond. This is why d AOs ("polarization functions") have to be introduced in ab initio treatments of carbon compounds if angle strain is to be taken adequately into account. The corresponding resonance integral $\beta(p_1p_2)$ will therefore deviate from the cos$\theta$ relationship, being greater when $\theta$ is near 0° or 180° and smaller near ±90° than the cosine relation implies. In the case considered above, the numerical values of the resonance integrals for dihedral angles of ±60° will be less than one-half those for 180° so the net contribution of the three hyperconjugative interactions will be stabilizing. Conversely, if the dihedral angles are 0° and ±120°, their net effect will be destabilizing. The combined effect of $\sigma$ conjugation and hyperconjugation in $CH_3CH_2X$ will therefore favor the conformation in which the methyl and $CH_2X$ groups are staggered, the eclipsed conformation being an energy maximum, i.e., a transition state for rotation about the C–C bond.

As is well-known, the preferred conformation of saturated carbon atoms linked by a C–C bond is staggered, the barrier to rotation being typically ca. 3 kcal/mol. However, while the effect is very well-known, it has not yet been satisfactorily explained in terms of simple PMO theory. It is now seen to follow as a direct consequence of the interplay between $\sigma$ conjugation and hyperconjugation predicted by PMO theory, when the theory is properly applied. The effect is small because it depends on the small differences in angular dependence between AOs in molecules and

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(44) (a) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122. (b) Wood, J. T.; Arney, J. S.; Cortes, D.; Berson, J. A. *Ibid.* **1978**, *100*, 3855.

(45) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

(46) (a) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 5246. (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *Ibid.* **1980**, *102*, 939. (c) Doubleday, Jr., C.; McIver, Jr., J. W.; Page, M. *Ibid.* **1982**, *104*, 3768.

(47) (a) Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Chem. Soc.* **1974**, *96*, 5240. (b) Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *Ibid.* **1974**, *96*, 5242. (c) Dewar, M. J. S.; Kirschner, S. *Ibid.* **1974**, *96*, 5244.

(48) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 5069.

(49) Unpublished work by E. F. Healy.

(50) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2931.

corresponding hydrogen-like AOs, arising from the lower symmetry of the potential field in which molecular electrons move.

According to this model, a trans hyperconjugative interaction between two bonds in a paraffin leads to a stabilization of ca. 0.5 kcal/mol and a cis interaction to an equal destabilization. However, the 3-fold potential field should also tend to make the lobes of p AOs differ in size, this again increasing the strength of bonds formed by them. If so, the determining factor in rotational barriers will be the stabilization arising from interactions of groups trans to one another rather than repulsions when they are cis. The effect is thus entirely distinct from steric interactions.

As is also well-known, the most stable configuration of a linear paraffin is one in which the carbon atoms are not only staggered but are also all trans to one another, each gauche interaction between CC bonds in a paraffin leading to a destabilization of ca. 0.5 kcal/mol.[15] This *gauche effect* has been generally attributed to steric repulsions between hydrogen atoms in the gauche conformers; cf. the repulsions commonly thought to exist between axial hydrogen atoms (H*) in the chair conformation (**35**) of cyclohexane where all the CC:CC interactions are gauche. Although this explanation is quoted in all the standard texts, it is far from plausible because the axial hydrogen atoms in **35** are in fact too far apart. Since the distance between them (2.5 Å) is greater than the sum (2.4 Å) of their Van der Waals radii, any residual Van der Waals force between them should be *attractive*, not repulsive. Furthermore, if the axial hydrogen atoms in **35** really do repel one another, replacement of one of them by methyl should lead to a large increase in the repulsions. While the conformer (**36**) of methylcyclohexane with methyl equatorial is more stable than that (**37**) with methyl axial, the energy of isomerization is only 1.74 kcal/mol,[51] corresponding to 0.87 kcal/mol per axial H/$CH_3$ interaction. This is very little more than the postulated H–H repulsion energy. In cases where there are genuine steric repulsions between hydrogen atoms, as in biphenyl (**38**), replacement of hydrogen by methyl has a much larger effect.

A more plausible explanation for the stability of trans conformers can be given in terms of the interplay between σ conjugation and hyperconjugation discussed above.

Hyperconjugative stabilization arises from interactions between bonds that are trans to one another and such interactions are expected to be greater when the bonds interacting are of similar type. A trans conformation about a given CC bond in a linear paraffin leads to a trans CC:CC interaction and two trans HC:CH interactions whereas a gauche conformation leads to two CC:CH interactions and one HC:CH one. Since a CC:CH interaction is expected to be less than the mean of the CC:CC and CH:CH ones, the net stabilization should be greater in the former case.

### Lone Pairs: The Anomeric Effect

Stereochemical studies have shown that lone pairs of electrons seem to have surprisingly large steric requirements, too large to be reasonably attributed to simple steric effects. The observations can be explained immediately in terms of the interplay between σ conjugation and hyperconjugation invoked in the previous section.

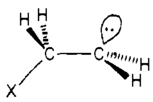
Lone pair electrons of second period atoms occupy hybrid AOs and can therefore interact σ conjugatively with adjacent σ bonds, just like the unpaired electrons in pyramidal radicals. Thus ethyl anion (**39**) is isoconjugate with allyl anion (**40**), just as ethyl radical (**5**) is isoconjugate with allyl radical (**21**). In **39**, as in **5**, there is also the possibility of hyperconjugation between the lone pair electrons and an adjacent CC σ bond. Again as in **5**, σ conjugation will synergize hyperconjugation if the latter involves the bond trans to the lone pair. Since σ conjugation remains unaffected by rotation about σ bonds, the geometry will be determined, as in the case of **5**, by hyperconjugation, being such as to place the bond best fitted to interact with the lone pair trans to it. For reasons indicated above, CH should be the worst possible choice. In **41**, the group X should therefore tend to be trans to the lone pair electrons (see **42**). Since the same result would follow if there were a steric repulsion between X and the lone pair, it is easy to see why the observed geometries have been interpreted in such terms. According to the present analysis, the geometries are determined by the stabilizing effect of substituents trans to the lone pair electrons, not by repulsions between the substituent and the lone pair when they are gauche to one another.

$CH_2{=}CH{-}CH_2^-$

40

$XCH_2CH_2^-$

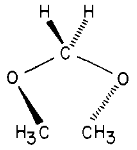
41



42

$CH_3OCH_2OCH_3$

43



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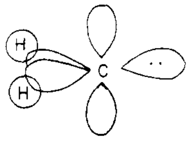

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Similar "steric" effects should occur for the same reason in the case of lone pairs of neutral atoms, in particular nitrogen and oxygen. A striking example is provided by acetals, which tend to have conformations that are staggered about both the CO bonds. For example, the preferred[53] conformation of dimethoxymethane (**43**) is the all-gauche **44**. This is what would be expected from the arguments given above. One lone pair of each oxygen atom should be trans to the adjacent CO bond, leaving only positions gauche to it for the methyl group. The situation here is indeed especially favorable for hyperconjugation because both of the terminal atoms in the corresponding allyl-like systems are the same.

The gauche orientation adopted by groups attached to oxygen in acetals was first recognized in carbohydrate chemistry and termed the *anomeric effect*.[53] While theoretical calculations reproduce the observed behavior of systems of this kind, no convincing explanation has yet been given in terms of the current molecular model. The one usually cited[54] was based on second-order perturbation theory and consequently depended on assessments of the energies of the specific orbitals involved. This, like other similar explanations, is unsatisfactory in the sense that the arguments used would not have led to a convincing prediction of the phenomenon in question if it had not already been known. According to the interpretation given here, the anomeric effect is the expected consequence of interactions that are also responsible for many of the other stereoregularities exhibited by saturated molecules.

Lone pair σ-conjugative interactions also lead to anomalous stability in molecules where two or more oxygen or fluorine atoms are attached to the same carbon atom, a well known effect illustrated by eq 12–16. These show heats of reaction ($\Delta H$,

$$CH_4 + CH_2F_2 \rightarrow 2CH_3F;\ \Delta H,\ -4.2 \qquad (12)$$

$$2CH_4 + CHF_3 \rightarrow 3CH_3F;\ \Delta H,\ -19.4 \qquad (13)$$

$$3CH_4 + CF_4 \rightarrow 4CH_3F;\ \Delta H,\ -33.4 \qquad (14)$$

$$CH_4 + CH_2(OCH_3)_2 \rightarrow 2CH_3OCH_3;\ \Delta H,\ -13.2 \qquad (15)$$

$$2CH_4 + CH(OCH_3)_3 \rightarrow 3CH_3OCH_3;\ \Delta H,\ -32.2 \qquad (16)$$

kcal/mol) for isodesmic reactions where $\Delta H$ would vanish if

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[51] Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278.

[52] Astrup, E. E. *Acta Chem. Scand.* **1973**, *27*, 3271.

[53] Lemieux, R. U.; Koto, S. *ACS Symp. Ser.* **1979**, *87*.

[54] David, S.; Eisenstein, O.; Hehre, W. J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 3806.

additivity held. The values of $\Delta H$ thus indicate the specific stabilization due to lone pair $\sigma$ conjugation. The thermochemical data are from ref 15, except for methyl orthoformate.[55]

The numbers of lone pair/bond interactions in $CH_2X_2$, $CHX_3$, and $CX_4$ are 2, 6, and 12, respectively. The values of $\Delta H$ in eq 12–16 are indeed approximately in the ratio 1:3:6, the lone pair/bond interaction energy being about 3 kcal/mol for F–CF and about 12 kcal/mol for O–CO.

Since lone pair $\sigma$ conjugation leads to a transfer of charge, the effect of such $\sigma$ conjugation between a lone pair of X and the CY bond in X–CRR–Y should be greater, the more electronegative Y and the less electronegative X. The stabilization should then be especially large in molecules such as $R_2NCH_2OR$ or $ROCF_3$. No thermochemical data seem to be available to test this prediction.

## $\sigma$ Conjugation in Carbenes

Another related phenomenon, which likewise has not yet been explained convincingly in terms of the current model, is the fact that triplet carbenes, including methylene ($CH_2$) itself, are nonlinear.

The nonlinearity of singlet $CH_2$ is easily understood.[3] Bivalent carbon has the valence state $(1s)^2(2s)(2p)^2$. The bonds in singlet carbene should therefore be formed by the singly occupied 2p AOs of carbon, the corresponding bond angle being consequently 90°. Repulsions between the electrons forming the CH bonds will naturally tend to open up the HCH bond angle, leading to a corresponding change in the hybridization of the carbon AOs used to form them. The change in hybridization involves, however, a partial promotion of electrons from the carbon 2s AO to the 2p AO. Consider, for example, the case where the CH bonds are formed by $sp^3$ hybrid AOs, each one-quarter 2s. Between them they use up half of the carbon 2s AO. Since the orbitals of $CH_2$ must be either symmetric, or antisymmetric, with respect to reflection in the plane of symmetry in which the nuclei lie, one of the orbitals of $CH_2$ must be the 2p carbon AO which alone is antisymmetric. The fourth carbon AO must therefore contain the remaining half of the 2s AO, i.e., it must be half s and half p and hence a sp hybrid AO. Since the latter is lower in energy than the 2p AO, it will be doubly occupied, the 2p AO remaining empty (**45**). The effective valence state of the carbon atom is then

$$(sp^3)^2(sp)(p) \text{ or } s^{1.5}p^{2.5} \qquad (17)$$

corresponding to promotion of half an electron from the 2s AO to the 2p AO. The amount of promotion increases with the bond angle, a linear geometry corresponding to the valence state $sp^3$ with promotion of a whole electron. Since the promotion energy in carbon is very high, the tendency to a 90° bond angle is strong. The actual value of the HCH bond angle (103.2°)[56] is evidently determined by a balance between the opposing effects of repulsions and promotion. The bond angles in $H_3N$ and $H_2O$ can be interpreted[3] in a similar manner. Since the lengths of bonds involving hydrogen are much greater in hydrides of elements of the later periods, the repulsions between the hydrogen atoms must be correspondingly smaller and the tendency for the HXH bond angle to increase at the expense of (ns np) promotion correspondingly less. The bond angles in such compounds ($H_2S$, $H_3P$) are indeed close to 90°. Similar considerations should apply in the case of dihydrides of the Group IV elements. While experimental data are lacking, near-Hartree-Fock ab initio calculations[57] predict bond angles for $SiH_2$ (93.5°) and $GeH_2$ (92.9°) that are close to 90°.

Triplet $CH_2$, however, is derived from a valence state of carbon in which all four AOs are singly occupied. This corresponds in all cases to quadrivalent carbon, one electron being promoted from the 2s AO to a 2p AO, regardless of the HCH bond angle. Since the CH bonds will still repel one another and since bonds formed by carbon are stronger the greater the s character of the carbon AO used to form them,[9] it would seem that the most stable geometry for triplet carbene should be linear, the CH bonds being formed by sp hybrid AOs of carbon. It was indeed assumed for many years that this is the case. Herzberg[56] in particular originally interpreted the vibronic spectrum of triplet carbene in terms of a linear geometry. ESR studies by Wasserman et al.[58] showed, however, that triplet carbene is in fact bent, the HCH angle being ca. 136°, a conclusion subsequently confirmed by Herzberg and Johns[59] from a reinterpretation of its vibronic spectrum.

No satisfactory explanation of this surprising result has as yet been given in terms of the current molecular model. Here $\sigma$ conjugation again provides an immediate answer.

If triplet carbene were linear, the unpaired electrons would necessarily occupy 2p AOs. The $\sigma$-conjugative interactions between them and the CH bonds would then vanish. While one of the carbon AOs must be a pure 2p AO, for reasons indicated above, the other AO will develop s character if the HCH bond angle is less than 180°. Since such a change will lead to $\sigma$-conjugative stabilization without any promotion of the carbon 2s electrons, it is expected to be energetically favorable. Furthermore, since the intraatomic resonance integral between two hybrid AOs of a carbon atom is greater the greater their s character, as indicated by the increase[9] in the strength of bonds formed by carbon with an increase in the s character of the AOs used to form them, $\sigma$-conjugative stabilization should be greatest when the 2s AO is shared evenly between the three relevant AOs, i.e., when all three are of $sp^2$ type, corresponding to a HCH bond angle of 120°. The fact that the observed bond angle (136°) is somewhat greater than 120° can of course be explained in terms of the factors noted above, i.e., repulsions between the electrons forming the CH bonds and the fact that such bonds are stronger the greater the s character of the carbon AOs used to form them.

The potency of $\sigma$ conjugation is indicated very clearly by the fact that triplet diphenylcarbene also has a bent structure. The linear isomer would be more strongly stabilized by $\pi$ conjugation if the phenyl groups were orthogonal, one interacting with each unpaired electron, because the resonance energy of two benzyl radicals is greater than that of one diphenylmethyl radical.[3] $\sigma$-Conjugative stabilization of the bent structure outweighs the increase in $\pi$-conjugation energy that would be available if the molecule were linear.

Analogy with the hydrides of group 5/6 elements suggests that the bond angles in triplet states of divalent compounds of the heavier group 4 elements, e.g., $SiH_2$, should be close to 120°. While no reliable experimental values are available, theoretical calculations[60,61] have predicted bond angles of 117.6° and 118.6° for triplet $SiH_2$ and triplet $GeH_2$, respectively. The value calculated in the same way for $CH_2$ (129.5°) was a little less than that observed (136°).[58,59]

## Chelotropic Reactions

$\sigma$ conjugation can be used to explain the course of chelotropic reactions in a manner which demonstrates their analogy to other cycloadditions.

In reactions of this kind, e.g., the addition of sulfur dioxide to **33** to form a cyclic sulfone (**46**), the chelotropic reagent is a species $XY^2$ which can be represented by a structure where X has two AOs available for forming $\sigma$ bonds, one of the AOs being filled and the other empty; cf. the representation of sulfur dioxide in **47**, dative $\pi$ bonds to sulfur being ignored. Such a species is analogous to singlet carbene and will have a similar structure, one of the AOs (A in **47**) being of p type and empty while the other (B) is a filled hybrid AO. Previous discussions[62,63] of chelotropic

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(55) Pihlaja, K.; Tuomi, M.-L. *Acta Chem. Scand.* **1971**, *275*, 465.

(56) Herzberg, G. "Electron Spectra and Electronic Structures of Polyatomic Molecules"; Van Nostrand: Princeton, NJ, 1966; p 491 and p 584.

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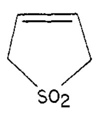
(62) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.



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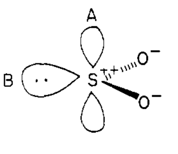

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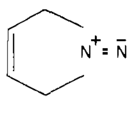

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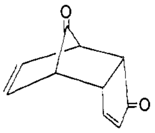

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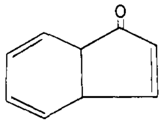

50

reactions have been based on these AOs, each of which can interact with the terminal 2p AOs of the polyene to form a cyclic conjugated system (see Figure 6a). Assuming that the reaction is pericyclic and that the transition state therefore has such a cyclic conjugated structure, the reaction will be "allowed" if the two cyclic conjugated systems are aromatic and "forbidden" if they are antiaromatic.[63]

The transition state can, however, be treated in an alternative way, the orbitals, A and B, being replaced by linear combinations, $\phi_1$ and $\phi_2$, given by

$$\phi_1 = (1/\sqrt{2})(\mathrm{A} + \mathrm{B});\ \phi_2 = (1/\sqrt{2})(\mathrm{A} - \mathrm{B}) \qquad (18)$$

As Figure 6b shows, each of these equivalent hybrid AOs overlaps with the 2p AO of just *one* terminal carbon atom in the polyene. Since $\phi_1$ and $\phi_2$ are hybrid AOs, σ conjugation will occur between them, leading to a cyclic conjugated system with two orbitals more than that in the original polyene. This system is isoconjugate with the cyclic conjugated system in the transition state for a synchronous $[2n + 2]$ π cycloaddition of the same polyene to ethylene. The chelotropic reagent bears the same relationship to ethylene as does a $-\mathrm{CH_2}-$ unit in a paraffin to a $=\mathrm{CH}-\mathrm{CH}=$ unit in a conjugated polyene. The transition state for the chelotropic addition of $\mathrm{SO_2}$ to **33** is thus isoconjugate with the transition state for the Diels Alder addition of ethylene to **33**. A similar relationship will of course also hold between chelotropic reactions and π cycloadditions of other conjugated polyenes. The rules for the stereochemistry of addition should therefore be the same in both cases, as indeed they are. Thus, in the case of a polyene, $(\mathrm{C{=}C})_n$, where the number ($n$) of C=C bonds is even ($=2m$), there are $4m$ conjugated atoms and consequently $4m$ p AOs. Since the chelotropic agent, or ethylene, contributes two AOs, the cyclic TS for either reaction will contain $(4m + 2)$ AOs and hence will be aromatic if it is of Hückel type, all the AOs in it overlapping in phase.[3] Such reactions should therefore take place place by suprafacial addition, as indeed they do. Conversely, when $n$ is odd ($=2\,m - 1$), the cyclic transition state contains $4m$ AOs and should be aromatic only if it is of anti-Hückel type. Such reactions take place, if at all, only by antarafacial addition.

This analysis shows that there is no need to regard chelotropic reactions as an independent group of pericyclic processes. They are isoconjugate with typical $[n + 2]$ π cycloadditions, a relationship conveniently indicated by classing them as $[n + 1]$ cycloadditions. Similar remarks naturally also apply to other reactions that are commonly described as chelotropic or reverse chelotropic processes, e.g., the loss of carbon monoxide or nitrogen from molecules such as **48** or **49** to form **33** or **50**.

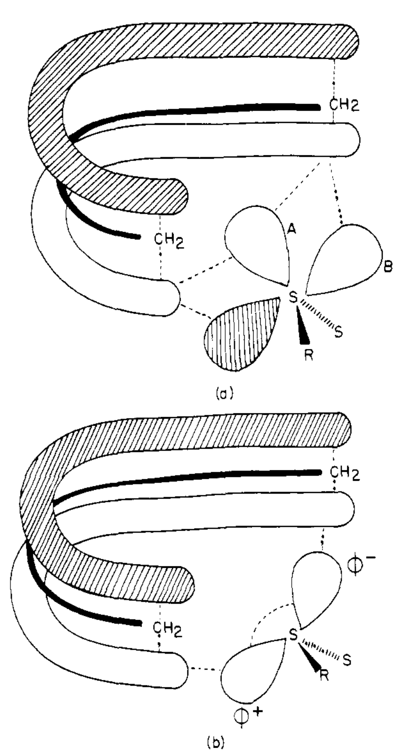

**Figure 6.** Description of a chelotropic transition state (a) in conventional terms and (b) in terms of σ conjugation.

## Summary and Conclusions

The astonishing progress made by organic chemistry over the last century has been due mainly to the effectiveness of the molecular models that organic chemists have developed to assist their thought processes. The model currently used by organic chemists in their research is based on the concept of localized bonds, combined with simple procedures for estimating the effects of departures from "localization" in specific cases. While this model has proved very successful, there are a number of places where it seems to fail. Some of these have been explained, not always convincingly, in terms of more complex models which are usually too complicated to be used by chemists as a basis for chemical thinking. Here attention has been drawn to an aspect of the current molecular model which has been known in principle for many years but ignored because its chemical significance was not appreciated, i.e., the fact that resonance integrals between different hybrid AOs of a given atom do not vanish even if the AOs are orthogonal. Recognition of this fact leads to the realization that there is no basic difference between saturated molecules and ones containing conjugated multiple bonds. Both types exhibit "bond localization" to comparable extents, using the term in its conventional sense, and the interactions between the "localized" σ bonds in saturated molecules are in fact at least as big as those between the "localized" π bonds in conjugated systems. PMO theory shows, however, that the interactions between adjacent "localized" bonds are approximately constant and can therefore be absorbed into the empirical values of bond properties, e.g., bond energies and bond lengths. This unification of normal conjugation (*π conjugation*) and σ conjugation leads to simple and convincing explanations of a number of apparent anomalies in organic chemistry which have remained unexplained in terms of the current qualitative molecular model used by organic chemists and which indeed have usually been ignored for lack of an explanation. Examples treated here include the unexpected stabilities of compounds containing three-membered rings, the pyramidal structures of radicals and biradicals, the staggered arrangement of bonds in saturated molecules and the *gauche* and anomeric effects, the unexpected geometry of triplet carbene, and the relationship between chelotropic reactions and other cycloadditions. The concept of σ conjugation therefore seems a useful addition to

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[63] Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.

current chemical theory and greatly limits the region where more complex, and correspondingly less visualizable, models need to be used.

This work also has possible implications for molecular mechanics, which is in effect a mathematical formulation of the localized bond model. The arguments presented here suggest that some at least of the problems currently being encountered in parametrizing such treatments may well be due to the current neglect of $\sigma$ conjugation. Attempts to include small ring compounds in such schemes, without reference to the apparently large $\sigma$-aromatic stabilization of three-membered rings, must, for example, greatly distort the treatment of angle strain. Problems may also arise from the description of rotation about single bonds in terms of 3-fold barriers. The analysis given here suggests that such barriers might be simulated more effectively by a superposition of 1-fold barriers, using a sharper function than a simple cosine function; for example, $\cos\theta|\cos\theta|$. Adoption of such a scheme might well overcome some of the difficulties presented by heteroatoms in such treatments.

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# Structure of Meerwein's Ester and Its Benzene Inclusion Compound

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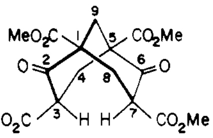
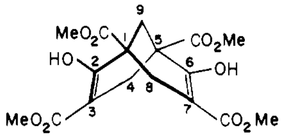
*Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and the Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110. Received May 19, 1983*

**Abstract:** The structure of Meerwein's ester (**1**) has been established by spectroscopic means (NMR, IR) and by single-crystal X-ray diffraction. In solution and in the solid state, **1** exists as a dienol (**1b**), which is stabilized by conjugate chelation. Crystals of the benzene solvate of **1** are orthorhombic, space group *Pnaa*, $a = 11.867$ (2), $b = 12.667$ (1), and $c = 25.601$ (3) Å, with four stoichiometric benzene molecules per molecule of **1**. The ester molecules are located on crystallographic 2-fold rotation axes and are sheathed in a channel of benzene molecules (Figure 3). In this unusual inclusion compound, it is not clear whether **1** is the host or the guest molecule.

In 1913 Meerwein and Schürmann[2a] described a one-step synthesis (from methyl malonate and formaldehyde) of an ester, since known as "Meerwein's ester" (**1**), that they identified as 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione (**1a**) and



1a



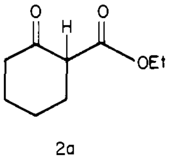
1b

that has proven its versatility as a key intermediate in the synthesis of a wide variety of bicyclo[3.3.1]nonane[3] and adamantane[4,5] derivatives.

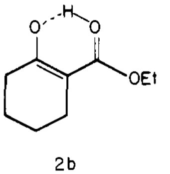
The structure (**1a**) assigned to Meerwein's ester has stood unchallenged to this day. We now present conclusive evidence that the ester is in fact completely enolized, both in the solid state and in solution, and that its structure must therefore be revised to that of 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene-2,6-diol (**1b**). In addition, we describe the structure of the benzene solvate of **1**, whose packing arrangement is unusual for an organic inclusion compound.

## Results and Discussion

**Nuclear Magnetic Resonance Spectra.** The $^1$H NMR spectrum of **1** in CDCl$_3$ features a sharp singlet at $\delta$ 12.14 due to the enolic protons in **1b**. This chemical shift is in excellent agreement with the value of 12.12 ppm observed for the hydroxyl proton in the enol form of a related cyclic $\beta$-keto ester, 2-carbethoxycyclohexanone (**2b**).[6] The presence of the diketo form of Meerwein's ester (**1a**) would have been revealed by a multiplet centered near 3.2 ppm due to the protons at C-3 and C-7, as observed for the $\alpha$-hydrogen in the keto form of 2-carbethoxycyclohexanone (**2a**).[6] However, no such signal was observed for **1**, even at low temperatures in CD$_2$Cl$_2$ or in methanol.



2a



2b

Furthermore, the signal at 12.14 was found to be insensitive to changes in concentration, suggestive of strong intramolecular hydrogen bonding. The $^1$H NMR evidence thus indicates that

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(1) (a) Princeton University. (b) Hoffmann-La Roche Inc.

(2) (a) Meerwein, H.; Schürmann, W. *Justus Liebigs Ann. Chem.* **1913**, *398*, 196. (b) See also: Meerwein, H. *J. Prakt. Chem.* **1922**, *104*, 161. Landa, S.; Kamýček, Z. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1320. Schaefer, J. P.; Honig, L. M. *J. Org. Chem.* **1968**, *33*, 2655.

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(4) For reviews, see: Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 286. Fort, R. C., Jr.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277. Fort, R. C., Jr. "Adamantane"; Marcel Dekker: New York, 1976.

(5) Meerwein's ester was the starting material for the first synthesis of an adamantane derivative [Böttger, O. *Ber. Dtsch. Chem. Ges.* **1937**, *70*, 314] and for the first synthesis of adamantane itself [Prelog, V.; Seiwerth, R. *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 1644].

(6) Rhoads, S. J. *J. Org. Chem.* **1966**, *31*, 171. See also: Forsên, S.; Merênyi, F.; Nilsson, M. *Acta Chem. Scand.* **1964**, *18*, 1208.

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