π-Electrons in Three Dimensions

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"Planar, monocyclic conjugated systems are aromatic if they contain $(4n + 2)$ π-electrons". The Hückel rule[1] is the most famous guiding principle in organic chemistry, yet in the past 25 years it has become apparent that there is a defect in its statement. It is not that the generality of the rule has been seriously questioned, but rather its restriction to *planar* conjugated systems.

As always, the area was pioneered by chemists with the imagination and courage to attempt the synthesis of new classes of molecules. Although many pieces of work could be cited in this connection, I found the bridged annulenes of Boekelheide[2] and Vogel[3] and the homoaromatic species[4] of Winstein[5] to be the most compelling. Finally in 1985 Smalley and co-workers[6] produced evidence for the generation of a spheroidal (condensed) aromatic molecule: icosahedral C_{60}.

BOEKELHEIDE (1963)

VOGEL (1964)

PETTIT (1962)
WINSTEIN (1959-69)

[SMALLEY (1985)]
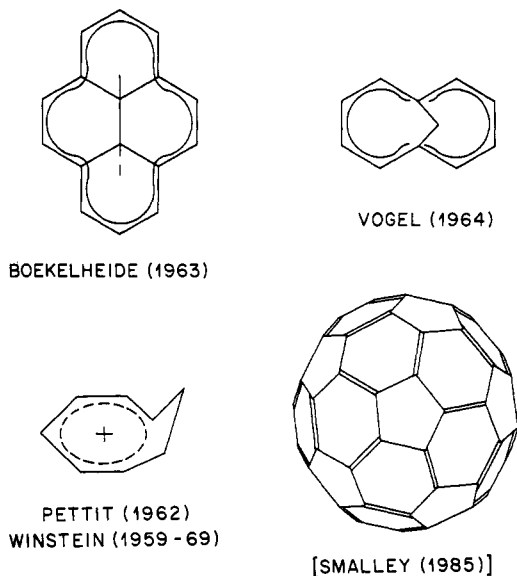
The preceding discussion focused on static structures, but in fact the transition states of many chemical reactions are commonly classified in terms of their aromatic character[7,8] in consonance with the Woodward–Hoffmann rules.[9] The structures of these transition states are necessarily nonplanar and frequently involve the interconversion of σ- and π-bonds along the pathway between reactants and products.

My attention was first drawn to this problem by L. T. Scott[10] in connection with the calculated structures[11] (Figure 1) of three bridged [10]annulenes.[3,12–14] He noted that the geometries[11] obtained by K. Raghava-

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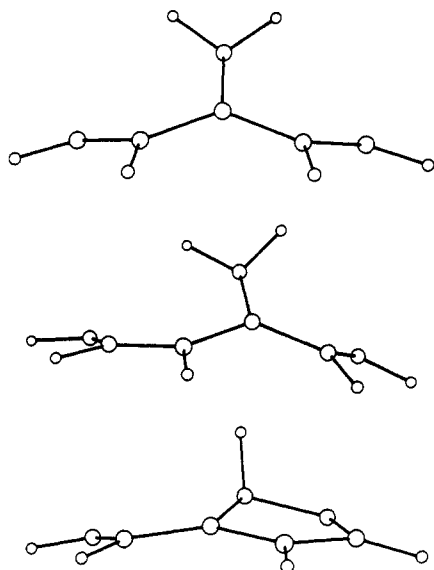
chari and myself implied a particularly severe distortion of the conjugated periphery of these aromatic systems. The traditional measure of the conformational inhibition of resonance in such molecules has been the π-orbital misalignment as expressed by the peripheral (termed formal) dihedral angles around the skeletal framework (τ, Figure 2). Two of the bridged annulenes in question exhibited formal dihedral angles in excess of 40°, and if it is assumed that these figures provide a real measure of the π-orbital misalignment, it is extremely difficult to rationalize this finding with the experimental and theoretical investigations with regard to the aromatic character of these compounds.

Pyramidalization

The point at issue in such nonplanar molecules revolves around the direction of the π-orbitals at the individual carbon atoms in the path of conjugation. As noted above, the misalignment angles between the π-orbitals has been traditionally taken from the formal dihedral angles or from some combination of all four possible dihedral angles that may be defined for a nonplanar conjugated system [C1–C2–C3–C4 (formal), C1–C2–C3–H3, H2–C2–C3–C4, and H2–C2–C3–H3 in Figure 2]. We, however, sought a direct measure of the direction of the π-orbital at each carbon atom in a nonplanar conjugated system and chose to express this as the π-*orbital axis vector* (POAV). In a planar molecule such as benzene, each of the π-orbitals (and POAVs) is perpendicular to the molecular plane. The POAV at each carbon atom makes equal angles of 90° to the three σ-bonds. In order to define a POAV at a nonplanar conjugated carbon atom we adopted the simplest possible approximation by assuming that the π-orbital also makes equal angles to the three σ-bonds in nonplanar geometries[15,16] (Figure 3), and this is now

(1) Hückel, E. *Z. Phys.* **1931**, *70*, 204.
(2) Boekelheide, V. *Proc. Robert A. Welch Found., Conf. Chem. Res.* **1969**, *12*, 83.
(3) Vogel, E. *Proc. Robert A. Welch Found., Conf. Chem. Res.* **1969**, *12*, 215.
(4) Rosenberg, J. L.; Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 2842.
(5) Winstein, S. *Chem. Soc. Spec. Publ.* **1967**, *21*, 5.
(6) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.
(7) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.
(8) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272.
(9) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*, Verlag Chemie–Academic Press: Weinheim/Bergst, Germany, 1970.
(10) Scott, L. T., private communication, 1984.
(11) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289.
(12) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277.
(13) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216.
(14) McCague, R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 165, 175.

Figure 1. Projection on the plane bisecting the bridge group of the calculated structure[11] of each of the bridged [10]annulenes: 1,6-methano[10]annulene (**1**, top), 1,5-methano[10]annulene (**2**), and 1,4,7-methino[10]annulene (**3**).
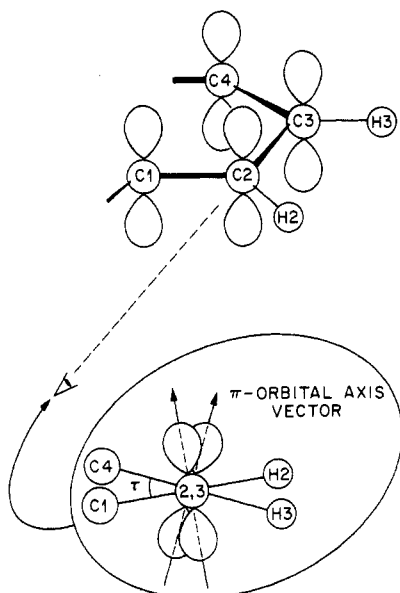

Figure 2. Definition of dihedral angles. The formal (skeletal) dihedral angle (τ, C1–C2–C3–C4) is equal to the misalignment angle between the π-orbital axis vectors (POAV) (and all of the other three dihedral angles) in the event that C2 and C3 are each in planar geometries. For C2 this would require that C1, C2, C3, and H2 be coplanar (*absence* of pyramidalization; see Figure 3).

known as the POAV1 analysis.[15] In planar systems this unique angle ($\theta_{\sigma\pi}$) is of course equal to 90° and for convenience we defined the pyramidalization angle, ($\theta_{\sigma\pi}$ − 90)°, which differs from 0° only in nonplanar conjugated systems. The pyramidalization angle provides a convenient index of the degree of nonplanarity at a conjugated carbon atom.

Let us now apply this simple geometrical analysis to the structures of the three bridged [10]annulenes and calculate the two quantities that have been defined: the pyramidalization angle ($\theta_{\sigma\pi}$ − 90)° and the POAV1.[15] They are displayed in Figures 4 and 5, the latter pa-
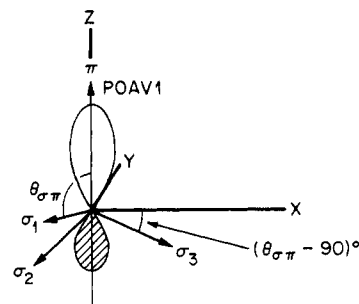
(15) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137.
(16) See also: Radziszewski, J. G.; Downing, J. W.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594.

Figure 3. Definition of $\theta_{\sigma\pi}$ [angle made by the π-orbital to each of the σ-bonds], ($\theta_{\sigma\pi}$ − 90)° [pyramidalization angle], and POAV1. In planar geometries, note that $\theta_{\sigma\pi}$ = 90° and ($\theta_{\sigma\pi}$ − 90)° = 0°. The POAV1 is taken to be perpendicular to the local (X,Y) plane in this construction.
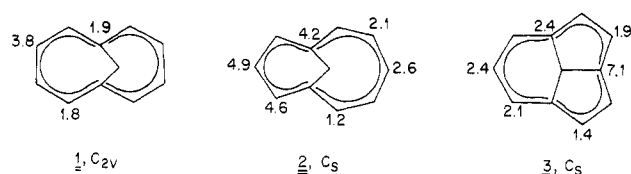

Figure 4. Pyramidalization angles [($\theta_{\sigma\pi}$ − 90)°; see Figure 3] calculated from the geometries found for 1–3.
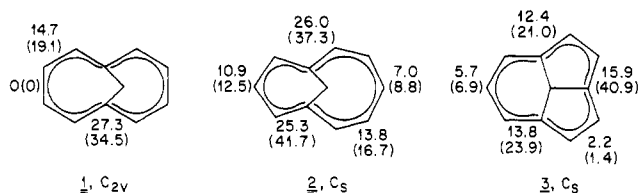

Figure 5. Peripheral dihedral angles (deg) calculated from the geometries found for 1–3. The lower (parenthesized) value corresponds to the formal dihedral angle (τ, Figure 2), while the upper value is the dihedral angle made by adjacent POAV1 (Figure 3) around the periphery.

rameter in the form of dihedral angles between POAV at adjacent pairs of conjugated carbon atoms (Figure 2). Two factors are immediately apparent: pyramidalization is an important feature of the structures of these molecules, even at unconstrained carbon atoms, and the π-orbital misalignment inferred from the POAV analysis is significantly reduced from that obtained by a consideration of the (parenthesized) formal dihedral angles included in Figure 5. The conclusion is inescapable: the molecules choose to distort so as to maximize favorable π-orbital overlap and aromatic character. In retrospect this is not a particularly surprising result; rather it is the degree to which these effects are operative that is unexpected—particularly when it is recalled that the π-orbital overlap scales as the cosine of the POAV misalignment angle. These are not small effects, and it is likely that the bridged annulenes 1–3 owe their stability, if not their existence, to the improvement of overlap brought about by pyramidalization.

Rehybridization

Up until this point the development has been purely geometrical. It is now appropriate to turn to a consideration of the change in electronic structure that is brought about by pyramidalization of a carbon atom. In a planar conjugated system such as benzene the carbon atoms are considered to be sp² hybridized so that each carbon atom possesses three σ-bonds com-
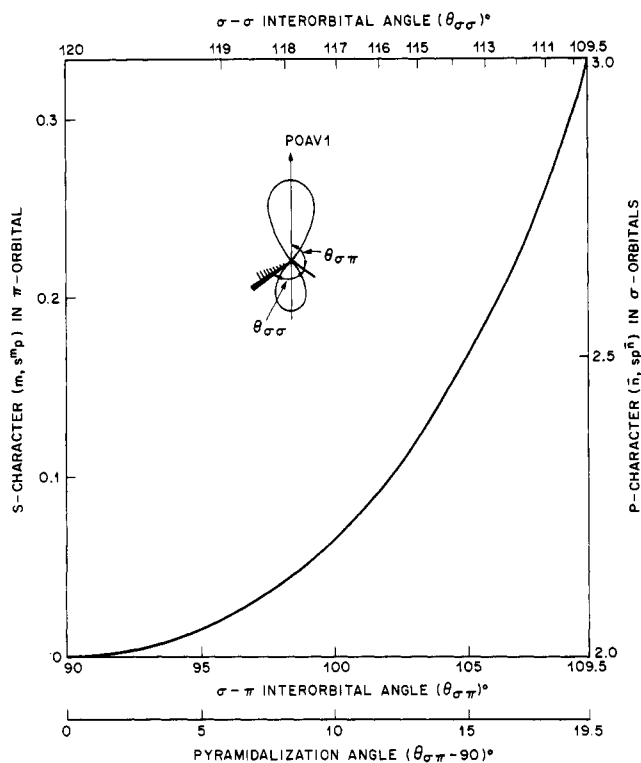
Figure 6. Relationship between the σ–σ and σ–π interorbital angles and the hybridization at a carbon atom between the extremes of sp² (planar geometry) and sp³ hybridization (tetrahedral geometry) in C_{3v} symmetry.

Figure 7. POAV1 hybridizations calculated from the geometries found for 1–3. The upper values correspond to the π-orbital hybridization [m in Figure 6 ($m = 0.0$ for planarity)], whereas the lower entries refer to the group-average σ-orbital hybridization [$\bar{n}$ in Figure 6 ($\bar{n} = 2.0$ for planarity)].

Figure 8. Orbital orthogonality, a basis for the definition of a π-orbital and for the separation of σ- and π-orbitals which is applicable in all (1–3) dimensions.

posed of sp² hybrids and a pure p-orbital for π-bond formation. The primary response of a conjugated carbon atom to a deviation from planarity is a change in the balance between the σ(sp²)- and π(p)-hybridization which is the rule in planar situations. In fact it is possible to relate the modified σ- and π-hybridizations directly to the pyramidalization angle $(\theta_{\sigma\pi} - 90)°$.[15,17] This dependence is shown graphically in Figure 6 for the case of local C_{3v} symmetry (equal σ-bond angles). It may be seen that the σ–σ and σ–π bond angles are directly related to the σ- and π-hybridizations. Note that it is most convenient to express the π-hybridization as the fractional s character $(m, s^m p)$. This is necessary because in the alternative notation (utilized for the σ-hybridization: n, sp^n) the fractional p character of the π-orbital would tend to infinity as planarity is approached. Figure 6 encompasses the full range of hybridizations between the limiting cases of pure sp² and sp³.

In situations that deviate from C_{3v} symmetry it is still possible to define a pyramidalization angle and to carry through the (POAV1) analysis as outlined above.[15–17] In this case a group-average σ-hybridization ($\bar{n}$, sp$^{\bar{n}}$) is obtained (see later). The results of the POAV1 analysis of hybridization for the bridged [10]annulenes are shown in Figure 7. Although we remarked earlier on the magnitude of the pyramidalization and concomitant improvement in π-orbital alignment in 1–3 (Figures 4 and 5), Figure 7 indicates that this is achieved with a modest degree of rehybridization. This point is made clear in Figure 6, where it may be seen that the degree of pyramidalization is very sensitive to the amount of rehybridization in the early part of the curve (close to
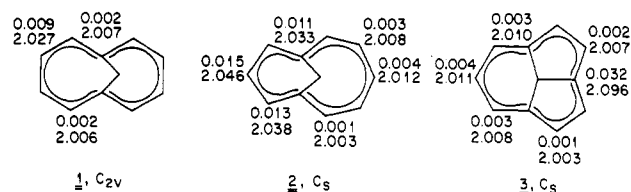
planarity). For example, a pyramidalization angle of 9.7°, which is halfway between planar and tetrahedral carbon, is achieved with π-orbital s character of $m = 0.0626$, which is <19% of the s character required for complete pyramidalization to tetrahedral carbon. Even for icosahedral C_{60} with a pyramidalization angle of 11.6°, the POAV1 s character of $m = 0.0928$ corresponds to just 28% of the tetrahedral value.[18]

It is therefore apparent that π-orbital overlap in nonplanar conjugated organic molecules may be vastly improved at the relatively small energetic expense that accompanies modest rehybridization.

σ–π Separability

The preceding analysis provides a chemically appealing and heuristically useful model for the structure and bonding in nonplanar conjugated organic molecules. Nevertheless, a question that might be raised in the present context relates to the *existence* of π-orbitals (electrons) in nonplanar conjugated systems. In order to answer this question, it is appropriate to begin with a discussion of the origins of the terms σ- and π-orbitals (electrons) and the basis for their separation in the description of the electronic structure of molecules.

The assignment of quantum numbers to electrons in (diatomic) molecules was first addressed by Hund[19] and Mulliken,[20] beginning in 1928. It was shown that in the case of molecules whose nuclei lie along a straight line (one-dimensional), the orbital angular momentum operator (about the linear axis) commutes with the nonrelativistic molecular Hamiltonian operator. This is a powerful result because it allows the simultaneous specification of the orbital angular momentum (eigen-

(17) Haddon, R. C. *Chem. Phys. Lett.* 1986, *125*, 231; *J. Am. Chem. Soc.* 1986, *108*, 2837.

(18) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* 1986, *125*, 459; 1986, *131*, 165.
(19) Hund, F. *Z. Phys.* 1928, *51*, 279.
(20) Mulliken, R. S. *Phys. Rev.* 1928, *32*, 186.

values Σ, Π, Δ, ...) and energy of the states of this class of molecules. It immediately motivates the separation of electrons into groups according to their orbital angular momenta, which in the present context merely involves a division between σ- and π-electrons (Figure 8). It should be noted, however, that even in the one-dimensional case, the Σ,Π classification applies to the energies of the states of a molecule; it does not imply the existence of σ and π orbitals and electrons and therefore offers no support for the proposition that the energies of the π-electrons are independent of the energies of the σ-electrons, and the same remarks apply to π-electron calculations of other molecular properties. Thus, even under the most rigorous conditions (one-dimensional), the case for σ–π separability remains empirical (and will become more so, as the scope of the classification is broadened).

Planar (two-dimensional) geometries were first considered by Hückel[21] in 1930, one year before the publication of his paper on the $(4n + 2)$ π-electron rule.[1] Hückel considered the effect that converting acetylene to ethylene and carbon monoxide to formaldehyde would have on the degenerate pair of π-orbitals in these linear molecules. He concluded that one of the π-orbitals would become a part of the σ set of orbitals while the other would remain substantially unchanged, and σ–π separability was thereby extended into two dimensions.

The concept of σ–π separability is usually introduced in terms of the planar, two-dimensional case, and orbitals are classified in terms of symmetry on reflection through the plane of symmetry containing the conjugated atoms (Figure 8). Although the symmetry operator commutes with the molecular Hamiltonian, the orbital classification offered in two dimensions is not as powerful as the one-dimensional case. The plane(s) of symmetry present in cyclohexane do not offer a particularly useful orbital classification in the present context.

It is therefore quite clear that the only rigorous result that obtains for the σ,π classification of one- and two-dimensional molecules relates to the electronic states (which may be observed by spectroscopy). It may be held that this motivates the treatment of σ- and π-electrons as separate entities, but a different viewpoint is adopted in the present article. *The success of σ–π separability may be attributed to the orthogonality of the σ- and π-orbitals.* The overlap integrals between σ- and π-orbitals are identically zero. There is a long tradition of using the overlap integral to measure the bonding and interaction between orbitals,[22] and it therefore comes as no surprise that orbitals without overlap may be treated independently. It is important to note that while the symmetry allows a classification into σ- and π-orbitals, the presence of symmetry is not the central issue; orbital orthogonality is the key to σ–π separability. If symmetry were the determining factor in allowing σ–π separability in benzene, the same classification should be effective in simplifying the treatment of planar (D_{6h}) cyclohexane, which has the
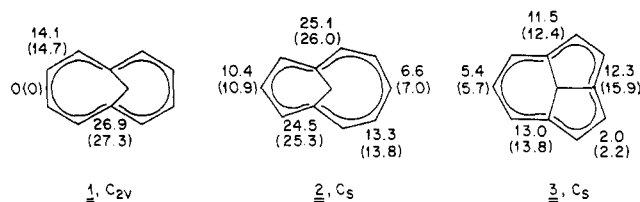

Figure 9. Peripheral POAV1 (parenthesized) and POAV2 (upper entry) dihedral angles (deg) calculated from the geometries found for 1-3.

same symmetry as benzene. In this geometry of cyclohexane the molecular symmetry plane divides the orbitals into a symmetric set ("σ") and an antisymmetric set ("π") just as in benzene. The symmetric group is composed of the six C–C orbitals plus six C–H orbitals whereas the antisymmetric group contains the remaining six C–H orbitals.[23] This separation has not been found useful in simple treatments of saturated hydrocarbons, and at the simplest level such calculations retain only the C–C orbitals, neglecting both the symmetric and antisymmetric C–H orbitals.[24]

Conservation of Orbital Orthogonality

If orbital orthogonality provides the fundamental basis of σ–π separability in one and two dimensions, then it also provides a mechanism for the extension of this principle into three dimensions (Figure 8). *The π-orbital at a nonplanar carbon atom is taken to be orthogonal to the three σ-orbitals.* In most situations the σ-orbitals may be taken to lie along the internuclear axes and with this construction it is possible to solve for the hybridization and directionality of the π-orbital.[17,25] This approach (termed the POAV2 analysis) is identical with the POAV1 analysis discussed earlier when the σ–σ bond angles are equal (C_{3v} symmetry) because in this case the orthogonality conditions are fulfilled when the π-orbital makes equal angles ($\theta_{\sigma\pi}$) to the three σ-orbitals (Figure 6).

As the POAV1 and POAV2 analyses differ only when there is inequality among the three σ-bond angles at a conjugated carbon atom, the two methods produce very similar estimates of the π-orbital misalignment angles in most nonplanar conjugated organic molecules.[17,25] The POAV1 (parenthesized) and POAV2 values of the π-orbital misalignment angles in 1-3 are compared in Figure 9, and as expected they are quite similar. However, each of the 12 independent π-orbital misalignment angles calculated for 1-3 is found to be lower in the case of the POAV2 analysis. This result suggests that the *conservation of orbital orthogonality is an important principle in nonplanar conjugated organic molecules.* It may be that orthogonal geometries minimize the electron–electron repulsions between orbital hybrids, along the line of argument utilized in the valence-shell electron pair repulsion (VSEPR) theory. However, it may be seen from Figure 9 that the con-

(21) Hückel, E. *Z. Phys.* **1930,** *60,* 423.

(22) (a) Pauling, L. *J. Am. Chem. Soc.* **1931,** *53,* 1367. (b) Slater, J. C. *Phys. Rev.* **1931,** *37,* 481. (c) Mulliken, R. S. *Phys. Rev.* **1932,** *41,* 67; *J. Chem. Phys.* **1951,** *19,* 900; *J. Phys. Chem.* **1952,** *56,* 295. (d) Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1952,** *20,* 837. (e) Hoffmann, R. *J. Chem. Phys.* **1963,** *39,* 1397.

(23) Jorgensen, W. L.; Salem, L. *The Organic Chemists' Book of Orbitals;* Academic Press: New York, 1973. Note the σ,π classification of the occupied orbitals of cyclopropane and cyclobutane and particularly cyclopentane and cyclohexane, which are nonplanar.

(24) (a) Hall, G. G. *Proc. R. Soc. London A* **1951,** *205,* 541. (b) Sandorfy, C. *Can. J. Chem.* **1955,** *33,* 1337. (c) Yoshizumi, H. *Trans. Faraday Soc.* **1957,** *53,* 125. (d) Klopman, G. *Tetrahedron (Suppl. 2)* **1963,** *19,* 111. (e) Herndon, W. C. *J. Chem. Educ.* **1979,** *56,* 448. (f) Honneger, E.; Yang, Z.; Heilbronner, E. *Croat. Chim. Acta* **1984,** *57,* 967. (g) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984,** *106,* 669.

(25) Haddon, R. C. *J. Phys. Chem.* **1987,** *91,* 3719; *THEOCHEM,* in press.

dition of orbital orthogonality (POAV2) is apparently more powerful than VSEPR requirements (equivalent to PAOV1)[25] in determining the orientation of the π-orbitals in nonplanar conjugated organic molecules.

The POAV1 and POAV2 analyses provide a unified definition for a π-orbital that is applicable in all dimensions: *a π-orbital is defined to be that hybrid orbital which is locally orthogonal to the σ-orbitals (POAV2)*, whereas from the standpoint of the POAV1 analysis the π-orbital is that hybrid orbital which makes equal angles with the σ-orbitals (as noted above, the POAV2 condition is apparently more powerful). It may be argued that these definitions represent a corruption of the terms σ and π. However, as the preceding discussion makes clear, the corruption of these terms began even before the scope of σ- and π-orbitals was extended from one to two dimensions; the arguments presented here merely continue this process to its logical conclusion.

Violations

There are some! It is implicitly assumed in the POAV analysis that the σ-bonds lie along the internuclear axes and that the dislocations in bonding are absorbed by the π-system alone. In fact the σ-bonds exhibit some deviation from the internuclear axes and as a result the π-orbital misalignment is further reduced. Thus the POAV analysis provides an upper bound for the π-orbital misalignment in nonplanar conjugated organic molecules.[17]

The effects of σ-bond bending on the POAV analysis have been assessed by model GVB calculations on twisted ethylene and found to be relatively minor.[17,26] This factor relates to the one-center orbital hybrids, and the more important violation of σ-π separability comes from the two-center orbital overlap terms. In a two-dimensional conjugated system, the π-orbitals are perpendicular to a common plane, and as a result there is *global* orthogonality between the σ- and π-orbitals throughout the molecule (Figure 8). That is, the overlap integral between *any* pair of σ- and π-orbitals is identically zero. This is not the case for nonplanar conjugated organic molecules where the π-orbitals are constructed to be orthogonal to the *local* one-center σ-orbitals, that is, at each individual carbon atom in the molecule. As a result there is no guarantee that the π-orbital at one carbon atom will be orthogonal to the σ-orbitals of the other carbon atoms in the molecule.

Deviations from global σ-π orthogonality are known to have important ramifications in certain situations. Nevertheless, the imposition of one-center orbital orthogonality (POAV2) provides the most logical and natural basis for the assessment of these effects.

Three-Dimensional (3D) HMO Theory

With π-orbitals defined in a consistent manner for all (1–3) dimensions, it seemed appropriate to extend the HMO theory into three dimensions.[26,27] This was accomplished by scaling the resonance integrals (β) in standard HMO theory by use of the overlap integrals

(26) (a) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676. (b) The PC version of program POAV3 (Fortran) is now available [QCMP044: Haddon, R. C. *QCPE Bull.* **1988**, 8]. The full POAV/3D-HMO analysis of the bridged [10]annulenes (1–3)[26a] required <15 s on an AT&T PC 6300.

(27) The 3D-HMO model should be distinguished from the extended-Hückel theory (EHT),[22e] in which all valence electrons (σ and π) are explicitly included in the calculation.
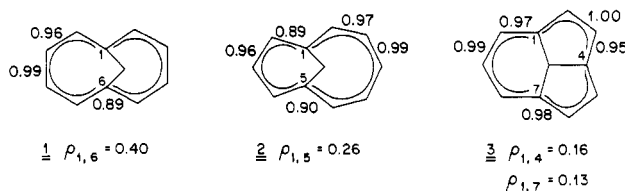
Figure 10. 3D-HMO reduced resonance integrals [ρ,β] calculated from the geometries found for 1–3. The peripheral (σ-bonded) quantities are ρ^R values, whereas the transannular analysis is in terms of ρ^B.

BOND	S, S	S, P_σ	P_σ, P_σ	P_π, P_π	TOTAL	ρ
1 – 2	0.001	−0.001	0.000	0.215	0.215	0.89
2 – 3	0.002	−0.003	0.001	0.243	0.243	0.96
3 – 4	0.003	−0.005	0.002	0.232	0.231	0.99
1 – 6	0.000	−0.010	0.082	0.027	0.099	0.40

Figure 11. Decomposition of the 3D-HMO ρ-values calculated from the geometry found for 1 in terms of the individual components of the overlap integral between POAV2 π-orbital hybrids.

calculated from the POAV π-orbital basis set. As the π-orbitals are no longer (necessarily) of pure p character, there are, in general, (s,s), (s,p_σ), (p_σ,p_σ), and (p_π,p_π) components to the overlap integrals between pairs of π-orbitals. Thus the π-orbital overlap integral between atoms i and j is given by $S_{ij} = (s^i,s^j) + (s^i,p_\sigma{}^j) + (s^j,p_\sigma{}^i) + (p_\sigma{}^i,p_\sigma{}^j) + (p_\pi{}^i,p_\pi{}^j)$, and this leads to the 3D-HMO (reduced) resonance integral $\beta_{ij} = (S_{ij}/S)\beta = \rho_{ij}\beta$, where S is the reference overlap integral and β the standard resonance integral of HMO theory. There are two possibilities for the choice of a reference overlap integral (S); in the first (S^B), the (p_π,p_π) overlap integral between nearest neighbors in benzene (R = 1.3964 Å) is utilized. The alternative choice (S^R) makes use of the (pure) (p_π,p_π) overlap integral evaluated for the bond length (R) in question. The first procedure (S^B) allows the treatment of π-orbital interactions between atoms without an intervening σ-bond, whereas utilization of S^R maintains contact with the body of HMO results for planar systems in which the resonance integrals were not adjusted for bond length.

The final quantity of interest is ρ_{ij} [=(S_{ij}/S^B) or (S_{ij}/S^R)], and in assessing nonbonded interactions a value of $\rho_{ij}{}^B > 0.2$ is recommended as a threshold (below which such effects are considered to be insignificant); note that the second-nearest-neighbor overlap integral in benzene leads to $\rho_{1,3}{}^B = 0.14$.

The 3D-HMO methodology is illustrated in Figure 10 by application to the three bridged [10]annulenes. The peripheral ρ values, which provide a measure of the resonance integrals, are within 2% of the cosines of the POAV π-orbital misalignment angles (Figure 9), and it is clear that these quantities are dominated by torsional distortions in the π-systems of the molecules. From the tabulation given for 1 in Figure 11 it may be seen that for directly (σ-bond) connected pairs of atoms (first three entries) the (p_π,p_π) component provides an excellent approximation to the total overlap integral for the π-bond. The cancellation of the σ-components

between nearest neighbors in the conjugated system appears to be a general feature of the bonding in these compounds. This result may be contrasted with the weight of the contributions to the transannular overlap integral (last entry in tabulation), where the σ-components dominate. On this basis a natural definition of homoconjugation within the POAV/3D-HMO theory emerges: the homoconjugate bond is characterized by an overlap integral between a pair of conjugated atoms in which the p_π,p_π contribution does not predominate.[26] This statement is in accord with the original characterization of the phenomenon as "...orbital overlap of a type intermediate between σ and π", as stated by Winstein.[5]

Finally it should be noted that it is the absence of global orthogonality in three dimensions (Figure 8) that gives rise to nonvanishing σ-contributions to the overlap integral between the locally orthogonal π-orbital hybrids (Figure 11). In two-dimensional situations, the overlap integral between the globally orthogonal π-orbitals is necessarily composed solely of the (p_π,p_π) component.

In terms of the threshold value $(\rho^B > 0.2)$ for a transannular interaction, both 1 and 2 qualify as homoconjugated species. This finding is in accord with recent studies that have led to the terms homonaphthalene[28] and homoazulene[13,29] for these molecules. On this basis only compound 3 qualifies as a true bridged [10]annulene.

Homoconjugation and Homoaromatic Character

The POAV analysis offers an analytical appoach to the characterization of the bonding in nonplanar conjugated organic molecules of known geometry, and even its extension to 3D-HMO theory introduces no adjustable parameters. As such the method provides an ideal basis for the classification of homoconjugated and homoaromatic molecules.

In assessing the workability of such an approach, it is appropriate to begin with the homotropenylium cation, the prima facie example of this phenomenon.[4,5,30] Theoretical calculations[31-33] and X-ray structures of two substituted derivatives of the compond[30,34,35] have provided evidence for two structures on the potential surface, with homoconjugate bond lengths of $R_{1,7} = 1.6$ and 2.3 Å, in qualitative correspondence with structures **4a** and **4c**. Recent calculations[36] with polarized basis sets and the inclusion of electron correlation effects, however, suggest a single minimum with $R_{1,7}$ in the vicinity of 1.7–2.0 Å, in support of formulation **4b**. The 3D-HMO ρ-values for the potential surface of 4, together with the calculated ring current $(J$, uncorrected for area) and the fractional π-component (π) of $\rho_{1,7}{}^B$, all referenced to the tropenylium cation, are shown in Figure 12. This analysis allows a reconciliation of all of the experimental data and leads to a complete theory
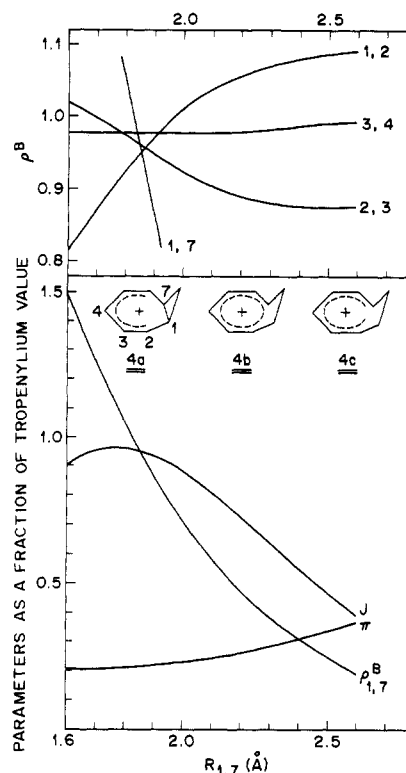

Figure 12. 3D-HMO analysis of the calculated geometries of the homotropenylium cation (4)[36] across the potential surface involving the 1–7 distance, where ρ^B is the measure of the resonance integral (β), J is the ring (bond) current (uncorrected for area), and π is the fractional contribution of the (p_π,p_π) overlap integral.

of the homotropenylium cation.[36] Perhaps most surprising is the distance dependence of $\rho_{1,7}{}^B$ and J. The 1–7 homoconjugate resonance integral $(\rho_{1,7}{}^B\beta)$ remains significant over the whole potential surface, and the homoconjugate linkage is the strongest π-bond in the molecule at $R_{1,7}$ distances <1.8 Å. This behavior arises from the superior orbital overlap properties of the σ-components involved in this bond. Note that the 3D-HMO ρ^B values indicate that the π-orbital resonance integrals of all bonds achieve a high degree of equalization in the range $R_{1,7} = 1.8$–2.0 Å. Furthermore the degree of inhibition of resonance in the molecule is small and uniformly distributed among all of the bonds in the molecule. This interpretation differs from the conventional Winstein picture of 4, in which the cyclic delocalization was only considered to be interrupted at the homoconjugate bond $(\rho_{1,7}{}^B = 0.73).$[5] Note that the σ/π composition of the homoconjugate resonance integral is fairly constant over the whole potential surface, but is dominated by the σ-component.

Unlike the homoconjugate resonance integral $(\rho_{1,7}{}^B)$ the ring current (J) does not exhibit a monotonic dependence on the value of $R_{1,7}$ and provides a good index of the degree of bond equalization and presumably (homo)aromatic character of the molecule.[36] Nevertheless the ring current is also significant over the whole potential surface and for the range $1.6 \leq R_{1,7} \leq 1.95$ Å the ring current is more than 90% of the tropenylium cation value.

The analysis suggests a $\rho_{1,7}{}^B \sim 1.0$ at the equilibrium geometry of the homotropenylium cation and thus the homoconjugate resonance integral is of much the same

(28) (a) Dewey, H. J.; Deger, H.; Frolich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412. (b) Roth, W. R.; Bohm, M.; Lennartz, H.-W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1007.
(29) Scott, L. T.; Oda, M.; Erden, I. *J. Am. Chem. Soc.* **1985**, *107*, 7213.
(30) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347.
(31) Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 5207.
(32) Haddon, R. C. *Tetrahedron Lett.* **1975**, 863.
(33) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.
(34) Childs, R. F.; Varadarajan, A.; Lock, C. J. L.; Faggiani, R.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 2452.
(35) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1986**, *108*, 3613.

(36) Haddon, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 1108.

strength as a normal π-bond, as in the rest of the molecule or the parent tropenylium cation itself.

The homotropenylium cation therefore sets the standard against which other homoconjugated species may be measured: $\rho_{homo}{}^B \sim 1.0$. Thus the homotropenylium cation emerges as an excellent approximation to the ideal homoaromatic species. Nevertheless the flatness of the potential surface[36] reemphasizes the statement that[33] "the very existence of homoaromaticity is a matter of a few kcal/mol".

Finally we consider the bicyclo[3.2.1]octa-3,6-dien-2-yl anion (5⁻) in which it has been argued that homoaromatic character is present[5,37] and absent.[38] The results of the POAV/3D-HMO analysis of the X-ray crystal structure[39] of (TMEDA)Li⁺·5⁻ are shown in Figure 13. It may be seen that in the solid state the homoconjugate resonance integral of 5⁻ is of about the same magnitude as those present in the bridged [10]-annulenes 1 and 2. In neutral molecules, such homo-
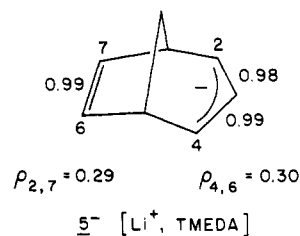

Figure 13. 3D-HMO ρ-values calculated from X-ray crystallographic structure[39] found for the bicyclo[3.2.1]octa-3,6-dien-2-yl anion with its (TMEDA)Li⁺ counterion.

conjugate interactions have been demonstrated to be important in the determination of one-electron properties, but of lesser significance with respect to many-electron properties such as the total energy.[28a,40–43]

Concluding Remarks

In this account of our research we have offered orbital orthogonality as a unifying principle for the existence of π-electrons (orbitals), which is applicable in one, two, and three dimensions. A π-orbital is defined to be that hybrid orbital which is locally orthogonal to the σ-orbitals. From this simple concept it has proved possible to provide an understanding of the structure and bonding in nonplanar conjugated organic molecules and to develop a complete theoretical description of the phenomenon of homoconjugation (homoaromaticity).

(37) (a) Brown, J. M. Occolowitz, J. L. Chem. Commun. 1965, 376; J. Chem. Soc. B 1968, 411. (b) Brown, J. M. Chem. Commun. 1967, 638. (c) Winstein, S.; Ogliaruso, M.; Sakai, M.; Nicholson, J. M. J. Am. Chem. Soc. 1967, 89, 3656. (d) Brown, J. M.; Elliott, R. J.; Richards, W. G. J. Chem. Soc., Perkin Trans. 2 1982, 485. (e) Washburn, W. N. J. Org. Chem. 1983, 48, 4287. (f) Christl, M.; Leininger, H.; Brückner, D. J. Am. Chem. Soc. 1983, 105, 4843. (g) Lee, R. E.; Squires, R. R. J. Am. Chem. Soc. 1986, 108, 5078.

(38) (a) Trimitsis, G. B.; Tuncay, A. J. Am. Chem. Soc. 1976, 98, 1997. (b) Trimitsis, G. B.; Zimmerman, P. J. Chem. Soc., Chem. Commun. 1984, 1506. (c) Grutzner, J. B.; Jorgensen, W. L. J. Am. Chem. Soc. 1981, 103, 1372. (d) Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. v. R. J. Am. Chem. Soc. 1981, 103, 1375. (e) Lindh, R.; Roos, B. O.; Jonsäll, G.; Ahlberg, P. J. Am. Chem. Soc. 1986, 108, 6554. (f) Schleyer, P. v. R.; Kaufmann, E.; Kos, A. J.; Mayr, H.; Chandrasekhar, J. J. Chem. Soc., Chem. Commun. 1986, 1583.

(39) Hertkorn, N.; Köhler, F. H.; Müller, G.; Reber, G. Angew. Chem., Int. Ed. Engl. 1986, 25, 468.

(40) Dewar, M. J. S. Molecular Orbital Theory of Organic Chemistry; McGraw-Hill: New York, 1969; Chapter 4.

(41) Heilbronner, E. In Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity; Bergmann, E. D., Pullman, B., Eds.; Academic Press: New York, 1971; p 58.

(42) Haddon, R. C. Aust. J. Chem. 1977, 30, 1.

(43) Scott, L. T. Pure Appl. Chem. 1986, 58, 105.