We conclude that the Creutz–Taube ion is electronically sort of a fancy version of the allyl radical, with the two termini coupled strongly via the bridge and with two allowed transitions ($B \rightarrow N$ and $N \rightarrow A$) arising from this coupling. The strong degree of delocalization might lead one to speculate about potentially exciting conductive properties of extended linear chains of this or related bridged species. However, more importantly, this piece of synthetic art of Creutz and Taube has in the last 17 years raised many important and fundamental questions about the way we interpret the results of a variety of common spectroscopic techniques and about the way we think of the very basic phenomena of spatial and temporal electron delocalization.

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Rehybridization and π-Orbital Overlap in Nonplanar Conjugated Organic Molecules: π-Orbital Axis Vector (POAV) Analysis and Three-Dimensional Hückel Molecular Orbital (3D-HMO) Theory

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Abstract: Nonplanarity in conjugated organic molecules such as the bridged annulenes, strained cycloalkenes, cyclophanes, π-complexes of organometallic and surface-bound alkenes and aromatics, and the transition states of most chemical transformations (particularly substitutions, additions, eliminations, and pericyclic reactions) plays a fundamental role in determining their chemistry. The primary response of conjugated systems to nonplanarity is a change in the balance between the $\sigma(sp^2)$ and $\pi(p)$ hybridization which is the rule in planar situations. In previous publications on this subject we have reported the development of the π-orbital axis vector (POAV) analysis which preserves σ–π separability in nonplanar geometries by appeal to the orbital orthogonality relationships. It is the primary hypothesis of the POAV analysis that the σ-bonds lie along the internuclear axes of the molecule. Thus, after structural adjustment, the remaining dislocations are construed to occur among the π-electrons. In the present paper a detailed analysis of these questions is presented in terms of electronic structure calculations on torsionally (C_2) twisted ethylene. The results are in excellent agreement with the assumptions and predictions of the POAV model and lend credence to the idea that torsionally twisted π-systems may be adequately mapped onto a minimal sp basis set (for analytical purposes) by the POAV theory. In the second part of the paper a number of nonplanar conjugated systems are analyzed with the three-dimensional (3D-) HMO theory. The 3D-HMO theory further quantities the POAV analysis by utilizing the local POAV hybrids to calculate overlap integrals between pairs of conjugated atoms. Suitably scaled, the overlap integrals provide reduced resonance integrals which allow a unified treatment of conjugated systems-planar and nonplanar. A natural definition of homoconjugation emerges from the analysis: 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.

Although planarity is considered to be the normal state of conjugated organic molecules containing formally sp^2 hybridized carbon atoms, reference to the literature shows that (with some notable exceptions) nonplanarity is the norm.[1] In many cases, the absence of a molecular symmetry plane containing the conjugated fragment of a molecule is of little consequence. The chemical ramifications of nonplanarity in conjugated organic molecules such as bridged annulenes,[2,3] strained cycloalkenes,[4-8] cyclophanes,[5] π-complexes[6] of organometallic[7] and surface-bound[8] alkenes and aromatics, and the transition states[9] of most chemical transformations (particularly substitutions, additions, eliminations and pericyclic reactions) are not so easily dismissed.

The primary response of conjugated systems to nonplanarity is a change in the balance between the $\sigma(sp^2)$ and $\pi(p)$ hybridization which is the rule in planar situations. In previous publications on this subject we have reported the development of the

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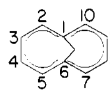
π-orbital axis vector (POAV) analysis[10-12] which preserves σ–π separability in nonplanar conjugated organic molecules by appeal to the orbital orthogonality relationships.[11,12] It is the primary hypothesis of the POAV analysis that the σ-bonds lie along the internuclear axes of the molecules. Thus, after structural adjustment, the remaining dislocations in bonding are construed to occur among the π-electrons. In a preliminary communication on this subject, electronic structure calculations for torsionally twisted ethylene were shown to produce results in excellent agreement with the assumptions and predictions of the POAV analysis.[11] The first part of this manuscript reports full details of this work together with results obtained with complete geometry optimization and extended and polarized basis sets.

The POAV analysis has shown the essential role of rehybridization in maintaining favorable π-overlap in the presence of conformational restraints in annulenes and alkenes, as expressed by the s-character, *m*, of the π-orbital (s^mp) and the improved π-orbital alignment as obtained from the dihedral angles (ϕ) between π-orbital axis vectors on adjacent conjugated carbon atoms. Such an approach provides a good picture of the maintenance of π-orbital overlap in twisted π-systems, but it seemed worthwhile to develop a general well-defined analysis of bonding in nonplanar conjugated systems which would also be applicable in cases involving the inclination of the π-orbitals along the internuclear axis (as found in tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**11**),[13] tricyclo[3.3.2.0^{3,7}]dec-3(7)-ene,[14] corannulene (**12**),[15] and icosahedral C_{60}[16]) and would therefore allow a uniform treatment of all distorted π-electron systems. This model, termed three-dimensional (3D)-HMO theory[17] is presented in the second part of the present paper and has already been prefaced in communications on the carbon spheroids[19] where the treatment finds natural application.



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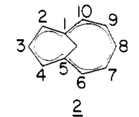

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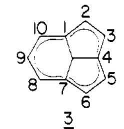

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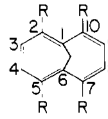

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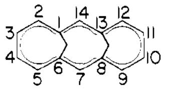

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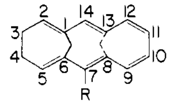
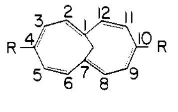
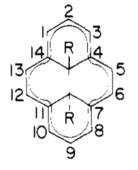


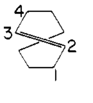
6, R = COOMe



7, R = Br



8, R = Et



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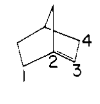

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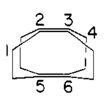

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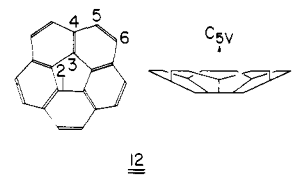

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[17] The 3D-HMO model should be distinguished from the Extended Huckel Theory (EHT)[18] in which all valence electrons (σ and π) are explicitly included in the calculation.

Theory

The POAV methodology for the calculation of the nonplanar hybrids and π-orbital axis vectors from the molecular geometry has been previously described,[10-12] and the FORTRAN computer program POAV2 which impliments this analysis is now available from QCPE.[20]

The 3D-HMO model further quantifies the analysis by utilizing the local POAV hybrids to calculate overlap integrals between pairs of conjugated atoms. Given the composition (s^mp) and orientation of the individual π-orbitals in a molecule it is straightforward to calculate the components of the sp Slater overlap integrals (carbon exponent of 1.625[21]) between pairs of atoms and apply the appropriate weighting coefficients (hybridizations; adopting the nomenclature of ref 12, the π-orbital atomic basis functions take the following form: $h_\pi = (m + 1)^{-1/2}[m^{1/2}s + p]$).

In the case of planar molecules this procedure simply reduces to the evaluation of a p_π, p_π overlap integral at a given internuclear separation. For benzene, with a bond length of 1.3964 Å,[22] the p_π, p_π overlap integral (S^B) is calculated to be 0.2458. This value can then be utilized to calculate a reduced resonance integral ($\rho\beta$) for a nonplanar π-bond with calculated overlap integral of S from the formula $\rho^B = S/S^B$; alternatively the relationship $\rho^R = S/S^R$ may be employed, where S^R is the pure p_π, p_π overlap integral for the bond length in question.[23] The latter approach allows direct comparison with the large body of HMO data already in the literature in which the resonance integral was not adjusted for bond length and has been utilized in the present study for all directly (σ-bonded) pairs of conjugated atoms.

While the overlap between directly bonded pairs of atoms should always be included in an HMO calculation, it is clearly necessary to arrive at a threshold value for the inclusion of transannular interactions. This is best achieved by a consideration of the ρ^B values (overlap integrals scaled by the benzene nearest neighbor (1,2) overlap integral). An absolute lower limit is provided by the 1,3 (next nearest neighbor) ρ^B value in benzene which is 0.140. At the same bond length as benzene, the cyclopentadienyl framework has a $\rho^B_{1,3}$ value of 0.195. Accordingly we have adopted a threshold value of 0.2 for ρ^B, for the inclusion of a transannular interaction in the HMO calculations. It should be noted that the $\rho^B_{1,3}$ value in cyclobutadiene is higher than this threshold.[27]

Finally is is appropriate to review the theoretical status of the POAV/3D-HMO model (as opposed to the *basic assumptions* of the theory which have been discussed previously[11,12] and are further treated herein).

The POAV model is nonparametric, and given the geometry of a conjugated molecule the analysis is uniquely determined.[12] Beyond this, the 3D-HMO theory requires an atomic Slater orbital exponent[21] for the evaluation of an overlap integral which must be scaled against a standard value. As this latter quantity itself

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Table I. Total Energies (hartree) for Torsionally (C_2) Twisted Ethylene

τ^a (deg)	HF/STO-3G// HF/STO-3G	GVB/STO-3G// HF/STO-3G	GVB/STO-3G// GVB/STO-3G	GVB/6-31G// GVB/6-31G	GVB/6-31G*// GVB/6-31G*	GVB/6-31G+5D// GVB/6-31G*
0	-77.07333	-77.17937	-77.18264	-78.10430	-78.13064	-78.13018
10	-77.07277	-77.17839	-77.18175	-73.10345	-78.12983	-78.12937
20	-77.06923	-77.17564	-77.17905	-78.10093	-78.12741	-78.12694
30	-77.06340	-77.17104	-77.17462	-78.09678	-78.12338	-78.12293
40	-77.05537	-77.16470	-77.16852	-78.09104	-78.11781	-78.11735
50	-77.04528	-77.15670	-77.16087	-78.08383	-78.11076	-78.11031
60	-77.03327	-77.14713	-77.15181	-78.07524	-78.10235	-78.10191
70	-70.01949	-77.13622	-77.14151	-78.06541	-78.09270	-78.09227
80	-77.00412	-77.12399	-77.13016	-78.05448	-78.08196	-78.08153
90	-76.98735	-77.11065	-77.11799	-78.04262	-78.07028	-78.06986

[a] Defined according to Figure 1.

Table II. Relative Energies (kcal/mol) for Torsionally (C_2) Twisted Ethylene

τ^a (deg)	HF/STO-3G// HF/STO-3G	GVB/STO-3G// HF/STO-3G	GVB/STO-3G// GVB/STO-3G	GVB/6-31G// GVB/6-31G	GVB/6-31G*// GVB/6-31G*
0	0.0	0.0	0.0	0.0	0.0
10	0.4	0.6	0.6	0.5	0.5
20	2.6	2.3	2.3	2.1	2.0
30	6.2	5.2	5.0	4.7	4.6
40	11.3	9.2	8.9	8.3	8.1
50	17.6	14.2	13.7	12.8	12.5
60	25.1	20.2	19.3	18.2	17.8
70	33.8	27.1	25.8	24.4	23.8
80	43.4	34.8	32.9	31.3	30.5
90	53.9	43.1	40.6	38.7	37.9

[a] Defined according to Figure 1.

is taken from a standard geometry, no adjustable parameters are introduced.

Calculational

Theoretical. Hartree-Fock (HF)[28] and generalized valence bond (GVB)[29] calculations were carried out with a version of the GAUSSIAN 82 program[30] modified for use on the CRAY X/MP computer. Standard STO-3G,[31] 6-31G,[32] 6-31G*,[33] and 6-31G+5D[33,34] basis sets were employed. The ethylene geometries were fully optimized within C_2 symmetry. In all GVB calculations the highest six electron pairs were split [GVB(6/12)], so that fission of the four C-H and the σ C-C bonds is treated on an equal basis with the dislocation of the π-bond.[11] Geometry optimizations and energy calculations with polarization functions were carried out with the 6-31G* basis set, but for the purposes of analysis of the wave function, a single calculation with 5 d-functions was employed (6-31G+5D).

Geometries. The calculated geometries of **1** (C_{2v}), **2** (C_s), **3** (C_s), **9** (C_2), and **10** (C_1) are already in the literature.[12,34] The experimental structures for **1**, **4**, **5**, **6**, **7**(C_2), and **8** were taken from X-ray crystallographic studies[35-40] and have been previously discussed.[12] The experimental geometries of **11**[13] and **12**[15] were obtained by an appropriate transformation of the published unit cell coordinates. The theoretical structure of icosahedral C_{60}[16,19,41] has been previously discussed.[19] The parameters obtained from the POAV and 3D-HMO analyses were symmetry averaged in the case of **1** ($C_1 \rightarrow C_{2v}$), **4** ($C_1 \rightarrow C_s$), **5** ($C_1 \rightarrow C_{2v}$), **6** ($C_1 \rightarrow C_s$), **8** ($C_2 \rightarrow C_{2h}$), **11** ($C_i \rightarrow D_{2h}$), **12** ($C_1 \rightarrow C_{5v}$).

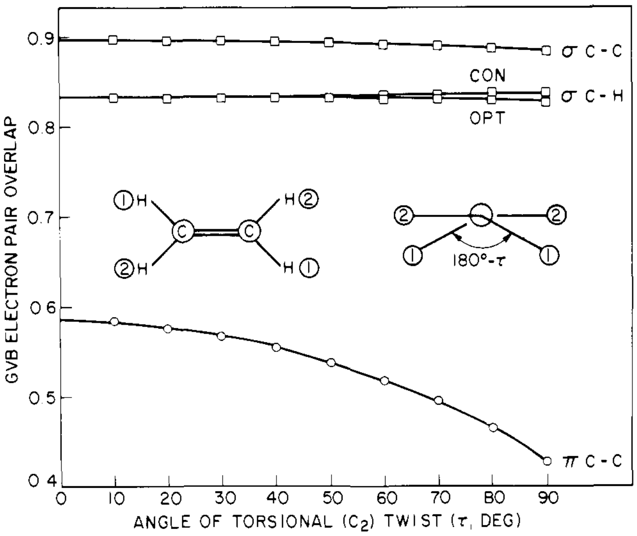

Figure 1. Overlap of the GVB/STO-3G electron pair functions of ethylene as a function of torsional (C_2) twist (τ). Con refers to bonds to hydrogen atoms (1), with dihedral angle constrained at (180-τ)°. Opt refers to bonds to hydrogen atoms (2), with optimized dihedral angle.

POAV and 3D-HMO Analyses. The equations required to effect the POAV and 3D-HMO analyses have been incorporated into a FORTRAN computer program entitled POAV3, which will be deposited with the Quantum Chemistry Program Exchange (QCPE).[42] The atomic coordinates of the molecule or molecular fragment of interest, are the only data which are required for the execution of the POAV3 program.

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Table III. Calculated Geometries at the HF/STO-3G, GVB/STO-3G, GVB/6-31G, and GVB/6-31G* Levels of Theory for Torsionally (C_2) Twisted Ethylene[a]

τ (deg)		C-H (Å)		C-C-H (deg)		τ (deg)
con	C-C (Å)	con	opt	con	opt	opt
0	1.306	1.082	1.082	122.2	122.2	0.0
	1.350	1.100	1.100	121.9	121.9	0.0
	1.351	1.091	1.091	121.8	121.8	0.0
	1.346	1.093	1.093	121.7	121.7	0.0
10	1.306	1.082	1.082	122.3	122.0	1.6
	1.348	1.100	1.101	121.9	121.8	2.4
	1.352	1.092	1.092	121.9	121.7	1.6
	1.347	1.093	1.093	121.8	121.6	2.0
20	1.307	1.082	1.083	122.5	121.6	3.2
	1.350	1.100	1.101	122.1	121.3	4.6
	1.353	1.092	1.092	122.1	121.3	3.0
	1.348	1.093	1.094	121.9	121.2	3.9
30	1.309	1.082	1.083	122.9	120.9	4.4
	1.353	1.100	1.101	122.4	120.6	6.4
	1.355	1.092	1.093	122.3	120.7	4.4
	1.350	1.093	1.095	122.2	120.6	5.3
40	1.311	1.082	1.084	123.5	120.0	5.4
	1.358	1.100	1.102	122.6	119.7	7.6
	1.359	1.092	1.094	122.7	119.9	5.4
	1.353	1.093	1.096	122.5	119.7	6.3
50	1.313	1.083	1.085	124.2	118.8	6.0
	1.364	1.100	1.104	122.9	118.6	8.4
	1.362	1.092	1.096	123.2	118.9	5.8
	1.357	1.093	1.098	122.9	118.7	6.8
60	1.315	1.083	1.087	125.1	117.5	6.4
	1.371	1.100	1.105	123.2	117.4	8.6
	1.367	1.092	1.098	123.6	117.8	5.8
	1.362	1.093	1.099	123.4	117.6	6.8
70	1.318	1.083	1.089	126.2	116.1	6.2
	1.380	1.100	1.106	123.6	116.1	8.2
	1.373	1.092	1.101	124.3	116.6	5.4
	1.368	1.093	1.101	124.0	116.3	6.4
80	1.321	1.083	1.091	127.5	114.6	5.8
	1.390	1.100	1.108	123.8	114.8	7.0
	1.379	1.092	1.103	124.8	115.4	4.4
	1.374	1.093	1.103	124.6	115.0	5.4
90	1.324	1.084	1.094	129.0	113.0	4.8
	1.404	1.100	1.110	123.7	113.7	4.8
	1.387	1.092	1.105	125.4	114.1	2.6
	1.381	1.094	1.106	125.2	113.7	3.8

[a] Geometrical parameters are defined according to Figure 1. The dihedral angle of the optimized C-H bonds (2) is taken in the same sense as that of the constrained C-H bonds (1).

The output from POAV3 consists of the information from POAV2[12,20] together with the data given in Table V. To run program POAV3 on the structures of all of the compounds reported herein required less than half a second of CRAY X/MP time. A PC version of the program is in preparation.

Results

GVB and POAV Analysis of Torsionally (C_2) Twisted Ethylene. Total energies are given in Table I and relative energies in Table II, for torsionally (C_2) twisted ethylene (as per the structure in Figure 1).[43] In assessing the importance of certain features of the wave function, it is convenient to begin with a consideration of the relative energies at $\tau = 90°$ (formal dihedral angle between constrained (trans) hydrogens of 90°) as a function of theoretical level in Table II. The energy improvement for this point ($\tau = 90°$) is 16 kcal/mol in passing between the HF minimal basis set (HF/STO-3G//HF/STO-3G) calculation and the GVB wave function with an extended and polarized basis set (GVB/6-31G*//GVB/6-31G*). Note that 11 kcal/mol of this difference is recovered by carrying out a GVB minimal basis set calculation at the HF minimal basis set geometry. A further half of the remaining discrepancy is removed by first optimizing the geometry with the GVB procedure. Thus even up to a torsional twist of 90°, basis set effects are responsible for only 2.7 kcal/mol in the relative energies. This observation provides strong support for a primary tenet of the POAV theory: for analytical purposes, torsionally twisted π-electron systems may be adequately mapped onto a minimal sp basis set. Further support for this point may be adduced from Table III, where it may be seen that the primary changes in the calculated structure once again occur between the HF/STO-3G and GVB/STO-3G calculations. It is of particular interest that the principal structural discrepancies at different theoretical levels occur between the calculated C-C bond length in twisted ethylene rather than among the various bond angles.

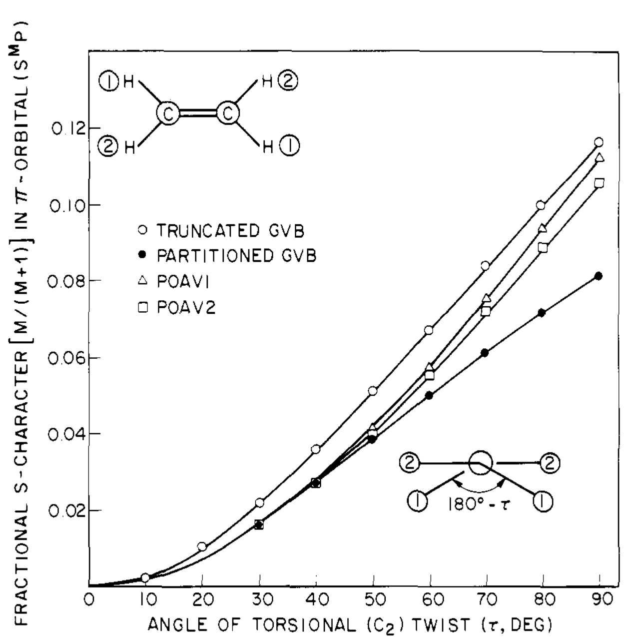

Figure 2. GVB/STO-3G and POAV fractional s-character [$m/(m+1)$, $s^m p$] in the π-orbital of ethylene as a function of the angle of torsional (C_2) twist (τ) at GVB/STO-3G equilibrium geometries.

As noted previously,[11] the generalized valence bond (GVB) method[29] provides the most appropriate energy calculation for the analysis of a torsionally twisted double bond. In particular the GVB wave function correctly describes bond-breaking processes (the limiting case for twisting of a double bond), and the resulting orbitals may be unambiguously identified as σ- and π-bonds. The overlap of the GVB electron pair functions provides a good index of the degree to which a particular bond in a molecule approaches the dissociation limit.[29] In a previous communication on this subject,[11] we analyzed the pair overlaps from GVB(6/12)/STO-6G wave functions obtained at HF/STO-3G optimized geometries as a function of the torsional angle (τ) in ethylene and noted the insensitivity of σ-bond overlaps to torsional twist in contradistinction to the behavior of the π-bond overlap, which was found to be considerably weakened at large values of τ. At that theoretical level the ratios of the orbital overlaps at $\tau = 90°$ to $\tau = 0°$ were found to be the following: σ C-C, 1.00; C-H constrained, 1.00; C-H optimized, 0.99; π C-C, 0.83.[11] In the present study with the GVB(6/12)/STO-3G wave function used both for the structures and analysis (Figure 1), the analogous results are as follows: σ C-C, 0.99; C-H constrained, 1.01; C-H optimized, 0.99; π C-C, 0.74. Thus although the dissociation of all bonds in the molecule can be correctly described by this wave function, only the π-bond is seriously weakened in such extreme geometries, hence reemphasizing a primary tenet of the POAV analysis: after structural adjustment, any remaining dislocations in bonding are primarily absorbed by the π-system.

Figure 2 shows the fractional s-character in the GVB/STO-3G wave function as a function of twist angle in ethylene, compared with the values obtained from applying the POAV analysis to the

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(43) See also ref 29.

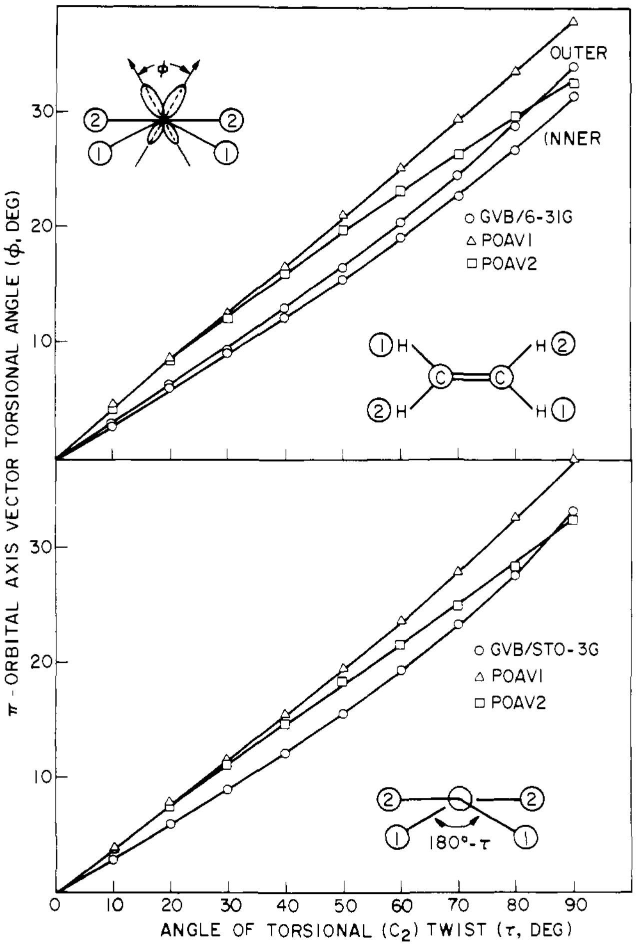

Figure 3. GVB and POAV calculated π-orbital axis vector torsional angles (φ) in ethylene as a function of torsional (C_2) twist (τ): GVB/STO-3G (lower) and GVB/6-31G (upper).

same GVB-optimized geometries. The GVB results were obtained by applying a Mulliken population analysis to the ethylene π-orbital. The truncated values shown in the figure include only the atomic terms and neglect the overlap contributions, whereas the partitioned results include the contributions from the standard Mulliken division of the overlap population. Given the local nature of the POAV analysis which is couched in terms of the atomic hybrids it would seem that the former quantity (truncated) provides the appropriate comparison. Nevertheless, for the regime of chemical interest, the POAV analysis is in good qualitative agreement with both measures of the GVB π-orbital s-character. Figure 2 firmly establishes rehybridization as the primary mechanism for the maintenance of favorable π-orbital overlap in nonplanar geometries.

The π-orbital axis vectors from the GVB wave functions and POAV analysis at the GVB equilibrium geometries are collected in Figure 3 in the form of π-orbital misalignment angles (φ). The π-orbital axis vectors are obtained directly from the GVB wave function in the form of the p coefficients; as the individual one-electron π-orbitals are not completely localized in the GVB calculation, the coefficients at each carbon are included in the analysis. The minimal basis set results (lower half of Figure 3) indicate that the POAV analysis provides an excellent qualitative picture of π-orbital misalignment in twisted π-systems. As suggested previously, for most systems of chemical interest the POAV analysis provides an upper bound for π-orbital misalignment (φ) in nonplanar conjugated organic molecules.[12] In the case of the POAV1 method the largest overestimation of φ is 4.8° in the vicinity of τ = 80°, whereas the POAV2 approach produces a value of φ which is too high by 2.7° at τ = 50°. The agreement among the POAV1, POAV2, and GVB analyses of π-orbital misalignment is even better at the GVB geometries than it was in the case of the previously reported HF structures.[11] As discussed above (see also ref 11), the GVB calculations may be expected to provide the most accurate picture of the structure of torsionally twisted ethylene.

The POAV analysis of higher level basis sets is less straightforward—in particular, split valence bases, where there is both an inner (I) and outer (O) set of sp functions (such as 6-31G), no longer give rise to a π-orbital axis vector. Instead the analogous quantity will in general follow a curved pathway from the nucleus.[44] Thus it becomes impossible to specify a unique angle for the π-orbital axis. Nevertheless, the trajectory of the π-orbital will always fall between the limits of the π-orbital axis vectors of the inner and outer components, as presented in the upper half of Figure 3. The participation of the inner and outer components of the GVB/6-31G wave function for ethylene is in the ratio of 0.55:0.45 and is invariant to the degree of twist (τ). The outer component produces a π-orbital misalignment angle (φ) in excellent agreement with the POAV analyses and is quite reminiscent of the GVB/STO-3G results shown below. The deviations for the inner component are a little larger, reaching a maximum value of 6.8° at τ = 80° (POAV1) and 4.1° at τ = 50° (POAV2).

The results in Figure 3, substantiate the idea that the π-orbital misalignment angles (φ) in twisted π-electron systems are considerably less than the formal dihedral angles would indicate. The various schemes which average the formal dihedral angles to obtain a measure of π-orbital misalignment fare much better but still represent a significant overestimate. For example, the (average) sum of the cis dihedral angles in ethylene at the GVB/STO-3G geometries are as follows: 0°(τ = 0°), 12.8°(τ = 30°), 26.8°(τ = 60°), and 42.6°(τ = 90°) (cf. the lower half of Figure 3).

All of the π-orbital axis vectors from the GVB/6-31G+5D, POAV1, and POAV2 analyses of the GVB/6-31G* equilibrium geometries lie within 1.2° of the corresponding GVB/6-31G values presented in Figure 3 and are therefore not displayed. This finding parallels the results given in Table II, where it may be seen that the progression from the 6-31G to the 6-31G* basis set changes the relative energies at τ = 90° by less than 1 kcal/mol.

Both of the POAV methods provide a good qualitative picture of the response of the electronic structure of a conjugated system to nonplanar distortions as judged by the preceding GVB analysis. The POAV1 approach[10] is easy to apply and conceptually straightforward and is adequate for many applications. However, the theoretical rigor of the POAV2 model[12] is manifest in its better quantitative agreement with the analysis of the GVB wave function (Figures 2 and 3). It is therefore apparent that the POAV2 analysis[11,12] must be the method of choice in numerical applications.

POAV/3D-HMO Analysis of Torsionally (C_2) Twisted Ethylene. The overlap integrals (S) between the POAV hybrids obtained at the GVB/STO-3G geometries for torsionally twisted ethylene are shown in Figure 4. Even at a formal dihedral angle (τ) of 90° it may be seen that the overlap integrals are 0.61 (POAV1 and POAV2) of their value at the planar geometry. The analogous quantities at the HF/STO-3G geometries are found to be 0.69 and 0.68, respectively, and it is apparent that the HF method seriously underestimates rehybridization effects at these extreme geometries (see above).

It is particularly interesting to note that the p_π, p_π component of the overlap integral (Figure 4) is an excellent approximation to the total value (s, s + s, p_σ + p_σ, s + p_σ, p_σ + p_π, p_π). This point will be returned to later, but the cancellation of the s, s + s, p_σ + p_σ, s + p_σ, p_σ contribution to the overlap integral appears to be a general feature.

3D-HMO Characterization of Homoconjugation. The results of the 3D-HMO analysis on compounds **1**–**12** are presented in Table V, and it may be seen that the results bear out the previous point to a remarkably high degree of accuracy: the p_π, p_π contribution provides a good approximation to the total overlap integral *for directly (σ-bond) connected pairs of conjugated atoms.*

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[44] Chipman, D. M.; Palke, W. E.; Kirtman, B. *J. Am. Chem. Soc.* **1980**, *102*, 3377.

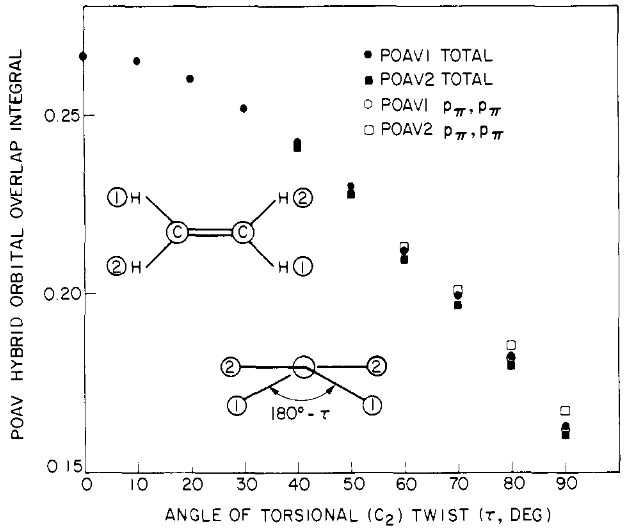

Figure 4. POAV hybrid orbital overlap integrals (p_π,p_π and total) in ethylene as a function of torsional (C_2) twist (τ) at GVB/STO-3G equilibrium geometries.

However, this is not the case for transannular interactions (see particularly compounds **1**, **5**, **6**, **7**, and **11**). A natural definition of homoconjugation within the POAV/3D-HMO theory therefore 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.*

POAV and 3D-HMO Analysis of Torsionally Twisted π-Electron Systems. In earlier papers we characterized the dislocations in π-bonding in nonplanar conjugated systems in terms of the π-orbital axis vector dihedral angles (ϕ) (Figure 3) between adjacent conjugated pairs of atoms. It is generally accepted that the degree of conjugation in twisted π-electron systems scales as the cosine function of the dihedral angle between adjacent pairs of p_π orbitals.[26] Given the cancellation of the other overlap components between directly bonded pairs of atoms found for the 3D-HMO model (discussed above), it is natural to investigate the relationship between the POAV values of ϕ and the 3D-HMO reduced resonance integrals (ρ). In fact, *for compounds **1-8** the cosine of the π-orbital axis vector torsional misalignment angle (ϕ) is within 2% of the ρ^R value* of all directly σ-bonded pairs of conjugated atoms. This approach fails, of course, for homoconjugate bonds (discussed above) and torsionally aligned systems (**11** and **12**).

Sense of the POAV. It is convenient to associate a sense (as well as a direction) with the π-orbital axis vector. *The positive sense of the POAV is defined to lie toward that lobe of the p-orbital which has the same sign as the s-orbital.* Within this definition, therefore, the relative senses of the POAV between a pair of atoms may be obtained directly by inspection of the sign of the s,s overlap integral. It may be seen (Table V) that the signs are overwhelmingly positive, and, therefore, it is apparent that *the POAVs tend to be of the same sense (and direction).* The two principal exceptions are provided by compounds **4** and **6**, and it may be seen that the change in POAV sense occurs at the weakest bond (site of interruption in conjugation).

Discussion

One-Center POAV Analysis. The one-center POAV analysis of compounds **1**, **4-8**, **11**, and **12** is summarized in Table IV; the values for **1-3**, **9**, and **10** were presented in a previous paper.[12] These results provide a convenient index of the rehybridization which is dictated by conformational restraint and/or the drive to maintain conjugation.[10,12] In the previous studies it was noted that 1,4,7-methino[10]annulene (**3**) possessed the most rehybridized carbon atom of any structurally characterized molecule yet to be examined with the POAV model. However, the degree of rehybridization in **3** is surpassed by both the basal 5-MR in **12** and the double-bonded carbons in **11**. This latter result is particularly significant in that **11** contains isolated double bonds, which are further destabilized by the (antihomoaromatic) transannular interaction.[13,45] An analysis of the presumed structure of icosahedral C_{60} gave values of $\theta_{\sigma\pi} = 101.6°$, $m = 0.09275$ (POAV1),[19] and $m = 0.08773$ (POAV2), where $\theta_{\sigma\pi}$ is the pyramidalization angle and m is the s-content in the π-orbital ($s^m p$).

Table IV. POAV One-Center Analysis[a]

mol	center	POAV1 $\theta_{\sigma\pi}$	POAV1 m	POAV2 m
1	4	94.1	0.01056	0.01028
	5	91.9	0.00225	0.00224
	6	92.1	0.00267	0.00262
4	4	92.6	0.00477	0.00468
	5	93.4	0.00702	0.00656
	6	91.9	0.00221	0.00215
	7	96.5	0.02663	0.02628
	8	91.3	0.00109	0.00104
5	4	93.7	0.00845	0.00821
	5	91.3	0.00116	0.00115
	6	93.1	0.00592	0.00579
	7	94.2	0.01098	0.01070
6	4	91.4	0.00129	0.00123
	5	90.5	0.00017	0.00017
	6	90.9	0.00053	0.00052
	7	92.8	0.00493	0.00492
	8	91.5	0.00141	0.00139
	9	90.6	0.00028	0.00027
	10	92.5	0.00380	0.00374
7	4	91.5	0.00142	0.00132
	5	90.2	0.00002	0.00001
	6	90.2	0.00003	0.00003
	7	91.2	0.00094	0.00094
	8	90.1	0.00000	0.00000
	9	90.2	0.00002	0.00002
8	2	91.5	0.00131	0.00131
	3	90.5	0.00015	0.00015
	4	91.2	0.00084	0.00084
	5	90.3	0.00007	0.00007
11	2	99.9	0.06479	0.06240
12	3	98.2	0.04393	0.04073
	4	93.8	0.00878	0.00844
	5	91.7	0.00233	0.00224

[a] See ref 12 for details of notation. The s-character in the π-orbital is given by $m(s^m p)$, and the pyramidalization angle (between the π and group average σ-orbitals) is denoted $\theta_{\sigma\pi}$.

The fact that **11** is an isolable (though not particularly stable), compound[13] encourages the belief that icosahedral C_{60} will be characterized by the end of the decade.[46] Icosahedral C_{60} would possess the most rehybridization of any compound to be characterized (Table IV), but it is not subject to the transannular interactions of **11**, and in addition it possesses a degree of resonance stabilization.[16,19,41,46]

Two-Center POAV2/3D-HMO Analysis of Compounds 1-8. As noted above, the ρ^R values turn out to be very close to the cosine

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(45) Honegger, E.; Heilbronner, E.; Wiberg, K. B. *J. Electron Spectrosc., Relat. Phenom.* **1983**, *31*, 369.

(46) (a) Since submission of this manuscript Professor Greene has supplied us with the crystallographic unit cell coordinates of 9, 9′, 10, 10′ - tetradehydrodianthracene (Viavattene-Greene diene)[46b] which possesses a pair of isolated double bonds that are similarly disposed to those of compound **11**.[13] Analysis of the diene carbon atoms gives values of $\theta_{\sigma\pi} = 102.9°$, $m = 0.11715$ (POAV1), and $m = 0.11346$ (POAV2). It may be seen from Table IV that Viavattene-Greene diene exhibits a greater degree of rehybridization than **11** and all of the structurally characterized molecules yet to be examined with the POAV model. As may be seen in the text, *Viavattene-Greene diene surpasses the degree of rehybridization required in icosahedral C_{60}.* The isolation of this diene and the observations at the conclusion of the paper[46b] probably provide more hope for the eventual characterization of icosahedral C_{60} than the multitude of studies based on calculated (thermodynamic) resonance energies. (b) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

Table V. POAV/3D-HMO Analysis[a]

mol	geom	bond		R (Å)	overlap integrals					ρ^B	ρ^R
					s,s	s,p_σ	p_σ,p_σ	p_π,p_π	total		
1	HF/6-31G	3	4	1.423	0.0035	−0.0051	0.0015	0.2317	0.2316	0.942	0.986
					0.0034	−0.0053	0.0016	0.2316	0.2314	0.941	0.985
		4	5	1.380	0.0018	−0.0026	0.0007	0.2424	0.2424	0.986	0.959
					0.0018	−0.0027	0.0008	0.2429	0.2427	0.988	0.961
		5	6	1.407	0.0009	−0.0013	0.0004	0.2140	0.2139	0.870	0.885
					0.0009	−0.0013	0.0004	0.2148	0.2147	0.874	0.899
		1	6	2.246	0.0003	−0.0096	0.0827	0.0264	0.0998	0.406	2.023
					0.0003	−0.0095	0.0816	0.0268	0.0991	0.403	2.009
2	HF/6-31G	3	4	1.407	0.0056	−0.0079	0.0022	0.2323	0.2321	0.944	0.961
					0.0055	−0.0077	0.0021	0.2327	0.2327	0.947	0.963
		4	5	1.397	0.0048	−0.0068	0.0019	0.2181	0.2180	0.887	0.888
					0.0047	−0.0068	0.0019	0.2196	0.2194	0.893	0.894
		5	6	1.386	0.0013	−0.0018	0.0005	0.2227	0.2227	0.906	0.890
					0.0012	−0.0021	0.0007	0.2242	0.2240	0.912	0.896
		6	7	1.399	0.0006	−0.0009	0.0003	0.2370	0.2370	0.964	0.968
					0.0006	−0.0010	0.0003	0.2375	0.2374	0.966	0.970
		7	8	1.410	0.0014	−0.0020	0.0006	0.2373	0.2373	0.965	0.987
					0.0012	−0.0021	0.0007	0.2374	0.2373	0.965	0.987
		1	5	2.370	0.0010	−0.0158	0.0578	0.0231	0.0662	0.269	1.736
					0.0010	−0.0151	0.0547	0.0239	0.0646	0.263	1.694
3	HF/6-31G	4	5	1.402	0.0034	−0.0048	0.0013	0.2286	0.2285	0.930	0.938
					0.0030	−0.0045	0.0013	0.2323	0.2320	0.944	0.952
		5	6	1.414	0.0006	−0.0009	0.0003	0.2378	0.2378	0.967	0.997
					0.0006	−0.0007	0.0002	0.2379	0.2380	0.968	0.998
		6	7	1.407	0.0008	−0.0012	0.0003	0.2352	0.2351	0.957	0.973
					0.0007	−0.0009	0.0002	0.2361	0.2362	0.961	0.977
		7	8	1.387	0.0013	−0.0018	0.0005	0.2413	0.2412	0.982	0.967
					0.0011	−0.0021	0.0007	0.2419	0.2416	0.983	0.968
		8	9	1.409	0.0012	−0.0018	0.0005	0.2385	0.2384	0.970	0.990
					0.0012	−0.0018	0.0005	0.2386	0.2386	0.971	0.991
		1	4	2.371	0.0010	−0.0075	0.0123	0.0339	0.0396	0.161	1.044
					0.0008	−0.0060	0.0092	0.0349	0.0389	0.158	1.025
		1	7	2.550	0.0002	−0.0037	0.0142	0.0227	0.0334	0.136	1.287
					0.0002	−0.0033	0.0131	0.0230	0.0330	0.134	1.270
1	expt	3	4	1.418	0.0041	−0.0060	0.0017	0.2333	0.2332	0.949	0.984
					0.0040	−0.0060	0.0018	0.2333	0.2331	0.948	0.983
		4	5	1.376	0.0020	−0.0028	0.0008	0.2429	0.2429	0.988	0.956
					0.0019	−0.0030	0.0009	0.2433	0.2432	0.989	0.957
		5	6	1.405	0.0010	−0.0014	0.0004	0.2152	0.2152	0.875	0.888
					0.0010	−0.0015	0.0004	0.2161	0.2160	0.879	0.892
		1	6	2.235	0.0003	−0.0107	0.0853	0.0267	0.1016	0.413	2.012
					0.0003	−0.0105	0.0840	0.0270	0.1008	0.410	1.998
4	expt	3	4	1.355	0.0015	−0.0021	0.0006	0.2613	0.2613	1.063	0.991
					0.0015	−0.0022	0.0006	0.2612	0.2611	1.062	0.991
		4	5	1.453	0.0021	−0.0030	0.0009	0.1737	0.1736	0.706	0.777
					0.0020	−0.0026	0.0007	0.1734	0.1734	0.706	0.776
		5	6	1.364	0.0017	−0.0023	0.0006	0.2550	0.2549	1.037	0.983
					0.0016	−0.0028	0.0010	0.2544	0.2542	1.034	0.980
		6	7	1.473	−0.0028	0.0041	−0.0012	0.1048	0.1049	0.427	0.487
					−0.0027	0.0044	−0.0015	0.1072	0.1074	0.437	0.498
		7	8	1.347	0.0021	−0.0031	0.0008	0.2553	0.2553	1.039	0.956
					0.0021	−0.0032	0.0009	0.2554	0.2552	1.038	0.956
		8	9	1.469	0.0003	−0.0005	0.0002	0.2169	0.2169	0.882	0.998
					0.0003	−0.0005	0.0002	0.2169	0.2169	0.882	0.998
		1	6	2.298	0.0002	−0.0086	0.0740	0.0246	0.0902	0.367	2.038
					0.0002	−0.0084	0.0728	0.0249	0.0896	0.364	2.023
5	expt	3	4	1.403	0.0034	−0.0048	0.0014	0.2400	0.2399	0.976	0.987
					0.0033	−0.0053	0.0017	0.2398	0.2395	0.974	0.985
		4	5	1.370	0.0013	−0.0018	0.0005	0.2470	0.2470	1.005	0.961
					0.0012	−0.0019	0.0006	0.2476	0.2475	1.007	0.963
		5	6	1.412	0.0010	−0.0014	0.0004	0.2142	0.2142	0.871	0.895
					0.0010	−0.0013	0.0004	0.2155	0.2155	0.877	0.901
		6	7	1.393	0.0033	−0.0047	0.0013	0.2406	0.2405	0.979	0.973
					0.0032	−0.0053	0.0017	0.2409	0.2405	0.978	0.973
		1	6	2.360	0.0006	−0.0125	0.0662	0.0219	0.0762	0.310	1.958
					0.0006	−0.0123	0.0655	0.0221	0.0759	0.309	1.949
6	expt	3	4	1.351	0.0016	−0.0023	0.0006	0.2636	0.2635	1.072	0.994
					0.0016	−0.0024	0.0007	0.2635	0.2634	1.072	0.994
		4	5	1.441	0.0004	−0.0005	0.0002	0.1982	0.1982	0.806	0.870
					0.0004	−0.0006	0.0002	0.1988	0.1988	0.809	0.872

Table V (Continued)

					overlap integrals					
mol	geom	bond		R (Å)	s,s	s,p_σ	p_σ,p_σ	p_π,p_π	total	ρ^B	ρ^R
		5	6	1.346	0.0003	−0.0004	0.0001	0.2622	0.2622	1.067	0.980
					0.0003	−0.0004	0.0001	0.2624	0.2624	1.068	0.981
		6	7	1.489	−0.0009	0.0014	−0.0004	0.0520	0.0520	0.212	0.247
					−0.0009	0.0014	−0.0004	0.0528	0.0529	0.215	0.252
		7	8	1.346	0.0007	−0.0010	0.0003	0.2630	0.2630	1.070	0.984
					0.0007	−0.0010	0.0003	0.2630	0.2630	1.070	0.984
		8	9	1.458	0.0001	−0.0001	0.0000	0.1925	0.1925	0.783	0.870
					0.0001	−0.0001	0.0000	0.1929	0.1929	0.785	0.872
		9	10	1.344	0.0001	−0.0001	0.0000	0.2664	0.2664	1.084	0.994
					0.0001	−0.0002	0.0001	0.2666	0.2665	1.084	0.994
		10	11	1.454	0.0005	−0.0007	0.0002	0.2214	0.2214	0.901	0.993
					0.0005	−0.0007	0.0002	0.2214	0.2213	0.901	0.992
		1	6	2.417	0.0001	−0.0050	0.0517	0.0218	0.0686	0.279	1.987
					0.0001	−0.0050	0.0511	0.0220	0.0682	0.278	1.976
		8	13	2.483	0.0000	−0.0026	0.0421	0.0201	0.0596	0.242	1.989
					0.0000	−0.0026	0.0417	0.0202	0.0594	0.242	1.981
7	expt	1	2	1.335	0.0000	0.0000	0.0000	0.2718	0.2718	1.106	0.999
					0.0000	0.0000	0.0000	0.2718	0.2718	1.106	0.999
		2	3	1.458	0.0000	0.0000	0.0000	0.1494	0.1494	0.608	0.675
					0.0000	0.0000	0.0000	0.1494	0.1494	0.608	0.675
		3	4	1.323	0.0000	−0.0001	0.0000	0.2763	0.2763	1.124	0.995
					0.0001	−0.0001	0.0000	0.2764	0.2764	1.125	0.995
		4	5	1.464	0.0001	−0.0001	0.0000	0.1721	0.1721	0.700	0.786
					0.0001	−0.0001	0.0000	0.1733	0.1733	0.705	0.792
		5	6	1.338	0.0000	0.0000	0.0000	0.2705	0.2705	1.101	0.999
					0.0000	0.0000	0.0000	0.2705	0.2705	1.101	0.999
		6	7	1.449	0.0001	−0.0001	0.0000	0.2227	0.2227	0.906	0.990
					0.0001	−0.0001	0.0000	0.2228	0.2228	0.906	0.991
		1	7	2.417	0.0001	−0.0042	0.0513	0.0210	0.0682	0.277	1.979
					0.0001	−0.0042	0.0512	0.0210	0.0681	0.277	1.975
8	expt	2	3	1.398	0.0002	−0.0003	0.0001	0.2446	0.2446	0.995	0.998
					0.0002	−0.0003	0.0001	0.2446	0.2446	0.995	0.998
		3	4	1.392	−0.0001	0.0002	−0.0001	0.2457	0.2457	1.000	0.993
					−0.0001	0.0002	−0.0001	0.2456	0.2456	0.999	0.993
		4	5	1.399	0.0001	−0.0001	0.0000	0.2423	0.2423	0.986	0.991
					0.0001	−0.0001	0.0000	0.2422	0.2422	0.986	0.991
		5	6	1.395	0.0000	0.0000	0.0000	0.2442	0.2442	0.994	0.991
					0.0000	0.0000	0.0000	0.2442	0.2442	0.994	0.991
		4	14	2.555	0.0001	0.0008	0.0029	0.0250	0.0288	0.117	1.120
					0.0001	0.0008	0.0029	0.0250	0.0288	0.117	1.122
9	HF/6-31G	2	3	1.324	0.0100	−0.0137	0.0035	0.2517	0.2515	1.024	0.908
					0.0100	−0.0151	0.0043	0.2521	0.2512	1.022	0.907
10	HF/6-31G	2	3	1.343	0.0610	−0.0749	0.0174	0.1625	0.1660	0.675	0.618
					0.0574	−0.0740	0.0178	0.1584	0.1595	0.649	0.594
11	expt	2	3	1.354	0.0261	−0.0352	0.0091	0.2405	0.2405	0.979	0.912
					0.0252	−0.0438	0.0146	0.2366	0.2326	0.946	0.881
		2	5	2.394	0.0055	−0.0555	0.1336	−0.0010	0.0826	0.336	2.283
					0.0053	−0.0540	0.1314	−0.0016	0.0811	0.330	2.240
		2	6	2.751	0.0029	−0.0290	0.0708	−0.0018	0.0430	0.174	2.560
					0.0028	−0.0290	0.0732	−0.0013	0.0457	0.187	2.727
12	expt	2	3	1.413	0.0168	−0.0235	0.0065	0.2244	0.2242	0.912	0.937
					0.0156	−0.0178	0.0040	0.2270	0.2288	0.931	0.957
		3	4	1.378	0.0080	−0.0111	0.0030	0.2438	0.2437	0.991	0.962
					0.0075	−0.0113	0.0030	0.2422	0.2414	0.982	0.953
		4	5	1.436	0.0014	−0.0021	0.0006	0.2225	0.2225	0.905	0.968
					0.0014	−0.0021	0.0007	0.2233	0.2232	0.908	0.971
		5	6	1.392	0.0006	−0.0009	0.0002	0.2466	0.2466	1.003	0.995
					0.0006	−0.0010	0.0003	0.2465	0.2464	1.003	0.994

[a] For each bond, the POAV2 results are given directly below the POAV1 values.

of the POAV misalignment angles (ϕ).[12] The lowest nearest neighbor ρ^R value in a fully cylically delocalized molecule occurs in compound **1**, which has $\rho^R_{5,6} = 0.889$ (HF/6-31G geometry) and 0.892 (experiment). The bridge carbon atoms (1 and 6) in this molecule exhibits little rehybridization, and it seems likely that the molecular structure reflects a delicate balance[34,47] between the foregoing effects and the presence of a strong homoconjugate interaction.

The nonaromatic compounds **4**[36] and **6**[48,49] are characterized by at least one symmetry related pair of low ρ values. In compound **4** it may be seem that $\rho^R_{4,5} = 0.776$ and $\rho^R_{6,7} = 0.498$, and in compound **6**, $\rho^R_{6,7} = 0.252$. Apparently ρ values of this mag-

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nitude are sufficient to overcome the drive for delocalization. The formally antiaromatic compound **7**,[50] possesses two sets of intermediate ρ values: $\rho^R_{2,3} = 0.675$ and $\rho^R_{4,5} = 0.792$. Nevertheless, rehybridization effects are at a minimum in this compound and there does not seem to be any obvious avoidance of conjugation in the molecule. Recent work favors the idea that the resonance energy of the higher antiaromatic annulenes may be near zero or even slightly positive.[51,52] At the other end of the scale compound **8**[53,54] possesses no ρ^R values less than 0.99.

Homoconjugation in Compounds 1–8. Up until 10 years ago, the known compounds with structural types exemplified by **1–8** were regarded as bridged annulenes; prototypes for the geometrically unattainable ideal D_{Nh} annulenes. In the last decade, the importance of transannular interactions has been fully recognized (although experimental evidence on this point has been available for some time).[55-61] For example, **1**[62] is now referred to as homonaphthalene,[60,63] **2**[64,65] as homoazulene,[65] and **5** as homoanthracene.[60]

In terms of our threshold value ($\rho^B > 0.2$) for a homoconjugate interaction, **1**, **2**, **4**, **5**, **6**, and **7** qualify as homoconjugated species. Of the [10]annulenes, therefore, only compound **3**[66] qualifies as a true bridged annulene, and in the case of the [14]annulenes, compound **8**[53,54] is the only true bridged annulene (in consonance with the above classification).[55-65]

A great deal of careful experimentation on these compounds has been documented in the literature, and a consensus has emerged as to the correct value of the transannular homoconjugate interaction in 1,6-bridged annulenes.[55-61,67] "The most likely value of the transannular resonance integral was estimated at about 40% of that between $2p_z$ orbitals on neighbors in benzene."[60] This definition corresponds precisely to our $\rho^B_{1,6}$ parameter, for which we calculate values of 0.403 (HF/6-31G structure) and 0.410 (experimental) for 1,6-methanol[10]annulene (**1**). Thus it appears that the experimental and theoretical estimates of this parameter are well reconciled. The transannular interaction in compound **5** turns out to be a little smaller with a $\rho^B_{1,6}$ value of 0.309. This is mainly due to the greater transannular distance in **5** ($R_{1,6}$ = 2.360 Å) than in **1** [$R_{1,6}$ = 2.246 (HF/6-31G geometry), 2.235 Å (experiment)], although there is a very slight POAV misalignment for the 1,6-interaction in **5** (the alignment is dictated by symmetry in **1**).

Table VI. POAV2/3D-HMO Total π-Electron Energies

mol	geom	no. of electrons	transannular intractn	energy (β)	
				calcd	ideal
9	HF/6-31G	2	–	1.814	2.0
10	HF/6-31G	2	–	1.188	2.0
11	expt	2	–	1.762	2.0
		4	+	3.524	4.0
1	HF/6-31G	10	–	12.017	12.944
			+	12.262	13.683
2	HF/6-31G	10	–	12.195	12.944
			+	12.229	13.364
3	HF/6-31G	10	–	12.650	12.944
1	expt	10	–	12.120	12.944
			+	12.364	13.683
4	expt	10	–	11.203	12.944
			+	11.402	13.683
7	expt	12	–	14.024	14.928
			+	14.061	15.618
5	expt	14	–	17.104	17.976
			+	17.390	19.314
6	expt	14	–	15.966	17.976
			+	16.181	19.314
8	expt	14	–	17.860	17.976
12	expt	20	–	27.906	28.737

It may be seen in Table V that for compounds **1**, **2**, **4**, **5**, **6**, and **7** the p_π, p_π overlap contribution amounts to less than half of the total homoconjugate overlap integral. This is in accord with the definition advanced in the Results section and the original characterization of this phenomenon as[68,69] "... orbital overlap of a type intermediate between σ and π."[68]

POAV2/3D-HMO Analysis of Compounds 9–12. To a first approximation, compounds **9–11** may be considered to provide a series of strained cycloalkenes with isolated double bonds.[4,13,14,70] As may be seen from Table V, the overlap in these conjugated systems is considerably reduced by the conformational restraints of the geometry. It was noted earlier that the amount of rehybridization in these compounds increases in the order: **9** < **11** < **10**, and it may be seen that the $\rho^B_{2,3}$ values follow the same sequence. This is in accord with their chemical stability: compound **10**[70d] has been identified only as a transient intermediate, and while **9**[70a] and **11**[13] are well-characterized compounds, the

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latter is known to be an extremely reactive molecule. Compound **11**, of course, possesses a significant transannular interaction ($\rho^{B}_{2,5}$ = 0.330, while $\rho^{B}_{2,6}$ falls below the threshold value of 0.2), and this is in qualitative accord with photoelectron spectroscopy studies.[45]

Compound **12**[15] is of interest because of its relationship to icosahedral C_{60}, but as may be seen from Tables IV and V, compound **11** is a better model for C_{60}[POAV2: $\rho^{R} = 0.911$ (5-MR/6-MR bond) and $\rho^{R} = 0.831$ (6-MR/6-MR), see also ref 19]. The prospects for isolation are encouraged by these results.

Total POAV2/3D-HMO π-Electron Energies. The total π-electron energies are given in Table VI, both with and without transannular homoconjugate interactions (ρ values below the threshold of 0.2, are neglected). It may be seen that all of the molecules lose π-electron energy as a result of nonplanarity, although in the case of compound **8**, the deviation from ideality is very small. While homoaromatic interactions have been shown to be significant in many of these compounds, the impact on total energies is seen to be relatively small. This is in accord with previous discussions of this dichotomy, in which attention is drawn to the distinction between one-electron properties (very sensitive to transannular interactions) and many-electron properties (relatively insensitive to secondary interactions).[60,71]

The total 3D-HMO π-electron energies may be expected to correlate with properties which depend on the collective behavior of the π-electrons. This follows as the POAV method utilizes the orbital orthogonality conditions to maintain σ–π separability in nonplanar conjugated organic systems. The exemplar for such properties in cyclically conjugated molecules is provided by the presence of an induced ring current.[72,73] Indeed this latter quantity has been shown to be directly related to the π-electron resonance energy of aromatic [4*n* + 2]annulenes.[74]

Previous empirical analyses of the ring currents of the compounds which have been examined[73,75] correlate rather well with the results in Table VI. Compound **8**, for example, was found to approach the maximum ring current expected for an ideal [14]annulene.[54,75] More recently the fraction of the maximum ring current for a [10]annulene has been found to be the following: **1**, 64%; **2**, 66%; **3**, 95%.[76] It should be pointed out, however, that the presence of transannular interactions complicates the comparison. In compounds **1** and **2** the transannular interaction stabilizes the molecule while quenching the ring current. The ring currents in compounds **4**[36] and **6**[48] are almost totally quenched. Compound **7** exhibits a paramagnetic ring current,[50] but a unified theory for π-electron energies and ring currents in antiaromatic annulenes has yet to be developed.

Unfortunately the results in Table VI cannot necessarily be expected to correlate directly with the stability and reactivity of the molecules. In the POAV model it is assumed that the σ-bonds lie along the internuclear axes of the molecule and the hybridization is constructed accordingly. In fact, deviations of up to 5° are found in the σ-bonds of torsionally twisted ($\tau = 90°$) ethylene. Thus it is likely that similar effects occur in other molecules discussed herein, and this is why a working threshold of $\theta_{ij} > 100°$ ($i \neq j \neq \pi$, σ-bonds) was recommended when the POAV method was introduced.[12] Thus the σ-system absorbs a degree of strain, and the dislocations in the π-system are further reduced. In the POAV model perfect σ-orbital following is assumed, and all dislocations are absorbed by the π-component, and this has been demonstrated to be a good approximation (see Results section and ref 11 and 12). Considered from the standpoint of the POAV model, the σ-destabilization takes the form of increased p-character and decreased s-character in the σ-hybrids. Thus this σ-contribution would have to be included in any direct comparison of the stability and reactivity of molecules. In the case of **9–11**, the two effects (rehybridization and π-bonding) parallel each other, and the comparison is on reasonably safe ground. The bridged [10]annulenes **2** and **3**, however, make use of considerably more rehybridization than **1**,[12] and it is apparent that this is an important factor in determining the chemical behavior of these compounds.[34,63] Although it is possible that a parameterization of the two effects could be found, for quantitative work on all-electron properties it would seem preferable to incorporate the POAV model into a molecular mechanics scheme.[77,78]

Conclusion

The POAV/3D-HMO theory is best characterized as an illustrative, semi-quantitative method for the classification of nonplanar conjugated organic molecules, at much the same level that standard HMO theory is now applied to provide a conceptual picture of planar π-systems. The POAV/3D-HMO analysis of compounds **1–12** yields few surprises: the molecules are found to be much the way the synthetic chemists, spectroscopists, and theoreticians have reported. Nevertheless, the focus is sharpened. The real value of the POAV/3D-HMO theory lies in the unified viewpoint which it offers for π-systems—planar and nonplanar.

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(78) A further refinement, along the lines of the Extended Huckel Theory,[17,18] would involve the evaluation of the off-diagonal matrix elements of the Hamiltonian by weighting the overlap integrals with suitably scaled valence orbital ionization potentials.