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Hybridization and the Orientation and Alignment of π-Orbitals in Nonplanar Conjugated Organic Molecules: π-Orbital Axis Vector Analysis (POAV2)

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Abstract: The concept of hybridization of atomic orbital basis functions to produce spatially directed wave functions with the orientation necessary for bond formation is fundamental to the modern understanding of the molecular and electronic structure of molecules. In the present article, we consider a bonding situation which has become increasingly important in recent years—nonplanar conjugated organic molecules, which are usually considered to possess formal sp^2 hybridization. It is shown that with a single assumption, it is possible to obtain analytical solutions for the hybridization in such compounds which in turn leads directly to the orientation of the π-orbital axis vectors (POAV) and hence to a measure of π-orbital alignment and overlap in distorted π-electron systems of known geometry. The π-orbital axis vector (POAV) analysis provides a vivid picture of the π-bonding in nonplanar conjugated organic molecules and the manner in which the σ-system has rehybridized and adjusted to facilitate the maintenance of favorable π-orbital overlap. The method is nonparametric and merely requires the atomic coordinates of the molecule or molecular fragment for its implementation (computer program POAV2 has been deposited with the Quantum Chemistry Program Exchange). The analysis is based on the sp hybrid orthogonality relationships and the geometry of the σ-skeleton. As such the method provides the most logical and natural bridge between the σ–π separability assumed in planar conjugated systems and the realistics of π-bonding in nonplanar situations. The analysis is not recommended in circumstances where the σ-bond angles are less than 100°, but with this proviso the method may be used with confidence. The general practice of quoting formal dihedral angles as a measure of π-orbital alignment or strain is strongly discouraged—such an approach is misleading, arbitrary, and equivocal. The POAV analysis has been used to provide insight into the electronic structure of a number of nonplanar conjugated organic systems of topical interest.

The concept of hybridization of atomic orbital basis functions to produce spatially directed wave functions with the orientation necessary for bond formation[1] is fundamental to the modern understanding of the molecular and electronic structure of molecules.[2-4] In general, however, it is not possible to assign hybridization (sp) from a consideration of molecular structure (or vice versa) in organic compounds of low symmetry (see below). In these cases, an energy calculation must be carried out to optimize the atomic orbital coefficients and the resulting wave function analyzed to provide an indirect index of the hybridization.[5-9] The maximum overlap method (MOM)[10] is a particularly successful variant of this approach in which the atomic hybridizations within the molecule are adjusted to maximize the total overlap of all bonds (suitably weighted by the empirical bond energies).

In the present article, we consider a bonding situation which has become increasingly important in recent years—nonplanar conjugated organic molecules,[11-13] which are usually considered to possess formal sp^2 hybridization. It is shown below that with a single assumption, it is possible to obtain analytical solutions for the hybridization in such compounds which in turn leads directly to the orientation of the π-orbital axis vectors (POAV) and hence to a measure of π-orbital alignment and overlap in distorted π-electron systems of known geometry.

In order to carry through this treatment, it is necessary to assume that the σ-bonds lie along the internuclear axes of the molecule. Thus the POAV model depends for its validity on the idea that the primary dislocations in bonding will occur among the π-electrons. In the main, this will take the form of torsional distortions, the energy of which is very much less than the energies required to bend σ-bonds in most situations. As shown below, it is quite evident that the more flexible σ-systems of many nonplanar conjugated organic molecules do much to accommodate the conformational preferences of the π-system, and this is re-

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flected by their structures and in deviations from pure sp^2 hybridization. The necessary rehybridization is often accomplished by movement of hydrogens or substituents which are not subject to conformational restraints, and it is primarily in this sense that the σ-system is seen to accommodate the more restrictive stereochemistry of the π-bonds.

Generalized valence bond (GVB) wave functions for torsionally twisted ethylene have been shown to produce results in excellent agreement with the assumptions and predictions of the POAV model.[14] While the calculations indicate that at a torsional twist angle (τ) of 90°, the carbon σ-bond deviates by 5° from the internuclear axis, analysis of the GVB electron pair functions shows that the dislocations in bonding which remain after structural adjustment are primarily absorbed by the π-system. The calculated amount of rehybridization in torsionally twisted ethylene (as measured by the s-character of the π-orbital) obtained from the POAV and GVB methods is in excellent agreement. In addition the torsional angles of the π-orbital axis vectors exhibit a maximum dispersion of 25% for τ values up to 90°. The results support the suggestion that the POAV model provides an upper bound for π-orbital axis vector torsional angles in the range $0° < \tau < 80°$.

An important aspect of the present analysis is the idea that even in a nonplanar conjugated organic molecule, it is still possible to divide the wave function into a sum of localized σ-hybrids which remain distinct from the π-orbital component. This is accomplished by choosing the atomic orbital hybrids to be orthogonal, for this ensures a separability of the bonds such that each makes its own individual contribution to the total electron density of the molecule.[5,15-18]

As a final note to this section, we inveigh against the general practice of quoting formal (heavy-atom skeleton) dihedral angles as a measure of π-orbital alignment and strain in nonplanar conjugated organic molecules. This procedure is misleading, arbitrary, and equivocal (see later and ref 19).

Theory

The orbitals for a conjugated nonplanar system take the form of eq 1 and 2 where h_1, h_2, and h_3 are the hybrid σ-orbitals, and p_1, p_2, and p_3 are p functions directed along the three internuclear axes to the adjacent atoms. Equation 2 contains the quantities of primary interest: the hybridization (λ_π) and direction of the π-orbital [p_π, π-orbital axis vector (POAV)].

$$\begin{aligned} h_1 &= N_1(s + \lambda_1 p_1) \\ h_2 &= N_2(s + \lambda_2 p_2) \\ h_3 &= N_3(s + \lambda_3 p_3) \end{aligned} \tag{1}$$

$$h_\pi = N_\pi(s + \lambda_\pi p_\pi) \tag{2}$$

The hybridizations are conveniently expressed as the p content of the σ-orbitals (sp^n) and the s content of the π-orbital ($s^m p$), which may be obtained from eq 3 and 4 such that the set (h_1, h_2, h_3, h_π) is normalized to sp^3.

$$m = (1/\lambda_\pi)^2 \tag{3}$$

$$n = \lambda_\sigma^2 \tag{4}$$

The orthogonality relationships (amongst the hybrids h_1, h_2, h_3 and h_π) take the form of eq 5 where the θ_{ij} are the angles between the hybrid orbital axes. There are six equations and six angles, three among the σ-orbitals (θ_{12}, θ_{23}, θ_{31}) and three between the σ-orbitals and the π-orbital ($\theta_{1\pi}$, $\theta_{2\pi}$, $\theta_{3\pi}$). Thus in general the problem is over-determined.[16]

$$1 + \lambda_i \lambda_j \cos \theta_{ij} = 0 \tag{5}$$

It is the central hypothesis of this paper that the hybridization and π-orbital orientation may be obtained from a consideration of the σ-orbitals in nonplanar conjugated organic molecules of known geometry.

POAV1. From eq 5 we may obtain π-orbital orthogonality relationships of the form given in eq 6. In a previous communication on this subject, we showed that it is possible to choose a POAV which makes equal angles ($\pi/2 + \theta$ in the previous notation) to the three internuclear axes ($\theta_{1\pi} = \theta_{2\pi} = \theta_{3\pi} = \theta_{\sigma\pi}$).[19,20] Clearly it follows from eq 6 that this approach (hereafter POAV1) is equivalent to the assumption of an (equal) average σ-bond hybridization in C_{3v} symmetry; that is, $\lambda_1 = \lambda_2 = \lambda_3 = (\bar{n})^{1/2}$ and $\theta_{12} = \theta_{23} = \theta_{31} = \theta_{\sigma\sigma}$, where $2 \sin (\theta_{\sigma\sigma}/2) = \sqrt{3} \sin \theta_{\sigma\pi}$.

$$\lambda_\pi = -\frac{1}{\lambda_1 \cos \theta_{1\pi}} = -\frac{1}{\lambda_2 \cos \theta_{2\pi}} = -\frac{1}{\lambda_3 \cos \theta_{3\pi}} \tag{6}$$

In the present notation, the POAV1 analysis[19] yields (eq 3 and 4) eq 7 and 8. While this approximation is probably adequate for many applications, an additional refinement is explored below.

$$m = \frac{2 \cos^2 \theta_{\sigma\pi}}{1 - 3 \cos^2 \theta_{\sigma\pi}} \tag{7}$$

$$\bar{n} = 3m + 2 \tag{8}$$

POAV2. Consider the σ-orbital orthogonality relationships expressed in eq 9.

$$\begin{aligned} 1 + \lambda_1\lambda_2 \cos \theta_{12} &= 0 \\ 1 + \lambda_2\lambda_3 \cos \theta_{23} &= 0 \\ 1 + \lambda_3\lambda_1 \cos \theta_{31} &= 0 \end{aligned} \tag{9}$$

They allow a self-consistent determination of the individual σ-orbital hybridizatons (sp^n) as

$$\begin{aligned} n_1 = \lambda_1^2 &= \frac{-(\cos \theta_{23})}{\cos \theta_{12} \cos \theta_{31}} \\ n_2 = \lambda_2^2 &= \frac{-(\cos \theta_{31})}{\cos \theta_{12} \cos \theta_{23}} \\ n_3 = \lambda_3^2 &= \frac{-(\cos \theta_{12})}{\cos \theta_{23} \cos \theta_{31}} \end{aligned} \tag{10}$$

Let

$$S(\lambda_\sigma) = \sum_{i=1}^{3} \frac{1}{1 + \lambda_i^2} \tag{11}$$

Then from the normalization requirement of the s content in the four hybrids, it is possible to obtain the π-orbital hybridization ($s^m p$).

$$S(\lambda_\sigma) + \frac{1}{1 + \lambda_\pi^2} = 1 \tag{12}$$

Thus

$$\lambda_\pi^2 = \frac{S(\lambda_\sigma)}{1 - S(\lambda_\sigma)} \tag{13}$$

and

$$m = 1/\lambda_\pi^2 = S(\lambda_\sigma)^{-1} - 1 \tag{14}$$

From a consideration of eq 6 and 9, it is possible to obtain additional relationships of the form shown in eq 15.

$$\begin{aligned} \cos \theta_{12} \cos \theta_{3\pi} &= \cos \theta_{31} \cos \theta_{2\pi} \\ \cos \theta_{23} \cos \theta_{1\pi} &= \cos \theta_{12} \cos \theta_{3\pi} \\ \cos \theta_{31} \cos \theta_{2\pi} &= \cos \theta_{23} \cos \theta_{1\pi} \end{aligned} \tag{15}$$

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If $x_i\boldsymbol{i} + y_i\boldsymbol{j} + z_i\boldsymbol{k}$ are unit vectors along the p_i (i = 1–3), then a set of homogeneous equations may be set up to solve for the components (x_π, y_π, z_π) of the POAV along p_π as shown in eq 16.

$$(x_3 \cos\theta_{12} - x_2 \cos\theta_{31})x_\pi + (y_3 \cos\theta_{12} - y_2 \cos\theta_{31})y_\pi + (z_3 \cos\theta_{12} - z_2 \cos\theta_{31})z_\pi = 0$$

$$(x_1 \cos\theta_{23} - x_3 \cos\theta_{12})x_\pi + (y_1 \cos\theta_{23} - y_3 \cos\theta_{12})y_\pi + (z_1 \cos\theta_{23} - z_3 \cos\theta_{12})z_\pi = 0$$

$$(x_2 \cos\theta_{13} - x_1 \cos\theta_{23})x_\pi + (y_2 \cos\theta_{31} - y_1 \cos\theta_{23})y_\pi + (z_2 \cos\theta_{31} - z_1 \cos\theta_{23})z_\pi = 0 \quad (16)$$

The determinant of coefficients vanishes, and in general it is possible to obtain nontrivial solutions for the components of p_π (hereafter POAV2).

Thus from the molecular geometry of a nonplanar conjugated system, it is possible to obtain the σ- and π-hybridizations (λ_1, λ_2, λ_3, λ_π) and the orientation of the π-orbital axis vector (p_π, POAV); these latter quantities may be used directly to obtain information on the π-orbital alignment and overlap in distorted π-systems.

Hybridization and Orthogonality. A masterful discussion of these concepts is provided in the book by McWeeny and Coulson,[15] and we shall be content to summarize the salient points.

It is important to bear in mind that hybridization merely provides a heuristically useful approach for understanding molecular shapes and the factors which determine the energy of molecules as a function of geometry. This explains the desirability of choosing orbitals which are localized in distinct spatial regions. In the present approach, we have extended these concepts via the orthogonality relationships and the known geometry of the σ-skeleton to provide information regarding the π-system, in a manner which preserves σ–π orthogonality which in turn is fundamental to the whole idea of σ–π separability in planar conjugated systems.

Limitations. As discussed above, it is implicity assumed in the present treatment that the dislocations in bonding are absorbed by the π-system alone. Thus in most cases,[14] *the POAV analysis provides a lower bound for the π-orbital alignment attained within nonplanar conjugated organic molecules.*

The absolute limitations to the application of the POAV analysis are provided by the orthogonality relationships of eq 9. Real hybrids cannot be obtained for σ-bond angles (θ_{ij}) < 90°.[21,22] In practice it seems that significant σ-bond orbital deviations from the internuclear axes occur at values of $\theta_{ij} < \sim 100°$,[14] and results obtained in this regime will need to be viewed with some caution (see, however, later discussion of this point).

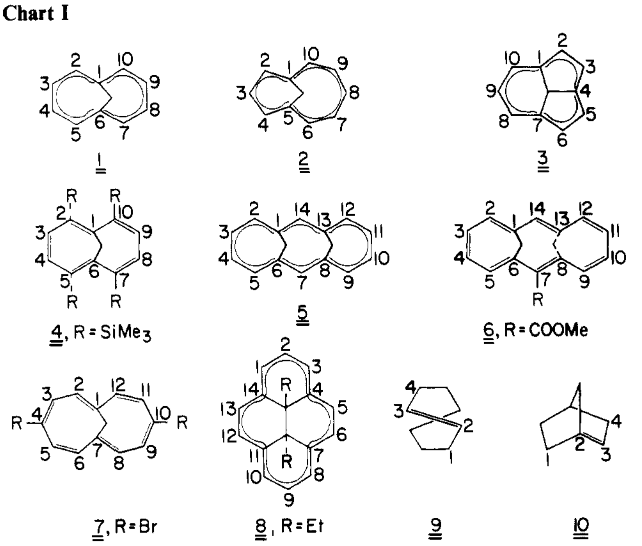
It should also be noted that in the limiting case of *planar* conjugated organic molecules such as *trans*-butadiene and benzene, both the POAV1 and POAV2 analyses produce pure p π-orbital axis vectors normal to the plane, leading to the conventional picture of perfect alignment among the π-orbitals; similarly, both methods yield pure sp^2 hybridization for the benzene σ-skeleton.

Also omitted from this treatment is any consideration of the importance of polarization functions in facilitating the bonding in nonplanar conjugated organic molecules (again, the point is taken up below).

Calculational

Theoretical Geometries. The Hartree–Fock (HF) calculations were carried out with a version of the GAUSSIAN 80 program[23] modified for use on the CRAY-1 computer. Standard STO-3G,[24] 6-31G,[25] and 6-31G* (6-31G+5D)[26] basis sets were utilized. The calculated structures of **1–3**, **9**, and **10** employed in this study were obtained by full geometry optimization at the HF/6-31G theoretical level within the specified symmetries (Chart I). The geometries of **1** (C_{2v}), **2** (C_s), and **3** (C_s) are already in the literature,[27] but the calculated structures of **9** (C_2) and **10** (C_1) have not been previously reported, and their atomic coordinates are included as supplemental information. The extended 6-31G basis set has been shown to provide a fairly reliable account of the geometries of conjugated organic molecules.[27] For analytical purposes, HF theoretical structures for **9** and **10** were also obtained with the STO-3G and 6-31G+5D basis sets. final total energies (hartrees): −307.38295, −310.92656, −311.05142 (**9**); −267.55055, −270.65358, −270.76751 (**10**) [HF/STO-3G, 6-31G, and 6-31G+5D, respectively]; −78.03136 (ethylene) [HF/6-31G+5D]. Calculated dipole moments (debye): 0.47, 0.84, 0.71 (**9**); 0.78, 1.47, 1.25 (**10**) [HF/STO-3G, 6-31G, and 6-31G+5D, respectively].

Chart I



Experimental Geometries. The experimental structures employed herein were taken from X-ray crystallographic studies.[28-33] The molecular atomic coordinates of 1,6-methano[10]annulene (**1**),[28] *syn*-1,6,8,13-bismethano[14]annulene (**5**),[30] 7-(methoxycarbonyl)-*anti*-1,6,8,13-bismethano[14]annulene (**6**),[31] 4,10-dibromo-1,7-methano[12]-annulene (**7**),[32] and *trans*-15,16-diethyldihydropyrene (**8**)[33] were obtained by an appropriate transformation of the published unit cell coordinates. Rectilinear atomic coordinates for 2,5,7,10-tetrakis(trimethylsilyl)-1,6-methano[10]annulene (**4**) were kindly supplied by Prof. Gieren.[29] The parameters obtained from the POAV analysis 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** ($C_1 \rightarrow C_s$), and **8** ($C_1 \rightarrow C_{2h}$).

POAV Analysis. The equations required to effect the POAV1 and POAV2 analyses have been incorporated into a Fortran computer program entitled POAV2, which has been deposited with the Quantum Chemistry Program Exchange (QCPE).[34] The atomic coordinates of the molecule or molecular fragment of interest are the only data which are required for the execution of the POAV2 program. The output from POAV2 consists of the information given in Tables I and II.

Results

The POAV analysis has been applied to a variety of nonplanar conjugated organic molecules in an effort to delineate and illustrate its range of application.

General. The results of the complete POAV analysis of the nonplanar conjugated systems **1–3**, **9**, and **10** at the theoretical geometries are given in Tables I and II. It may be seen that the POAV treatment provides a clear picture of the π-bonding in the

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Table I. One-Center POAV Analysis

		bond angles (θ_{ij}), deg						POAV2							
		substituents ($i \neq j \neq \pi$)[a,b]			POAV1			bond angles, deg							
compd	center[a]				$\theta_{\sigma\pi}$	$\bar{n}$	m	POAV1	substituents ($\theta_{i\pi}$)[a,c]			n_1	n_2	n_3	m
1	4	127.5	114.6	116.6	93.8	2.027	0.009 02	0.9	94.0	94.3	93.0	1.764	1.528	3.274	0.008 79
	5	122.5	118.2	119.0	91.8	2.006	0.002 09	0.1	91.9	91.9	91.7	1.911	1.814	2.344	0.002 08
	6	126.7	116.5	116.5	91.9	2.007	0.002 28	0.4	92.1	92.1	91.6	1.674	1.674	3.001	0.002 24
2	3	121.9	118.0	118.0	94.9	2.046	0.015 23	0.4	95.1	95.1	94.6	1.895	1.895	2.400	0.015 18
	4	116.7	119.1	122.3	94.6	2.038	0.012 83	0.5	94.1	94.5	94.9	2.448	2.029	1.723	0.012 76
	5	129.5	112.0	116.8	94.2	2.033	0.011 08	1.3	94.3	95.2	93.0	1.889	1.308	3.761	0.010 58
	6	123.5	119.7	116.7	91.2	2.003	0.000 87	0.1	91.3	91.2	91.1	1.643	1.996	2.484	0.000 86
	7	134.1	113.7	111.8	92.1	2.008	0.002 79	0.8	92.5	92.3	91.4	1.324	1.562	4.660	0.002 60
	8	138.5	110.4	110.4	92.6	2.012	0.004 16	1.2	93.0	93.0	91.4	1.336	1.336	6.135	0.003 73
3	4	143.8	105.5	105.5	97.1	2.096	0.031 88	4.3	98.3	98.3	92.7	1.239	1.239	11.257	0.025 89
	5	109.6	126.5	123.5	91.9	2.007	0.002 25	0.7	91.6	91.5	92.6	2.761	3.214	1.021	0.002 11
	6	110.2	123.8	125.8	91.4	2.003	0.001 14	0.5	91.1	91.1	91.8	3.040	2.747	1.064	0.001 08
	7	140.2	104.8	114.5	92.4	2.010	0.003 47	1.4	92.1	93.4	91.1	2.114	0.801	7.278	0.002 89
	8	118.3	122.4	118.9	92.1	2.008	0.002 68	0.2	92.1	91.9	92.2	1.906	2.338	1.827	0.002 67
	9	125.2	117.2	117.2	92.4	2.011	0.003 60	0.4	92.6	92.6	92.1	1.736	1.736	2.766	0.003 56
9	2[d]	121.7	115.8	119.1	96.1	2.069	0.023 10	0.7	96.0	96.7	95.5	2.127	1.698	2.483	0.022 96
	3	121.7	119.1	115.8	96.1	2.069	0.023 10	0.7	96.7	96.0	95.5	1.698	2.127	2.483	0.022 96
10	2[e]	114.7	103.7	108.2	110.0	3.084	0.361 32	6.7	109.1	115.7	104.2	3.176	1.809	5.645	0.340 50
	3[f]	106.7	122.8	120.0	100.9	2.240	0.079 96	4.4	98.7	98.0	105.2	3.217	3.776	1.061	0.073 40

[a] With center k, the sequence of skeletal atoms (largest ring) is taken to be: $k-1$, k, $k+1$, and the nonskeletal substituent (or hydrogen) denoted as $[k]$. [b] Bond angles taken in the sequence: $k-1,k,k+1$; $k-1,k,[k]$; $k+1,k,[k]$. [c] Substituents taken in the sequence: $k-1,k+1,[k]$. [d] Bond angles (θ_{ij}, deg, respectively): 121.2, 115.6, 119.9 (STO-3G); 121.6, 115.9, 118.9 (6-31G+5D). [e] Bond angles (θ_{ij}, deg, respectively): 114.2, 103.0, 108.0 (STO-3G); 114.6, 104.0, 108.3 (6-31G+5D). [f] Bond angles (θ_{ij}, deg, respectively): 107.1, 123.0, 119.4 (STO-3G); 106.5, 122.6, 119.9 (6-31G+5D).

molecules and the manner in which the σ-system has adjusted to facilitate the maintenance of favorable π-orbital overlap.

The angles between the σ- and π-orbitals ($\theta_{\sigma\pi}$) obtained from the POAV1 treatment provides a useful qualitative geometrical picture of the degree of rehybridization at a given conjugated atom.[19,20]

However, in cases where the σ-bond angles (θ_{ij}, $i \neq j \neq \pi$) are significantly different and the rehybridization substantial, the POAV1 and POAV2 π-orbital vectors show an appreciable dispersion and utilization of the latter quantity is recommended. This is also reflected in the differing σ–π orbital angles ($\theta_{i\pi}$) and σ-orbital hybridizations (n_i) obtained from the POAV2 analysis. Such behavior is illustrated by 1,4,7-methino[10]annulene (**3**) at the 4-position where the σ-bond angles are quite different and rehybridization is important; the resulting improvement in π-orbital alignment (Table II) is quite phenomenal. All of the bridged [10]annulenes[35-39] make use of rehybridization to improve π-orbital overlap,[19] and it seems likely that these and other compounds owe their stability if not their existence to such effects.

Particular attention is drawn to the variations in the four σ-bond dihedral angles and their relationship to the POAV values,[19] as presented in Table II. The $k-1$, $l+1$ entries are the traditional (termed formal) dihedral angles, and it is apparent that these quantities provide a completely misleading index of π-orbital alignment. In the aromatic bridged annulenes **1**–**3** and **5**, the formal dihedral angles are almost always greater than the POAV values. On the other hand, the nonaromatic compounds in this series (**4** and **6**), frequently exhibit bonds where the reverse holds true. Finally in the aromatic **8** and the antiaromatic **7**, there is little rehybridization—but for quite different reasons (see later).

trans-Cyclooctene (**9**)[40-42] and 1-norbornene (**10**)[43] allow an examination of the importance of rehybridization in a nonplanar isolated double bond. The effects are large—particularly in the case of the unknown **10**—as discussed by other authors.[11-13,20,41,44-50] It is interesting to note the substantial rehybrization which occurs in the unconstrained position, 3, of **10** in order to facilitate π-orbital overlap.

Limitations of the POAV Analysis. As noted earlier, two potential flaws may be envisaged in the POAV analysis: the possibility of σ-bond orbital deviations from the internuclear axes and the possible involvement of polarization functions in rehybridization. Note that both effects serve to further improve π-orbital overlap, and we stress again that in most cases[14] *the POAV analysis provides a lower bound for the π-orbital alignment attained within nonplanar conjugated organic molecules.* Nevertheless, we argue below that in the vast majority of cases, these complications are at least an order of magnitude lower in importance than the simple sp rehybridization treated within the POAV analysis.

The dihedral angles around the conjugated system of **1** are given in Table II for both the theoretical (HF/6-31G) and experimental (X-ray)[28] geometries. It may be seen that the largest disagreements among all of these angles in the two structures amount to 1.0°. Given the fact that the estimated standard deviations of the experimental bond angles are reported[28] as 0.2–1.6°, the agreement between the dihedral angles in the two structures is excellent. As the theoretical geometry is taken from a calculation which employed a basis set comprised of s and p functions alone, we conclude that polarization functions would exert a relatively minor influence on the calculated structure and rehybridization within the molecule. Further support for this point of view is

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Table II. Two-Center POAV Analysis

		dihedral (torsional) angles, deg							
		atom pair[a]		σ-bonds to					
compd	geom	*k*	*l*	*k* − 1,*l* + 1	*k* − 1,[*l*]	[*k*],*l* + 1	[*k*],[*l*]	POAV1	POAV2
1	HF/6-31G	3	4	0.0	13.8	13.8	0.0	0.0	0.0
		4	5	19.1	25.6	5.1	11.6	14.7	14.1
		5	6	34.5	27.6	28.0	21.1	27.3	26.9
2	HF/6-31G	3	4	12.5	27.7	4.7	10.5	10.9	10.4
		4	5	41.7	26.4	26.0	10.7	25.3	24.5
		5	6	37.3	33.0	21.4	17.1	26.0	25.1
		6	7	16.7	8.3	20.8	12.5	13.8	13.3
		7	8	8.8	1.9	17.0	6.4	7.0	6.6
3	HF/6-31G	4	5	40.9	34.4	9.2	2.6	15.9	12.3
		5	6	1.4	3.1	7.7	3.2	2.2	2.0
		6	7	21.0	11.3	16.3	6.7	12.4	11.5
		7	8	23.9	16.5	13.6	6.2	13.8	13.0
		8	9	6.9	1.7	14.0	5.3	5.7	5.4
1	exptl[28]	3	4	0.4	14.7	14.7	0.5	0.2	0.3
		4	5	20.1	26.6	4.9	11.5	15.2	14.6
		5	6	34.5	27.0	28.0	20.4	26.9	26.4
4	exptl[29]	3	4	1.1	6.8	11.8	6.1	2.9	3.3
		4	5	37.9	48.4	28.5	38.9	38.4	38.5
		5	6	17.7	10.6	4.6	2.5	8.2	8.5
		6	7	52.9	76.1	46.0	69.3	60.2	59.5
		7	8	4.1	0.8	25.5	20.1	12.5	12.9
		8	9	1.1	5.0	4.5	1.6	0.5	0.7
5	exptl[30]	3	4	0.9	14.8	12.3	1.9	1.4	1.6
		4	5	19.6	24.4	6.1	10.9	14.5	13.8
		5	6	33.9	23.6	29.3	18.9	25.8	25.1
		6	7	23.8	8.6	12.4	2.9	9.7	9.0
6	exptl[31]	3	4	0.7	8.8	9.1	0.4	0.1	0.1
		4	5	33.0	35.1	24.0	26.2	29.2	28.9
		5	6	15.0	9.6	12.8	7.3	10.9	10.7
		6	7	73.7	83.5	68.4	78.1	75.7	75.4
		7	8	15.3	11.9	5.5	2.1	8.6	8.6
		8	9	31.6	30.8	28.3	27.6	29.4	29.1
		9	10	8.6	3.1	9.5	4.0	5.9	5.6
		10	11	5.2	0.4	11.1	6.2	5.9	6.0
7	exptl[32]	1	2	4.3	4.0	0.1	0.4	2.0	2.0
		2	3	47.7	47.1	48.0	47.4	47.5	47.5
		3	4	8.2	2.2	8.8	2.8	5.0	4.6
		4	5	41.3	41.9	35.5	36.1	38.1	37.6
		5	6	2.2	3.0	1.5	2.4	2.3	2.3
		6	7	10.4	6.1	9.5	5.3	7.7	7.5
8	exptl[33]	2	3	3.5	1.6	5.3	0.2	1.8	1.8
		3	4	5.2	9.4	3.5	7.7	6.5	6.6
		4	5	4.7	5.9	8.8	10.0	7.5	7.6
		5	6	8.9	7.8	7.8	6.6	7.7	7.7
9	HF/STO-3G	2	3	39.6	18.3	18.3	2.9	18.0	17.8
	HF/6-31G	2	3	42.0	20.5	20.5	0.9	20.0	19.4
	HF/6-31G+5D	2	3	42.2	20.1	20.1	2.1	19.5	18.9
10	HF/STO-3G	2	3	86.8	51.2	20.8	14.9	36.7	36.6
	HF/6-31G	2	3	86.9	51.3	22.1	13.5	37.3	37.4
	HF/6-31G+5D	2	3	86.4	50.2	22.0	14.2	36.9	37.2

[a] See footnote *a* to Table I (note that $l = k + 1$).

provided by the calculated dihedral angles obtained for **9** and **10** as a function of basis set flexibility.

We begin by noting that the theoretical structure of **9** (Tables I and II) is in excellent agreement with previous experimental[41,42] and calcuated[48-50] geometries obtained for the molecule. Thus, an electron diffraction study[42] of **9** gave rise to a formal dihedral angle of 44.0 (0.4)° and double bond length of 1.332 (0.003) Å, whereas an X-ray crystallographic investigation[41] of a derivative of **9** produced values of 42.3 (0.3)° and 1.330 Å for the same quantities. The experimental dipole moment of 0.8 D[44] for *trans*-cyclooctene (**9**) is well reproduced by the calculations.

As may be seen from Table II, the flexibility of the basis set exerts a relatively minor influence on the dihedral angles obtained for **9** and **10**. In fact, there are larger adjustments in torsional angles in progressing from minimal (STO-3G) to extended (6-31G) sp basis sets (maximum difference: 2.2°) than occurs on the addition of polarizations functions (6-31G+5D) to the extended basis set (1.1°).

The calculated double bond lengths show the same insensitivity to basis set flexibility; in the series HF/STO-3G, 6-31G, 6-31G+5D, we find the values (in angstroms) 1.311, 1.324, 1.320 (**9**) and 1.336, 1.343, 1.335 (**10**). This trend is not significantly different from the double bond lengths (in angstroms) calculated for ethylene with the same basis sets: 1.305,[51] 1.322,[51] 1.317. It is therefore concluded (at least from a structural perspective) that polarization functions play a relatively minor role in the rehybridization of the types of compounds included in this work. Similar remarks apply to the question of σ-orbital deviations from the internuclear axes. If this phenomenon occurred to a significant extent, we again might expect large changes in the calculated structures as a function of basis set flexibility.[52] We have already remarked on the invariance of the dihedral angles of **9** and **10**

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to the theoretical level—the same behavior is observed for the σ-bond angles around the double bond in **9** and **10** and the maximum deviation among the three basis sets for these quantities is 1° (Table I). We have already stressed the absolute limitations to the application of the POAV analysis as provided by the orthogonality relationships (eq 9). Real hybrids cannot be obtained for σ-bond angles, θ_{ij} ($i \neq \theta \neq \pi$), less than 90°,[21,22] and we recommend a working threshold of 100°. The smallest σ-bond angle included in this study occurs in compound **10** (103.7°).

A further point should be made in connection with this question. Reference to the literature has not disclosed any examples of compounds in which the torsional forces produced by a twisted double bond have imposed a σ-bond angle of less than 100°. (Note that there are no torsional forces generated by the double bond in a molecule such as cyclopropene, and the strain cannot be relieved by rehybridization of the σ-orbital.) A leveling effect seems to be operative in the present instance. The fact that the above situation does not occur perhaps suggests that the torsional forces necessary to close up a σ-bond angle below 100° would lead to such π-destabilization that the molecule would be insolable.

Providing that the restriction on σ-bond angles is heeded [$\theta_{i,j} > 100°$ ($i \neq j \neq \pi$)], we believe that the POAV analysis may be used with confidence.

Discussion

Bridged [10]Annulenes (1–3). The calculated (HF/6-31G) structures of these three molecules have been previously discussed from the standpoint of the POAV1 analysis.[19] In fact it was this series of molecules which first alerted us to the inadequacies of conventional dihedral angles in the assessment of π-orbital overlap in nonplanar conjugated organic molecules. This is made apparent by inspection of the $k - 1, l + 1$ entries (formal dihedral angles) in Table II, where the usual very large dihedral angles appear at the bridge positions. Such degrees of π-orbital misalignment are not consonant with the chemical behavior of these molecules. These values become much more realistic when obtained from the POAV analysis. The empirical finding[53] that the fraction of the maximum ring current[54] for a [10]annulene follows the order **1**, 64%, **2**, 66%, **3**, 95%, is noteworthy in the present context. Such a sequence cannot be reconciled with the formal dihedral angles, but it coincides precisely with that predicted by the POAV analysis.[19] The importance of rehybridization in the periphery of **1** has been previously noted,[55–59] but apart from an MOM calculation,[58] quantitative treatments are lacking. It is also worth noting that the proportionality between the formal and POAV dihedral angles is poor, and thus attempts to scale the formal dihedral angles so as to obtain a true measure of π-orbital alignment[55] are not supported by the POAV analysis.

1,6-Bridged Annulenes (1, 4, 5, and 6). *syn*-1,6:8,13-Bismethano[14]annulene (**5**)[60] is seen to be rather similar to its lower homologue, 1,6-methano[10]annulene (**1**), although the π-orbital overlap within the conjugated segments common to both molecules may be fractionally better in the case of **5**. The only new feature is supplied by the inner conjugated segment of **5** which maintains good π-orbital alignment. Presumably this favorable situation persists in the higher homologues[61] of this compound.

The π-orbital overlap pattern exhibited by molecules **1** and **5** provides a strong contrast with that presented by 2,5,7,10-tetrakis(trimethylsilyl)-1,6-methano[10]annulene (**4**)[29] and 7-(methoxycarbonyl)-*anti*-1,6:8,13-bismethano[14]annulene (**6**).[31,62] Both of these compounds have been shown to be localized, nonaromatic polyenes.[29,31,62,63] In the case of **4**, the bulky substituents displace one another from the conformation in which the α-carbons would be able to effectively rehybridize so as to allow optimum π-orbital overlap with the 1,6-bridge-carbons (cf. **1**). As a result only one side of the molecule is able to maintain conjugation with the 1,6-carbon atoms and the rigid stereochemistry of the bridge dictates that this will be the α-carbon atoms whose substituents are displaced below the ring plane, thereby aligning the π-orbitals across the 1,2 and 5,6 bonds, but effectively deconjugating the 1,10 and 6,7 bonds for the converse reason. The steric effects extend to the 2,3 and 4,5 bonds which also suffer interrupted conjugation. It is interesting to note that the rehybridization in **4** is primarily dictated by the substitution pattern rather than the drive for conjugation—as reflected by the fact that most of the POAV π-orbital misalignment angles are *greater* than the formal dihedral angles. This may be contrasted with **1–3** and **5** in which the reverse is virtually universal.

Molecule **6** exhibits rather similar features to **4**, except that the localization in **6** arises solely from the orientation of the bridge groups. As may be seen from Table II, the *anti* arrangement makes continuous π-orbital overlap an impossibility. Note that there is relatively little rehybridization in the molecule—apparently the degree of delocalization is insufficient to demand the necessary structural deformations.

4,10-Dibromo-1,7-methano[12]annulene (7).[32,64] This formally antiaromatic molecule bears many similarities to the nonaromatic **4** and **6**. There are substantial interruptions in the conjugation, and rehybridization effects are small. It is apparent that the drive for delocalization in this compound is considerably reduced in comparison to the aromatic bridged annulenes **1–3** and **5**.

***trans*-15,16-Diethyldihydropyrene (8).**[65] The POAV results substantiate the evidence in favor of the idea that these compounds closely approach the geometry of an ideal annulene.[54,65–67] It is usually assumed that the π-orbital overlap (integral) in nonplanar conjugated organic molecules scales as the cosine function of the dihedral angle. The largest POAV value in **8** is less than 8°, which has a cosine greater than 0.99!

Conclusion

The π-orbital axis vector (POAV) analysis provides a vivid picture of the π-bonding in nonplanar conjugated organic molecules and the manner in which the σ-system has rehybridized and adjusted to facilitate the maintenance of favorable π-orbital overlap. The method is nonparametric and merely requires the atomic coordinates of the molecule or molecular fragment for its implementation. The analysis is based on the sp hybrid orthogonality relationships and the known geometry of the σ-skeleton. As such the method provides the most logical and natural bridge between the σ–π separability assumed in planar conjugated systems and the realistics of π-bonding in nonplanar situations. The analysis is not recommended in circumstances where the σ-bond angles are less than 100°, but with this proviso the method may be used with confidence. The general practice of quoting formal dihedral angles as a measure of π-orbital alignment or strain is strongly discouraged—such an approach is misleading, arbitrary, and equivocal.

The POAV analysis has been shown to provide insight into the electronic and molecular structure of a number of nonplanar conjugated organic systems of topical interest (**1–10**).

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