

corresponding fashion as required by the virial theorem. This behavior is, for example, found with the carbon bound protons. The decrease in kinetic energy (and increase in total energy) with increasing electron population at oxygen requires that the effective size of the oxygen increases more rapidly than the increase in population.

One question of recent interest has been the origin of the difference in acidity between alcohols and carboxylic acids.²⁰ The more recent conclusion is that the polarization of the carbonyl group is the major factor, and that carboxylate resonance is at best a minor factor. This question may now be examined in terms of the atom energies. In going from ethanol to acetic acid, one major change in energy is that of the hydroxy proton. Its energy increases by 227 kcal/mol on ionization in ethanol, and it increases by only 206 kcal/mol in acetic acid. Thus, one-half of the total difference in ionization energy of acetic acid vs ethanol is accounted for by the ground-state difference in energy between the two protons that will be lost on ionization. The same trend is found in comparing methanol with fluoromethanol. Trifluoromethanol does not fit this pattern, and as noted above, the bonding and charge distribution for this alcohol is quite different than that for the others.

Conclusions

The change in C-O bond length on going from an alcohol to its alkoxide ion is only to a small extent affected by the nature of the substituents. A hydrogen, methyl group, or fluorine is approximately equally effective. The usual effect on the charge

distribution is transfer of charge density from the alcohol carbon to the attached groups, which leads to a reduction in the classical electrostatic energy, and to an internal attractive coulombic interaction, which leads to a short C-O bond in the alkoxide. The charge transfer from carbon to its substituents probably results from a repulsive interaction between the lone pair electrons and the backsides of the C-X bond orbitals. A somewhat different pattern of charge shifts was found with trifluoromethanol, presumably because of the very low electron population at the carbon in the alcohol. A large part of the difference in ionization energies between alcohols and carboxylic acids is found in the difference in hydroxyl proton energies.

Calculations

The calculations were carried out with GAUSSIAN-86²¹ and were run on MicroVax and Trace7/200 computers. Standard basis sets were used.² The analysis of the wave functions was carried out with the PROAIMS programs.²²

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Supplementary Material Available: Calculated vibrational frequencies for methanol, methoxide ion, trifluoromethanol, and trifluoromethoxide ion (1 page). Ordering information is given on any current masthead page.

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Measure of Nonplanarity in Conjugated Organic Molecules: Which Structurally Characterized Molecule Displays the Highest Degree of Pyramidalization?

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Abstract: A set of vectors reciprocal to those pointing along the internuclear axes from a conjugated carbon atom are introduced. The resultant of the reciprocal vectors is shown to define the π -orbital axis vector at a nonplanar conjugated atom. The quantities introduced in the transformation are sufficient to define all of the popular measures of pyramidalization in nonplanar conjugated organic molecules and to allow comparisons between the different schemes. The measures of nonplanarity are divided according to isotropy, and it is shown that there is a high degree of correlation between the different scales of pyramidalization, particularly in the case of the isotropic analyses. The compound reported by Greene and co-workers in 1974, 9,9',10,10'-tetrahydro-dianthracene (**2**) is established as possessing the most pyramidalized carbon atoms of all structurally characterized molecules. All measures of pyramidalization concur with this assessment and with the finding that the degree of pyramidalization in this compound surpasses that which is required in icosahedral C₆₀.

The pathways of many organic chemical reactions involve π -electron systems that undergo drastic deviations from planarity, and the same situation prevails in the formation of the carbon spheroids such as icosahedral C₆₀. It is now becoming clear, however, that substantially nonplanar conjugated organic molecules can actually be isolated and subjected to (structural) characterization. When the geometrical features of this diverse class of compounds are examined, it would be useful to identify a simple, easily conceptualized parameter for the measurement of the degree of nonplanarity.

Since interest in these compounds arose in a number of distinct connections, the nonplanarity has been assessed from different standpoints—some of which have depended on local symmetry for their application. Nevertheless, in situations where the different indices overlap in their applicability, it is of some interest to seek relations among these different measures and to enquire as to whether they lead to the same general scale of nonplanarity.

A measure that has found particular favor relates to the degree of pyramidalization, although this term has been used in a number of different connotations. In fact it was a recent paper on

crystallographically determined π -pyramidalization angles (ϕ) by Paquette and co-workers¹ that stimulated the present study; these workers reported the structure of an interesting new sesquiorbornatriene (**4**, $\phi = 32.4^\circ$) together with a pyramidalization scale based on the literature values of structurally characterized, nonplanar alkenes. In particular they cited the modest value given for the π -pyramidalization angle in 9,9',10,10'-tetrahydrodianthracene (**2**, $\phi = 19.7^\circ$),² which was synthesized and structurally characterized by Greene and co-workers² in 1974. Yet the π -orbital axis vector (POAV) analysis of this molecule implies a degree of pyramidalization that is greater than that of all of the structurally characterized molecules yet examined and surpasses the degree of pyramidalization required in icosahedral C_{60} .³ It therefore seemed worthwhile to subject the various pyramidalization schemes to a rigorous analysis and to assess their predictive value.

Theory

In this section I show that the quantities introduced in the Appendix are sufficient to define all current measures of the degree of pyramidalization in nonplanar conjugated organic molecules.

In the expanded notation, the general π -orbital axis vector⁴⁻⁶ is the vector area of the triangle (\vec{a}_π) formed by the termini of \vec{v}_1 , \vec{v}_2 , and \vec{v}_3 and may be expressed as

$$\vec{v}_\pi = \vec{a}_\pi = \vec{a}_{12} + \vec{a}_{23} + \vec{a}_{31} \quad (1)$$

and

$$\vec{V}_\pi = \vec{v}_\pi / N \quad (2)$$

where N is the appropriate normalization constant for \vec{v}_π [$N = (\vec{v}_\pi \cdot \vec{v}_\pi)^{1/2}$].⁶

As may be seen from eq 1, the π -orbital axis vectors are collinear with the resultant of the reciprocal vectors introduced in the Appendix

$$\vec{v}_\pi \propto \vec{v}_1^* + \vec{v}_2^* + \vec{v}_3^* \quad (3)$$

Three distinct situations may be identified for choosing the lengths of the \vec{v}_i .

POAV1:

$$\vec{v}_1(1) = \vec{V}_1 \quad \vec{v}_2(1) = \vec{V}_2 \quad \vec{v}_3(1) = \vec{V}_3 \quad (4)$$

POAV2:

$$\begin{aligned} \vec{v}_1(2) &= (\cos \theta_{23}) \vec{V}_1 & \vec{v}_2(2) &= (\cos \theta_{31}) \vec{V}_2 \\ \vec{v}_3(2) &= (\cos \theta_{12}) \vec{V}_3 \end{aligned} \quad (5)$$

Real:

$$\vec{v}_1(R) = R_1 \vec{V}_1 \quad \vec{v}_2(R) = R_2 \vec{V}_2 \quad \vec{v}_3(R) = R_3 \vec{V}_3 \quad (6)$$

Substitution of these relations into eqs 1 and 2 leads directly to $\vec{v}_\pi(1)$, $\vec{V}_\pi(1)$ (POAV1), $\vec{v}_\pi(2)$, $\vec{V}_\pi(2)$ (POAV2), $\vec{v}_\pi(R)$, and $\vec{V}_\pi(R)$ (Real). The former four quantities have been discussed previously, but the remaining two vectors are introduced here for the first time. They arise from eq 6, where the generating vectors have their real lengths in some coordinate system; for example, the R_i could be bond lengths to adjacent atoms in angstroms.

In the POAV1 theory, the π -orbital axis vector makes equal angles with the three σ -bonds,^{7,8} so that $\theta_{1\pi} = \theta_{2\pi} = \theta_{3\pi} = \theta_{\sigma\pi}$ and the pyramidalization angle is defined as $(\theta_{\sigma\pi} - 90^\circ)$. In the present context it is convenient to use the following expression

$$\cos \theta_{\sigma\pi} = \vec{V}_1 \cdot \vec{V}_\pi \quad (7)$$

$$= \vec{V}_1 \cdot \vec{a}_{23} / N \quad (8)$$

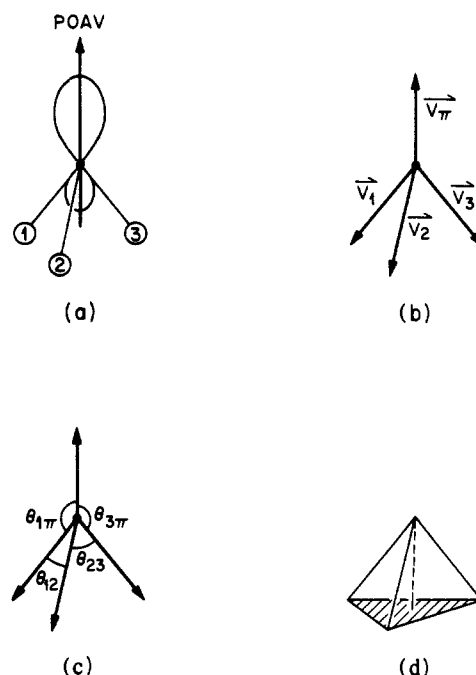


Figure 1. (a) π -Orbital axis vector (POAV) shown for a nonplanar conjugated carbon atom (\bullet) bonded to atoms 1, 2, and 3 (pyramidalization has been exaggerated for clarity). (b) \vec{V}_1 , \vec{V}_2 , and \vec{V}_3 are unit vectors lying along the internuclear axes to the adjacent atoms 1, 2, and 3, whereas \vec{V}_π is the general unit POAV. (c) Four of the six interorbital angles. θ_{12} and θ_{23} are angles among the σ -bonds, whereas $\theta_{1\pi}$ and $\theta_{3\pi}$ are angles between the σ -orbitals and the π -orbital. The remaining two angles (not shown) are θ_{31} and $\theta_{2\pi}$. (d) Tetrahedron of volume T (solid lines), triangle of area A (cross-hatched), and altitude of height H (dashed line), defined in the POAV analysis.

A relationship analogous to eq 8 may be derived in the POAV2 theory, but the three angles $\theta_{1\pi}$, $\theta_{2\pi}$, and $\theta_{3\pi}$ remain distinct in the general case.⁵ When the degree of nonplanarity in nonplanar conjugated organic molecules is compared with POAV2 theory, it appears preferable to focus on the degree of rehybridization as expressed by the s character in the π -hybrid.

As noted in the Appendix, the volume of the tetrahedron (Figure 1d) defined by \vec{v}_1 , \vec{v}_2 , and \vec{v}_3 is given by

$$t = \vec{v}_1 \cdot (\vec{v}_2 \times \vec{v}_3) / 6 \quad (9)$$

From eqs 4–6, it is clear that eq 9 will serve to generate three distinct tetrahedral volumes

$$T(1) = \vec{V}_1 \cdot (\vec{V}_2 \times \vec{V}_3) / 6 = T \quad (10)$$

$$T(2) = -\cos \theta_{12} \cos \theta_{23} \cos \theta_{31} T \quad (11)$$

$$T(R) = R_1 R_2 R_3 T \quad (12)$$

in an obvious notation, where T is taken to be positive.

As noted previously, the π -orbital axis vector (eq 1, Figure 1) is given by the vector area of the triangle (magnitude A) formed by the termini of the \vec{v}_i (the base of the tetrahedron). The areas are given by

$$A(1) = (\vec{v}_\pi(1) \cdot \vec{v}_\pi(1))^{1/2} \quad (13)$$

$$A(2) = (\vec{v}_\pi(2) \cdot \vec{v}_\pi(2))^{1/2} \quad (14)$$

$$A(R) = (\vec{v}_\pi(R) \cdot \vec{v}_\pi(R))^{1/2} \quad (15)$$

The altitudes of the tetrahedra (H) then follow

$$H(1) = 3T(1) / A(1) \quad (16)$$

$$H(2) = 3T(2) / A(2) \quad (17)$$

$$H(R) = 3T(R) / A(R) \quad (18)$$

The real altitude $H(R)$ has been extensively utilized by Bürgi, Dunitz, and co-workers⁹ and given the symbol Δ .

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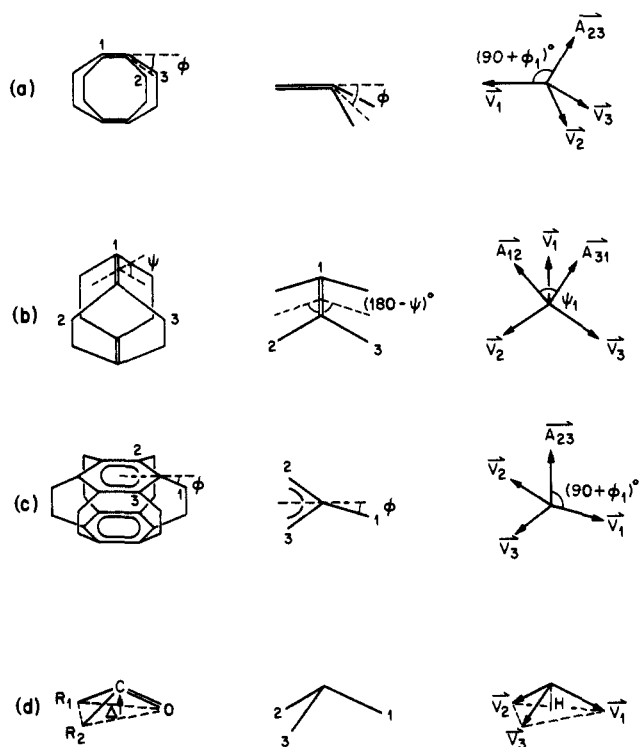


Figure 2. Key: first column, conventional usage of the quantities (a) ϕ , (b) Ψ , (c) ϕ , and (d) Δ ; second column, detail of this construction; third column, reformulation in terms of quantities introduced in this study.

If we define the angle $(90 + \phi_1)^\circ$, as shown in Figure 2, where \vec{A}_{23} is a unit vector perpendicular to \vec{V}_2 and \vec{V}_3 (eq A.6), then

$$\cos(90 + \phi_1) = \vec{V}_1 \cdot \vec{A}_{23} \quad (19)$$

$$= \vec{V}_1 \cdot (\vec{V}_2 \times \vec{V}_3) / \sin \theta_{23} \quad (20)$$

$$= -6T / \sin \theta_{23} \quad (21)$$

Note that an identical relationship may be obtained for ϕ_2 and ϕ_3 by cyclic permutations of the subscripts and that these expressions are independent of the local symmetry.

The angle ϕ has been referred to as the π -pyramidalization angle and employed by a number of groups^{1,2,10-13} in assessing nonplanarity in conjugated organic molecules. The usual constructions are given in Figure 2 and depend on local C_{2v} symmetry at the conjugated atom. Equation 21 may be regarded as a generalization of this treatment; the form of this relationship may be compared with the formula for the σ, π -pyramidalization angle defined in POAV theory (eqs 7 and 8).

The flap or hinge angle Ψ is often used^{1,14-16} in conjunction with the π -pyramidalization angle ϕ and is exemplified in Figure 2.

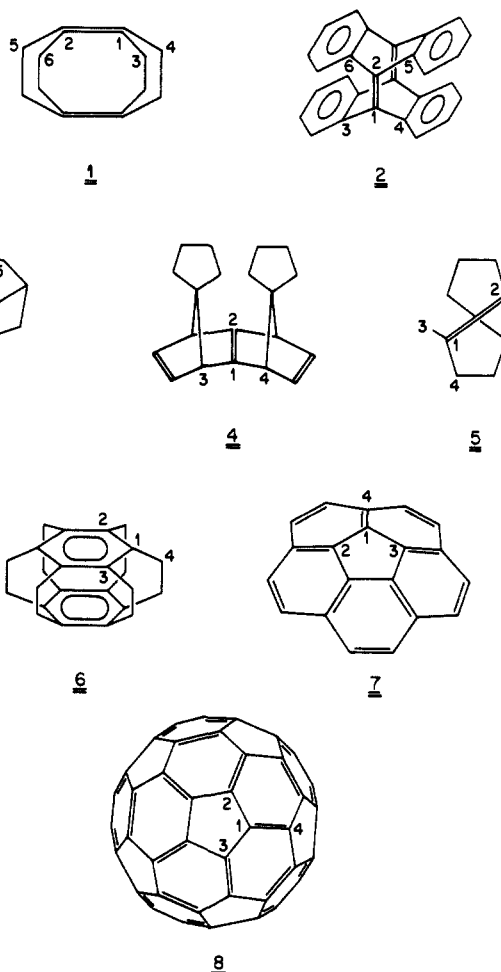


Figure 3. Numbering scheme employed in Table 1.

The two-center dihedral angle across the common bond 1 and between σ_2^A and σ_2^B with centers at atoms A and B may be expressed as¹⁷

$$\cos \tau_{\sigma_2^A \sigma_2^B} = -\vec{A}_{12}^A \cdot \vec{A}_{12}^B \quad (22)$$

The corresponding one-center dihedral angle may be identified with Ψ

$$\cos \Psi_1 = \vec{A}_{31} \cdot \vec{A}_{12} \quad (23)$$

Again, the corresponding quantities Ψ_2 and Ψ_3 may be obtained by cyclic permutation of the subscripts, and the expressions are independent of the local symmetry.

Calculations

Geometries. The model structures C(d) and C(g) refer to diamondoid carbon (tetrahedral sp^3 carbon with three σ -bonds), and graphitic carbon (planar sp^2 carbon), respectively. The bond angles in C_{60} (8, Figure 3)¹⁸ are uniquely determined by the geometry, although the results were checked on two C_{60} structures^{19,20} in the literature. I am grateful to Professor Schulman for supplying the HF/STO-3G structure for 8.¹⁹ The geometry of *trans*-cyclooctene (5) was taken from the gas-phase electron diffraction study by Traetteberg.²¹ All of the remaining structures were obtained by a transformation of the unit cell coordinates obtained by X-ray crystallography. The fractional coordinates and unit cell dimensions of 1,¹² 3,¹³ and 7²² were taken from the literature. I am grateful to Professors Boekelheide, Greene, and Paquette for supplying

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Table I. Pyramidalization Schemes

molec	c	order ^a of subs	bond angles (deg)							bond angles (deg)			angles (deg)			POAV1 tetrahedron			
			substituents			POAV1				POAV2 $\theta_{\sigma\pi}^*$			$(90 + \phi)$		ψ	alt <i>H</i>	area <i>A</i>	vol <i>T</i>	
			θ_{ij}	σ -bonds	$\Sigma\theta_{ij}$	$\theta_{\sigma\sigma}$	$3\theta_{\sigma\sigma}$	$\theta_{\sigma\pi}$	<i>m</i>	$\theta_{\sigma\pi}^*$	<i>m</i>	$(90 + \phi)$	ψ						
C(d)			109.5	109.5	109.5	328.4	109.5	328.4	109.47	0.3333	109.5	109.5	109.5	0.3333	144.7	60.0	0.3333	1.155	0.1283
2	1	2, 3, 4	109.1	118.1	117.7	345.1	115.1	345.2	103.04	0.1201	106.3	101.4	101.2	0.1164	125.9	45.3	0.2256	1.229	0.0924
		1, 5, 6	118.5	109.2	118.1	345.7	115.3	345.8	102.75	0.1142	106.0	101.0	100.9	0.1105	125.2	44.5	0.2208	1.232	0.0906
8	1	2, 3, 4	108.0	120.0	120.0	348.0	116.0	348.1	101.64	0.0928	99.5	99.5	105.5	0.0877	121.7	41.8	0.2018	1.239	0.0833
		1, 2, 3, 4	120.6	110.0	120.6	351.2	117.1	351.3	99.93	0.0653	102.6	98.4	98.4	0.0629	117.4	35.8	0.1724	1.255	0.0721
1	2	1, 5, 6	120.6	110.1	120.7	351.3	117.1	351.4	99.86	0.0643	102.5	98.4	98.4	0.0619	117.2	35.5	0.1712	1.256	0.0717
		1, 2, 3, 4	107.7	122.4	123.1	353.1	117.7	353.2	98.72	0.0494	96.8	96.7	102.1	0.0456	113.6	32.6	0.1516	1.258	0.0636
7	1	2, 3, 4	107.4	138.5	107.7	353.6	118.0	354.1	98.15	0.0427	93.8	99.5	99.6	0.0367	121.7	22.5	0.1417	1.229	0.0581
		1, 2, 3, 4	119.7	117.8	118.2	355.7	118.6	355.7	96.96	0.0308	97.1	97.0	96.7	0.0307	110.9	23.5	0.1213	1.280	0.0517
4	1	2, 3, 4	107.4	138.5	107.7	353.6	118.0	354.1	98.15	0.0427	93.8	99.5	99.6	0.0367	121.7	22.5	0.1417	1.229	0.0581
		1, 2, 3, 4	119.7	117.8	118.2	355.7	118.6	355.7	96.96	0.0308	97.1	97.0	96.7	0.0307	110.9	23.5	0.1213	1.280	0.0517
6	1	2, 3, 4	118.4	115.8	121.9	356.1	118.7	356.1	96.61	0.0276	97.2	95.9	96.6	0.0274	109.1	23.3	0.1151	1.281	0.0491
		1, 2, 3, 4	112.1	133.8	110.9	356.9	119.0	357.0	95.79	0.0210	93.5	96.8	96.5	0.0194	110.7	17.1	0.1010	1.264	0.0425
3	1	2, 3, 4	110.9	138.0	110.1	359.0	119.7	359.1	93.14	0.0061	91.7	93.7	93.6	0.0054	102.0	9.1	0.0548	1.263	0.0231
		1, 2, 3, 4	120.0	120.0	120.0	360.0	120.0	360.0	90.0	0.0	90.0	90.0	90.0	0.0	90.0	0.0	0.0	1.299	0.0
C(g)			120.0	120.0	120.0	360.0	120.0	360.0	90.0	0.0	90.0	90.0	90.0	0.0	90.0	0.0	0.0	1.299	0.0

^a For carbon atom 1 in molecule 2, the order 2, 3, 4 implies pairs of substituents in the order 2,3; 3,4; 4,2 (θ_{ij}) and single substituents in the order 2, 3, 4 ($\theta_{\sigma\pi}$).

data for molecules 6,²³ 2,² and 4,¹ respectively.

Many of the molecules characterized by X-ray crystallography have their gas-phase symmetry lowered by the crystalline environment. In our previous studies^{3,5} we averaged the results of the analyses over symmetry-related atoms and bonds, but in the present work, the results are taken directly from the transformed crystallographic data in order to make the discussion concrete. For molecules 1 and 2, the analyses of the two crystallographically distinct carbon atoms are both reported, whereas for molecules 6 and 7, which possess six and five distinct carbon atoms, respectively, only the results for the most pyramidalized atom are included.

Computational Methods. The equations necessary to effect the analyses derived above were incorporated into the POAV3 program²⁴ and will be made available in the next release.

Results and Discussion

The results of the analysis are collected in Table I; the molecules are listed in descending order of their degree of pyramidalization, as expressed by the quantity $\theta_{\sigma\pi}$. Reference to the table shows that the following measures of pyramidalization exhibit the same monotonic dependence: $\Sigma\theta_{ij}$, $\theta_{\sigma\sigma}$, $\theta_{\sigma\pi}$, $m(\text{POAV1})$, $m(\text{POAV2})$, H , and T . All of these quantities have been introduced in the theory section with the exception of $\Sigma\theta_{ij}$, which is the sum over the bond angles at the conjugated carbon atom ($\Sigma\theta_{ij} = \theta_{12} + \theta_{23} + \theta_{31}$, Figure 1c). In turn, the quantity $\alpha(\text{av})$,²⁵ which in our notation is equal to $1/3\Sigma\theta_{ij}$, is closely related to $\theta_{\sigma\pi}$.²⁵ It may be seen that $3\theta_{\sigma\pi}$ (from POAV1 theory) and $\Sigma\theta_{ij}$ are within 0.1° for all C atoms, with the exception of molecule 4 in which the bond angles (θ_{ij}) are very different.

At this point it is appropriate to divide the pyramidalization schemes according to *isotropy*. The pyramidalization measures that fall in monotonic sequence in Table I are *isotropic*; that is, they do not depend on the selection of a bond, or pair of bonds in their calculations, but weight all three bonds on a reasonably even basis (symmetric with respect to interchange of substituents (labels)). The quantities ϕ and Ψ , however, are not symmetric in substituents (*anisotropic*), and the specification of a bond, or a pair of bonds, is necessary for their definition (eqs 21 and 23). As noted in the introduction, this feature is according to design, as these quantities were introduced in the context of a class of molecules with a unique bond direction for the assessment of pyramidalization.

The anisotropic measures of pyramidalization are therefore suitable for compounds 1–5, which possess a unique path of conjugation, but are less appropriate for molecules 6–8, which have two (6) and three (7 and 8) conjugated bonds to the atom in question. In the case of these latter molecules the values quoted in the table are in accord with standard usage and refer to $(90 + \phi_4)^\circ$ and Ψ_4 (numbered according to structures in Figure 3).

The remaining quantities are calculated as follows: $(90 + \phi_2)^\circ = 110.5^\circ$ (6), 116.9° (7), 125.3° (8); $(90 + \phi_3)^\circ = 110.6^\circ$ (6), 117.1° (7), 125.3° (8); $\Psi_2 = 23.9^\circ$ (6), 28.6° (7), 37.4° (8); $\Psi_3 = 23.8^\circ$ (6), 28.3° (7), 37.4° (8). In this sense, therefore, the anisotropic quantities do not provide a unique measure of the pyramidalization of an atom, and this point is clear from the defining equations (Theory section).

Nevertheless, the pyramidalization sequence given by all of the schemes in the table show a very high degree of correlation, and compound 4 alone is responsible for most of the disagreement. As noted above, this is due to the very different bond angles in this molecule.

Before leaving the discussion of the various measures of pyramidalization in conjugated organic molecules, it is appropriate to turn to a point raised in the introduction:²⁶ the identification of a generally applicable, simple, easily conceptualized parameter for the measurement of the degree of nonplanarity. The last point is the most difficult to assess as it is dependent on the focus of the application, although molecular geometric and electronic structure form the basis for much of contemporary chemistry. The first requirement effectively eliminates the anisotropic quantities (ϕ and Ψ) from consideration as these parameters only apply to a particular class of molecules. The quantity $\Delta(H(R))$ in our notation is dependent on bond length, although $H(1)$ and $H(2)$ remove this objection. Nevertheless the limiting values of these parameters at the tetrahedral geometry are not immediately obvious, and therefore, the degree of pyramidalization is difficult to ascertain. The simplest and most widely available piece of information that pertains to the structure of molecules are the (experimental) bond angles subtended at a given atom (θ_{ij}), and the sum of these quantities ($\Sigma\theta_{ij}$) offers a particularly straightforward approach to the problem. Alternatively, an average bond angle ($1/3\Sigma\theta_{ij}$) may be introduced (α_{av} in the terminology of Nelsen²⁵), and in order to express deviations from planarity this may be cast in the form $(120 - 1/3\Sigma\theta_{ij})^\circ$. The only drawback to this scheme is the focus on the σ -bonds. As its name implies the π -orbital axis vector (POAV) analysis was introduced with the express purpose of providing information about the π -orbitals in nonplanar conjugated organic molecules. For the assessment of geometric structure (pyramidalization), $\theta_{\sigma\pi}$, the σ - π interorbital angle of POAV1 theory is the most generally applicable, simple, and easily conceptualized parameter for the measurement of the degree of nonplanarity, whereas from the standpoint of electronic structure, the s character from POAV2 theory (which is based on the hybridization theory of Pauling) is most appropriate. Both of these quantities are presented in Figure 4 for the structures considered in this paper. The σ - π interorbital angle is displayed in the form of $(\theta_{\sigma\pi} - 90)^\circ$, the σ , π -pyramidalization angle defined for POAV1 theory. The s character of POAV2 theory is represented in the form of the fractional s character of the π -orbital ($m/(m+1)$), hybridization

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(26) This section was added at the request of the reviewers and incorporates some of their suggestions.²⁵

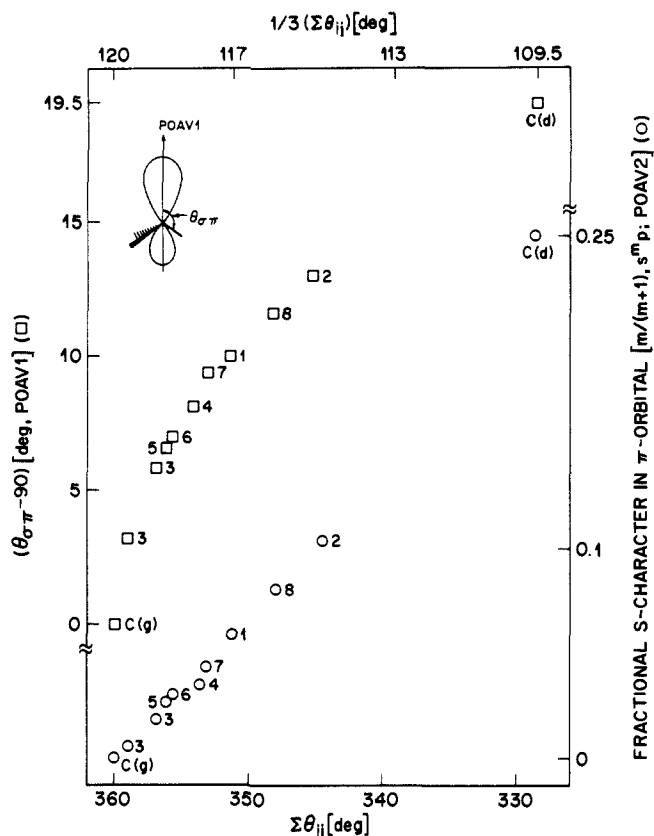


Figure 4. POAV1 σ,π -pyramidalization angle $(\theta_{\sigma\pi} - 90)^\circ$ and POAV2 π -orbital fractional s character $[(m/m + 1), s^m p]$ as a function of the sum of bond angles $(\sum\theta_{ij})$ at the conjugated carbon atom.

$s^m p$), which has been shown to scale with orbital energy in certain compounds.²⁵ It is interesting to note that from the geometric standpoint, the structures of conjugated organic molecules have achieved 67% of the nonplanarity at tetrahedral carbon, whereas from an electronic standpoint this figure is reduced to 42%.

As a final point we speculate on the limits to nonplanarity in conjugated organic molecules. Clearly the answer to this question will be mediated by considerations of resonance, steric hindrance, and reaction pathways available to candidate molecules. As far as gas-phase stability is concerned, it appears that, for the carbon spheroids, the smallest structure attainable falls in the vicinity of C_{32} and C_{28} .²⁷ For these two species, values of $(\theta_{\sigma\pi} - 90)^\circ = 16.0^\circ, 17.1^\circ$ and $(m/m + 1) = 0.1264, 0.1401$ (C_{32}, C_{28}) may be estimated,²⁰ which correspond to 82%, 88% and 51%, 56%, respectively, of the limiting (tetrahedral) values of the geometric and electronic structure measures discussed above.

It was noted in the introduction that the POAV analysis of molecule **2** implies a degree of pyramidalization that is greater than that of all of the structurally characterized molecules yet examined and surpasses the degree of pyramidalization required in icosahedral C_{60} .³ Reference to the table shows that *all other measures of pyramidalization are in concurrence with this assessment*. In the original publication on this compound a pyramidalization angle of $\phi = 19.7^\circ$ ($(90 + \phi)^\circ = 109.7^\circ$) was quoted, and this erroneous value has apparently carried forward through the literature for the past 15 years.

Concluding Remarks

By extending the concept of the π -orbital axis vector, new relationships were obtained for the σ,π -pyramidalization angle of POAV theory. In addition it was shown that the POAV may be written as the resultant of a set of vectors reciprocal to the σ -bonds that gave rise to the idea of a volume, an altitude and a basal area associated with the tetrahedron defined by the σ -bonds of a nonplanar conjugated atom. With these constructs it proved possible to establish relationships between the σ,π -pyramidalization angle of POAV theory and other definitions of pyramidalization. 9,9',10,10'-Tetrahydrodianthracene is established as possessing the most pyramidalized carbon atoms of all structurally characterized molecules. No particular problems are anticipated in the isolation of icosahedral C_{60} .

Appendix

In this section I expand our previous treatment of the π -orbital axis vector (POAV) analysis of nonplanar conjugated organic molecules⁴ so as to make contact with previous treatments of pyramidalization.

As before,^{5,6} let $\vec{V}_1, \vec{V}_2,$ and \vec{V}_3 be unit vectors lying along the three σ -orbitals (taken to be directed along the internuclear axes to the adjacent atoms) radiating from a conjugated atom (Figure 1), and let $\vec{V}_\pi, \vec{V}_\pi(1),$ and $\vec{V}_\pi(2)$ be unit π -orbital axis vectors (general, POAV1 and POAV2, respectively). The corresponding quantities in lower case ($\vec{v}_1, \vec{v}_2, \vec{v}_3, \vec{v}_\pi, \vec{v}_\pi(1),$ and $\vec{v}_\pi(2)$) will be taken to have the same direction as the unit vectors, but with a magnitude to be defined below.

At this point it is useful to introduce a set of reciprocal vectors (\vec{v}_i^*)

$$\begin{aligned}\vec{v}_1^* &= \frac{\vec{v}_2 \times \vec{v}_3}{\vec{v}_1 \cdot (\vec{v}_2 \times \vec{v}_3)} \\ \vec{v}_2^* &= \frac{\vec{v}_3 \times \vec{v}_1}{\vec{v}_1 \cdot (\vec{v}_2 \times \vec{v}_3)} \\ \vec{v}_3^* &= \frac{\vec{v}_1 \times \vec{v}_2}{\vec{v}_1 \cdot (\vec{v}_2 \times \vec{v}_3)}\end{aligned}\quad (\text{A.1})$$

The denominator of eq A.1 is identified as the volume of the parallelepiped defined by $\vec{v}_1, \vec{v}_2,$ and \vec{v}_3 , which is in turn six times the volume of the tetrahedron (t) defined by $\vec{v}_1, \vec{v}_2,$ and \vec{v}_3 (Figure 1d). The numerators of eq A.1 are twice the vector areas of the triangles defined by $(\vec{v}_1, \vec{v}_2), (\vec{v}_2, \vec{v}_3),$ and (\vec{v}_3, \vec{v}_1) and will be denoted by $\vec{a}_{12}, \vec{a}_{23},$ and $\vec{a}_{31},$ respectively (in ref 6, the vector areas were symbolized by $\vec{A}_{12}, \vec{A}_{23}$ and \vec{A}_{31}). Thus

$$\vec{a}_{12} = \frac{1}{2}(\vec{v}_1 \times \vec{v}_2) \quad (\text{A.2})$$

$$\vec{a}_{23} = \frac{1}{2}(\vec{v}_2 \times \vec{v}_3) \quad (\text{A.3})$$

$$\vec{a}_{31} = \frac{1}{2}(\vec{v}_3 \times \vec{v}_1) \quad (\text{A.4})$$

The corresponding unit vectors takes the form

$$\vec{A}_{12} = (\vec{V}_1 \times \vec{V}_2) / \sin \theta_{12} \quad (\text{A.5})$$

$$\vec{A}_{23} = (\vec{V}_2 \times \vec{V}_3) / \sin \theta_{23} \quad (\text{A.6})$$

$$\vec{A}_{31} = (\vec{V}_3 \times \vec{V}_1) / \sin \theta_{31} \quad (\text{A.7})$$

where

$$\cos \theta_{ij} = \vec{V}_i \cdot \vec{V}_j \quad (\text{A.8})$$

and the angles among the σ -orbitals are denoted by $\theta_{12}, \theta_{23},$ and $\theta_{31},$ whereas the angles between the σ -orbitals and the π -orbital are denoted by $\theta_{1\pi}, \theta_{2\pi},$ and $\theta_{3\pi}$ (Figure 1c).

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