

COMMENTS

Comment on the Relationship of the Pyramidalization Angle at a Conjugated Carbon Atom to the σ Bond Angles

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The π -orbital axis vector (POAV) analysis provides a complete description of the electronic structure of nonplanar conjugated organic molecules,¹ and the current interest in fullerenes and carbon nanotubes has led to widespread application of the POAV method.^{2–10} As may be inferred from the name, the method is based on vector algebra, and the equations necessary to solve for the various quantities of interest (pyramidalization angles, dihedral angles, hybridizations, and resonance integrals) are best handled with a PC and the computer program POAV3.¹¹ The only quantities necessary for this analysis are the atomic coordinates of the atoms in the molecule or fragment. Thus, to solve for the pyramidalization angle and hybridization at a single nonplanar conjugated carbon merely requires the atomic coordinates of the conjugated atom and its three attached atoms (denoted 1, 2, and 3).

It has been pointed out that it would be useful to be able to calculate some of these quantities (particularly the POAV1 pyramidalization angle) directly from the three angles made by the σ -bonds (θ_{12} , θ_{23} , θ_{31}) at the conjugated carbon in question. This bond angle information is often available from geometry optimizations or X-ray crystal structures of molecules, whereas the underlying atomic coordinates are not reported.

In POAV1 theory the π -orbital axis vector is defined as that vector which makes equal angles ($\theta_{\sigma\pi}$) to the three σ -bonds at a conjugated carbon atom, and the pyramidalization angle is obtained as $\theta_p = (\theta_{\sigma\pi} - 90)^\circ$ (Figure 1).^{12,13} In the present manuscript we report the solution of the POAV1 equations in the absence of symmetry in terms of the σ -bond angles at a conjugated carbon atom.

For completeness we first give the solutions in the presence of symmetry. In the case of C_{3v} symmetry ($\theta_{12} = \theta_{23} = \theta_{31}$),¹³ the angle made by the π -orbital axis vector to the σ -bonds is given by

$$\cos(\theta_p) = \cos(\theta_{\sigma\pi} - 90) = (2/\sqrt{3}) \sin(\theta_{12}/2) \quad [C_{2v} \text{ symmetry}] \quad (1)$$

For C_{2v} symmetry ($\theta_{12} = \theta_{23}$ and θ_{31} unique),³ this quantity is given by

$$\cos(\theta_p) = \cos(\theta_{\sigma\pi} - 90) = \frac{2 \sin^2(\theta_{12}/2)}{\sqrt{4 \sin^2(\theta_{12}/2) - \sin^2(\theta_{31}/2)}} \quad [C_{2v} \text{ symmetry}] \quad (2)$$

In the general case ($\theta_{12} \neq \theta_{23} \neq \theta_{31}$, all bond angles unique), I first solve for unit vectors along the three σ -orbital directions (taken to be the internuclear vectors), in terms of the σ -bond angles, and then use these vectors in the standard analysis.^{13–15}

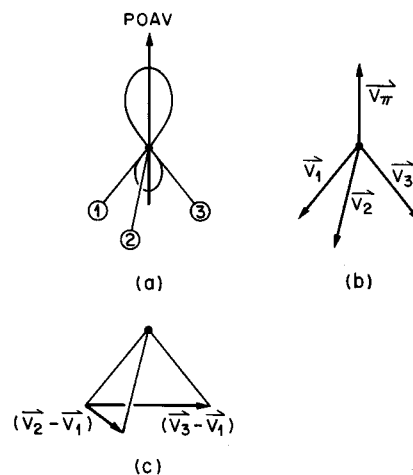


Figure 1. Vector construction of the POAV1 unit π -orbital axis vector (\vec{V}_π). Pyramidalization has been exaggerated for clarity. (a) The π -orbital axis vector (POAV) is shown for a conjugated carbon atom (\bullet) bonded to atoms 1, 2, and 3. (b) \vec{V}_1 , \vec{V}_2 , and \vec{V}_3 are unit vectors lying along the internuclear directions to the adjacent atoms 1, 2, and 3, whereas \vec{V}_π is the unit π -orbital axis vector. (c) A construction for the POAV1.^{12,14}

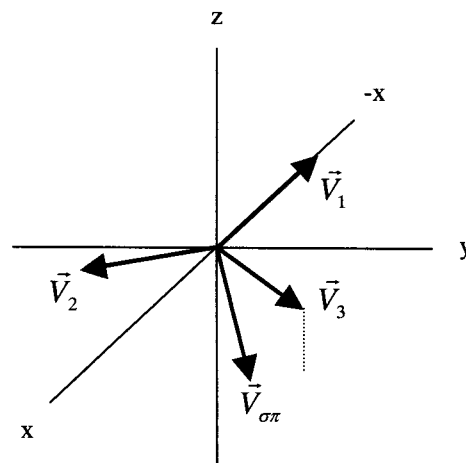


Figure 2. Coordinate system for the construction of the POAV1 π -orbital axis vector (\vec{V}_π) in terms of the σ -bond angles, where \vec{V}_1 , \vec{V}_2 , and \vec{V}_3 are unit vectors lying along the internuclear directions to the adjacent atoms 1, 2, and 3.

We recall that three points define a plane. We define our coordinate system such that the conjugated carbon atom is located at the origin, the first attached atom (number 1) lies along the $-x$ direction, the second attached atom (number 2) lies in the x,y plane (in the fourth quadrant), and the third atom (number 3) lies out of the x,y plane but with projection usually in the first quadrant of this plane (Figure 2). \vec{V}_1 , \vec{V}_2 , and \vec{V}_3 are unit vectors along these three directions, respectively. Let

$$\vec{V}_i = x_i \vec{i} + y_i \vec{j} + z_i \vec{k}$$

and

$$\vec{V}_i \cdot \vec{V}_j = \cos \theta_{ij}$$

Hence

$$\left[\begin{array}{ll} x_1 = -1 & y_1 = 0 \\ x_2 = -\cos\theta_{12} & y_2 = \sin\theta_{12} \\ x_3 = -\cos\theta_{31} & y_3 = (\cos\theta_{23} - \cos\theta_{12}\cos\theta_{31})/\sin\theta_{12} \end{array} \quad \begin{array}{l} z_1 = 0 \\ z_2 = 0 \\ z_3 = \sqrt{1 - \cos^2\theta_{31} - \left[\frac{\cos\theta_{23} - \cos\theta_{12}\cos\theta_{31}}{\sin\theta_{12}} \right]^2} \end{array} \right]$$

We can now form the POAV1 unit π -orbital axis vector (\vec{V}_π) by taking the normalized cross product of two vectors lying in the plane defined by the termini of \vec{V}_1 , \vec{V}_2 , and \vec{V}_3 (Figure 2)¹⁴

$$\vec{V}_\pi = (\vec{V}_2 - \vec{V}_1) \times (\vec{V}_3 - \vec{V}_1) / |(\vec{V}_2 - \vec{V}_1) \times (\vec{V}_3 - \vec{V}_1)|$$

or

$$\vec{V}_\pi = (\vec{V}_1 \times \vec{V}_2) \times (\vec{V}_2 \times \vec{V}_3) \times (\vec{V}_3 \times \vec{V}_1) / |(\vec{V}_1 \times \vec{V}_2) \times (\vec{V}_2 \times \vec{V}_3) \times (\vec{V}_3 \times \vec{V}_1)|$$

Thus

$$\vec{V}_\pi = \frac{(y_2 z_3) \vec{i} - z_3(x_2 - x_1) \vec{j} + [y_3(x_2 - x_1) - y_2(x_3 - x_1)] \vec{k}}{\sqrt{(y_2 z_3)^2 + [z_3(x_2 - x_1)]^2 + [y_3(x_2 - x_1) - y_2(x_3 - x_1)]^2}}$$

and

$$\cos(\theta_{\sigma\pi}) = \frac{\vec{V}_1 \cdot \vec{V}_\pi}{(x_1 y_2 z_3)} = \frac{(x_1 y_2 z_3)}{\sqrt{(y_2 z_3)^2 + [z_3(x_2 - x_1)]^2 + [y_3(x_2 - x_1) - y_2(x_3 - x_1)]^2}} \quad [\text{no } (C_1) \text{ symmetry}] \quad (3)$$

The hybridization of the π -orbital ($s^m p$) is then obtained as before^{12,13}

$$m = 2 \cos^2(\theta_{\sigma\pi}) / (1 - 3 \cos^2(\theta_{\sigma\pi}))$$

and the average hybridization of the σ -orbitals ($sp^{\bar{n}}$) is given by

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

The complexity of these equations makes their application tedious, and for this reason we have made available a Lotus wk1 spreadsheet in which these formulas have been entered. Keying in the three bond angles at a conjugated carbon atom will immediately give the pyramidalization angle and associated quantities. The wk1 spreadsheet was developed on an HP 200 LX PDA and can be opened in virtually any modern spreadsheet such as Lotus or Excel. This spreadsheet can be downloaded free of charge from the web site of Carbon Solutions, Inc. at <http://carbonsolution.com>.

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