

## **$\pi$ -Orbital conjugation and rehybridization in bridged annulenes and deformed molecules in general: $\pi$ -orbital axis vector analysis**

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**Abstract** – The field of bridged annulene chemistry began twenty years ago with the synthesis of 1,6-methanol[10]annulene, and since that time a great many variations on this theme have been reported. By their very nature it is usually impossible for these systems to attain complete coplanarity, and  $\pi$ -orbital misalignment often occurs in the periphery. In many cases these deformations have been confirmed by structural, spectroscopic and theoretical investigation, and it has often been noted that these compounds tolerate remarkably high  $\pi$ -orbital misalignment (as measured by the peripheral dihedral (torsional) angles), without quenching of the cyclic delocalization and aromatic character. It is the purpose of this communication to point out that in nonplanar conjugated molecules: (i) the skeletal dihedral angle may be a poor index of  $\pi$ -orbital alignment; (ii) rehybridization (from  $sp^2$ ) may have a significant effect on  $\pi$ -orbital alignment; (iii) the  $\pi$ -orbital alignment obtained in molecules such as the bridged annulenes is far better than hitherto realized. This process is accomplished by development of a general analytical method for the location of the  $\pi$ -orbital axis vector (POAV) in nonplanar conjugated molecules.

The field of bridged annulene chemistry began twenty years ago with the synthesis of 1,6-methanol[10]annulene,<sup>1</sup> and since that time a great many variations on this theme have been reported.<sup>2</sup> By their very nature it is usually impossible for these systems to attain complete coplanarity, and  $\pi$ -orbital misalignment often occurs in the periphery. In many cases these deformations have been confirmed by structural, spectroscopic and theoretical investigation,<sup>3–28</sup> and it has often been noted that these compounds tolerate remarkably high  $\pi$ -orbital misalignment (as measured by the peripheral (skeletal) dihedral angles), without quenching of the cyclic delocalization and aromatic character.<sup>29</sup>

It is the purpose of this study to point out that in nonplanar conjugated molecules: (i) the skeletal dihedral angle may be a poor index of  $\pi$ -orbital alignment; (ii) rehybridization (from  $sp^2$ ) may have a significant effect on  $\pi$ -orbital alignment; (iii) the  $\pi$ -orbital alignment obtained in molecules such as the bridged annulenes is far better than hitherto realized. This process is accomplished by development of a general analytical method for the location of the  $\pi$ -orbital axis vector (POAV) in nonplanar conjugated molecules.

We begin by noting that in order for the dihedral (torsional) angle to provide a unique and accurate picture of  $\pi$ -orbital alignment, each of the bonded pair of atoms must (separately) lie in the same plane as its nearest neighbors. Thus C1, C2, C3 and R2 (Figure 1) are required to be coplanar, as are C2, C3, C4 and R3 if the dihedral angle (usually taken as C1, C2, C3, C4) is to provide a meaningful index of  $\pi$ -orbital alignment. Clearly as the restriction on coplanarity is removed, the dihedral angle is no longer unique, and in general there exist four possible choices (C1, C2, C3, C4; C1, C2, C3, R3; R2, C2, C3, C4; R2, C2, C3, R3). The point really at issue of course, is the state of hybridization of C2 and C3, and a more fruitful approach is to pursue the  $\pi$ -orbital axis vector (POAV) directly, which is the real quantity of interest in the present context.

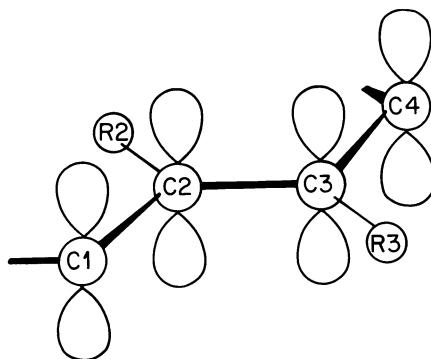


Figure 1. Dihedral angles in conjugated systems.

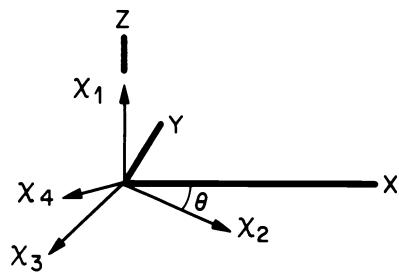


Figure 2. Hybrid orbitals  $\chi_1, \dots, \chi_4$  for hybridization intermediate between  $sp^2$  and  $sp^3$ .  $\chi_1$  is colinear with the  $\pi$ -orbital axis vector and is constructed so as to make an equal inclination to the edges of the trihedral angle formed by  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  and is defined to lie along the  $Z$ -axis.  $\theta$  is the angle of inclination made by  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  to the  $X$ ,  $Y$  plane.

The hybrid orbitals to carbon may be written:

$$\chi_1 = p_z$$

$$\chi_2 = \frac{1}{\sqrt{3}}(s + \sqrt{2}p_x)$$

$$\chi_3 = \frac{1}{\sqrt{3}}(s - \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{3}{2}}p_y) \quad (\text{pure } sp^2)$$

$$\chi_4 = \frac{1}{\sqrt{3}}(s - \frac{1}{\sqrt{2}}p_x + \sqrt{\frac{3}{2}}p_y)$$

and

$$\chi_1 = \frac{1}{2}(s + \sqrt{3}p_z)$$

$$\chi_2 = \frac{1}{2}(s - \frac{1}{\sqrt{3}}p_z + \sqrt{\frac{8}{3}}p_x)$$

$$\chi_3 = \frac{1}{2}(s - \frac{1}{\sqrt{3}}p_z - \sqrt{\frac{2}{3}}p_x - \sqrt{2}p_y) \quad (\text{pure } sp^3)$$

$$\chi_4 = \frac{1}{2}(s - \frac{1}{\sqrt{3}}p_z - \sqrt{\frac{2}{3}}p_x + \sqrt{2}p_y)$$

The general case,<sup>30</sup> for trigonal hybridization intermediate between  $sp^2$  and  $sp^3$ , is depicted in Figure 2, and the hybrid orbitals take the form

$$\chi_1 = As + Bp_z$$

$$\chi_2 = \frac{1}{\sqrt{3}}(Bs - Ap_z + \sqrt{2}p_x)$$

$$\chi_3 = \frac{1}{\sqrt{3}}(Bs - Ap_z + \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{3}{2}}p_y)$$

$$\chi_4 = \frac{1}{\sqrt{3}}(Bs - Ap_z - \frac{1}{\sqrt{2}}p_x + \sqrt{\frac{3}{2}}p_y)$$

where  $A = \sqrt{2} \tan\theta$ ,  $B = (1 - A^2)^{1/2}$  and the  $\pi$  and  $\sigma$  (average group) hybridizations<sup>30</sup> are given by  $m = A^2/B^2(s^n p)$  and  $n = 3m + 2(sp^n)$ , respectively. The  $\pi$ -orbital axis vector is obtained directly from the construction in Figure 2, and when these have been obtained<sup>31</sup> for the conjugated carbon atoms dihedral angles are readily derived which uniquely and accurately reflect the  $\pi$ -orbital alignment within the molecule.<sup>32</sup>

The application of this approach to the calculated structures<sup>28</sup> of 1,6-methano[10]annulene (**1**),<sup>1,2</sup> 1,5-methano[10]annulene (**2**)<sup>29,33</sup> and 1,4,7-methano[10]annulene (**3**)<sup>34,35</sup> is presented in Figures 3 and 4. The calculated geometry obtained for **1**<sup>28</sup> is in excellent agreement with a recent X-ray crystallographic study,<sup>9</sup> and it seems reasonable to assume that the calculated structures of **2** and **3** will prove to be similarly reliable.<sup>28</sup>

The conventional analysis based on peripheral dihedral angles suggests the usual very large values at the bridge positions for the  $\pi$ -orbital misalignment (Figure 3). These values become much more realistic when obtained by the POAV analysis. A very modest rehybridization Figures 4 and 5, is seen to lead to greatly improved  $\pi$ -orbital alignment, particularly in the case of **2** and **3**.

The chemical stability of the compounds is not a good index of the  $\pi$ -orbital alignments in the bridged annulenes (**1-3**) as **1** and **2** are known to possess transannular homoaromatic interactions.<sup>3-29</sup> Nevertheless the observation that **3** forms the first stable higher annulenol is noteworthy.<sup>29a,35,36</sup> Perhaps most relevant in the present instance is the empirical finding<sup>37</sup> that the fraction of the maximum calculated ring current<sup>38</sup> for a [10]annulene is as follows: **1**, 64%; **2**, 66%; **3**, 95%. This sequence is extremely difficult to reconcile with the conventional dihedral angles, but it coincides precisely with that predicted by the POAV analysis.

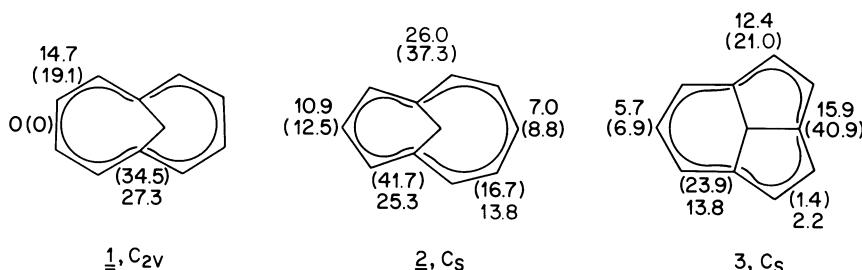


Figure 3. Conventional, peripheral dihedral angles (parenthesized), contrasted with POAV dihedral angles in **1-3**.

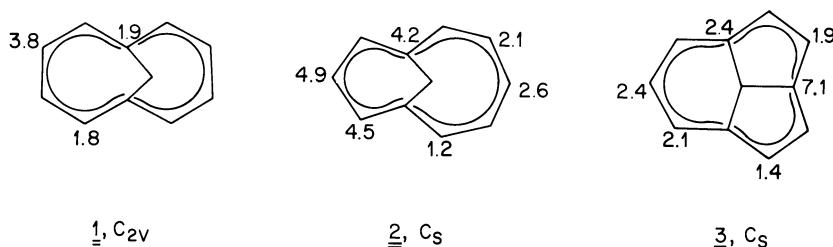


Figure 4. Peripheral angles of inclination ( $\theta$ , degrees) found for **1-3**.

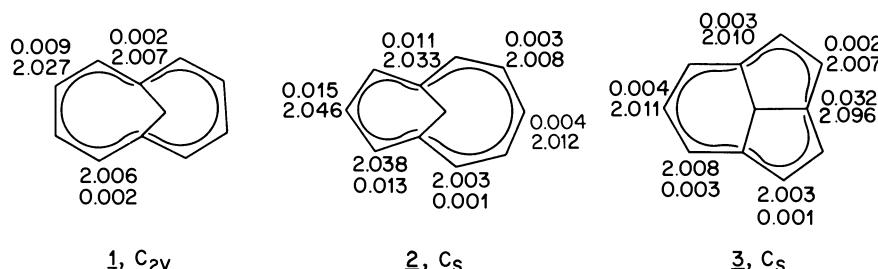


Figure 5. The  $\pi$  ( $s^m p^n$ ) and  $\sigma$  ( $sp^n$ , average group) hybridizations  $m$  and  $n$  calculated for **1-3** from the POAV analysis.

The question of rehybridization in the periphery of the bridged-[10]annulenes was first raised in connection with the interpretation of the photoelectron<sup>18</sup> and electron spin resonance<sup>18,39</sup> spectra of compounds such as **1**, where it was suggested that the  $\pi$ -orbital alignment might be better than indicated by the conventional analysis of peripheral dihedral angles.<sup>18</sup> The POAV analysis bears out this point but indicates that the effect is of even more significance in **2** and **3**.

Rehybridization in conjugated molecules has been mentioned in the literature<sup>40-45</sup> but does not seem to have received the attention it deserves. It seems clear that such effects are likely to be important in deformed conjugated molecules in general.

## APPENDIX

The suggestion that it is possible to construct a vector (POAV) which makes equal angles to three arbitrary vectors originating from a point, has been met with virtually uniform disbelief by our colleagues. This Appendix has been added to clarify the point. We begin by noting that it takes four points to define a sphere.

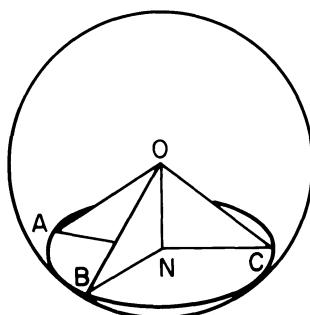


Figure 6. A construction for the POAV.

Consider the atom in question to be located at the center (O) of a sphere with arbitrary radius (Figure 6). Let the points of intersection of the bonds to the substituents with the surface of the sphere be denoted by A, B and C. These three points of intersection with the surface of the sphere define a circle. The vector which is normal to the ABC plane and passes through the center of the circle (N) also intersects the center of the sphere O. This vector is the axis of a right cone with vertex O and base ABC. It is the POAV. The construction is unique and involves no (symmetry) assumptions.

## ADDENDUM

After the completion of this manuscript we became aware of an analysis of bridgehead imines utilizing a similar approach:  
J. G. Radziszewski, J. W. Downing, M. Jawdosiuk, P. Kovacic and J. Michl, *J. Am. Chem. Soc.* **107**, 594 (1985).

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- [30] The problem is treated in  $C_{3v}$  symmetry as the location of the  $\pi$ -orbital ( $\chi_1$ ) axis vector is invariant to the angles made among the  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  vectors, providing  $\chi_1$  (separately) makes equal angles with  $\chi_2$ ,  $\chi_3$  and  $\chi_4$ . Effectively  $\chi_2$ ,  $\chi_3$  and  $\chi_4$  define a right cone and within this degree of freedom the directionality of the hybrids does not change the construction. A further discussion of this point is given in the Appendix.
- [31] The POAV (colinear with  $\chi_1$ ) is readily obtained from the cross-product  $(\lambda_2 - \lambda_3) \times (\lambda_4 - \lambda_3)$  where  $\lambda_2$ ,  $\lambda_3$  and  $\lambda_4$  are unit vectors along  $\chi_2$ ,  $\chi_3$  and  $\chi_4$ , respectively. Dihedral (torsional) angles follow directly: E. B. Wilson, Jr., J. C. Decius, and P. C. Cross "Molecular Vibrations," Dover: New York (1955), p. 60.
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