

C₆₀: Sphere or Polyhedron?

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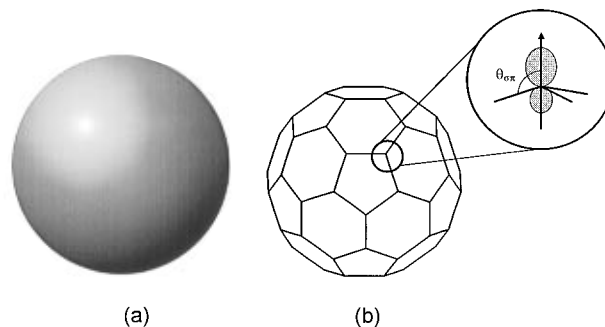
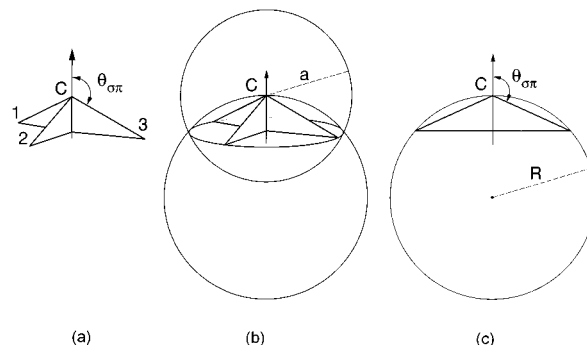
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In the original publication¹ on the subject, C₆₀ was depicted with the aid of a soccer ball, but this representation soon gave way to the familiar line drawing of chemical bonds between nuclei.² To a large extent this dichotomy in the representation of the fullerenes remains today, and it is the purpose of this paper to pose and address the question that appears in the title. Of course, in reality the answer is well-known, and neither the sphere (Figure 1a) nor the polyhedron (Figure 1b) represent C₆₀, which like other molecules exists as a collection of nuclei with an associated distribution of electron density. Nevertheless, it is of interest to consider which of these conventional representations is most relevant for the fullerenes and in particular the language most appropriate to the description of the shape of these molecules and the geometry of the carbon atoms.

The importance of this question is made apparent by an examination of the fullerene and buckybowl literature, in which the terms pyramidalization and curvature are often used interchangeably.^{3,4} The shape of these molecules is often described in terms of curvature, but the definition of this term requires a smooth surface for which a tangent line exists at every point on its graph. Thus, Figure 1a may be ascribed a curvature, whereas Figure 1b has zero curvature along the bonds, but an undefined curvature at the nuclei (vertices). On the other hand, Figure 1b shows pyramidalized carbon atoms, whereas this issue is not raised by Figure 1a. The pyramidalization angle (θ_p) obtained from the π -orbital axis vector (POAV) analysis has been shown to provide a useful index of the degree of nonplanarity and the strain energy at the individual carbon atoms in fullerenes.⁵ Thus, for C₇₀ and C₇₆ where the carbon atoms are no longer all equivalent, this analysis predicts the regio-chemical reactivity⁶ of these compounds toward certain reagents.^{5–7} But even here the POAV pyramidalization angle was referred to as the “local curvature”.⁶ 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 $\theta_p = (\theta_{\sigma\pi} - 90^\circ)$ (Figures 1 and 2).⁸ Thus, implicit in this definition is the assumption that the bonds lie along the internuclear axes, as in Figure 1b.⁹

It is possible to provide a unified approach to this question and to integrate these two descriptions, by a consideration of two important points. First, as noted above, if the method of analysis is to be chemically useful it must be local, and this requires a definition that distinguishes the environments of the individual atoms and bonds. Second, four points in 3D space define a sphere: the four points that will be of interest here are the coordinates of the conjugated atom in question (C) and its

Figure 1. Representations of C₆₀.Figure 2. Construction of the POAV1 pyramidalization angle [$\theta_p = (\theta_{\sigma\pi} - 90^\circ)$] and the local or atomic curvature [$\kappa = 1/R$], at a conjugated carbon atom C.

three directly bonded neighbors (atoms 1–3). With this basis in place we can proceed immediately to a unified approach to the problem, by the construction of two geometrically related spheres (Figure 2).

The POAV1 theory of pyramidalization may be related to the construction of a sphere of arbitrary radius with its center at point C.⁸ The intersection of the three bonds to the neighboring atoms with the surface of the sphere then defines a circle, and this circle together with the center of the sphere leads to a right cone. This cone generates the family of all bond directions for a given pyramidalization angle at the carbon atom C (Figure 2b).⁸

The spherical curvature implied by the carbon atom C and its three neighbors is simply obtained by the construction of that sphere (radius R), which has its surface defined by the coordinates of these four points. The general case is solved below, but for the purposes of illustration a slightly simpler case is treated here and in Figure 2. We set all of the bond

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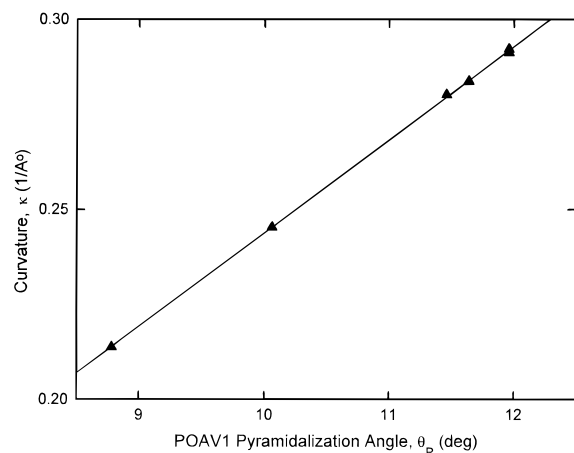


Figure 3. Plot of pyramidalization angle against curvature for C_{60} and C_{70} .

lengths to carbon C to be equal to a and define this to be the unit of radius of the sphere used in the POAV construction. This now leads to the construction shown in Figure 2b, and it is apparent from the orthographic projection of the lower sphere given in Figure 2c that

$$a/(2R) = \cos(180 - \theta_{\sigma\pi}) = \sin(\theta_{\sigma\pi} - 90) = \sin \theta_p \quad (1)$$

where R is the radius of the sphere given in Figure 2c. The curvature κ of this sphere is given by

$$\kappa = 1/R = \frac{2 \sin \theta_p}{a} \approx (2\theta_p)/a \quad (2)$$

Thus, there is an analytical relationship between the local or atomic curvature and the POAV pyramidalization angle for bonds of equal length; eq 2 also gives the relationship between the radii of the two spheres of Figure 2, which are equal when $2 \sin \theta_p = 1$, or $\theta_p = 30^\circ$. The POAV pyramidalization angle is a function of the bond angles at the conjugated carbon atom alone, because the bond lengths are ignored in this treatment. Since the curvature is defined by the real coordinates of all of the atoms, a length scale is implied. Nevertheless, in situations where the bond lengths are similar, the pyramidalization angle provides an index of local curvature as suggested by a number of authors, and it is clearly accurate to characterize the reactivity of the fullerenes in terms of atomic or local curvature. For C_{60} with bond lengths of 1.4 Å, we obtain $\theta_p = 11.64^\circ$, $R = 3.469$ Å, and $\kappa = 0.2882$ Å⁻².

In the general case we cannot use the construction of Figure 2, because with unequal bond lengths the coordinates of the atoms do not fall on the surface of the sphere defined in Figure 2b. Nevertheless the separate components of the Figure may be used to independently solve for the pyramidalization angle and the curvature. The pyramidalization angle is independent of bond lengths and may be found as before. Figure 2c is no longer valid for obtaining the curvature, and the general equation for a sphere must be utilized

$$(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2 = R^2 \quad (3)$$

where x_0 , y_0 , and z_0 are the coordinates of the center of the

sphere. When the coordinates of the four defining points (C, 1, 2, and 3 in Figure 2a) are utilized, a system of nonhomogeneous equations may be solved to obtain x_0 , y_0 , z_0 , and R ($=1/\kappa$), and this procedure has been incorporated into the latest version of the POAV3 program.¹⁰

It is of interest to test how well the relationship holds in practice. Utilizing the HF/3-21G geometry¹¹ for C_{60} with bond lengths of 1.367 and 1.453 (2) Å, we obtain $\theta_p = 11.64^\circ$, $R = 3.524$ Å, and $\kappa = 0.2837$ Å⁻², clearly showing the dependence of curvature on bond length. As a further test, Figure 3 shows a plot of θ_p versus κ for C_{60} and the five different carbon atoms in C_{70} obtained from HF/3-21G geometries.¹¹

An unconstrained fit to these data shows a straight-line correlation coefficient of 0.9999 and gives a line which passes through the origin within the standard error of the fit. The value of the bond length (using eq 2) obtained from the gradient of the line is $a = 1.422$ Å. This result may be compared with the mean bond length of 1.424 Å obtained by averaging over the 18 bond lengths implicit in the definition of the geometries of the six independent carbon atoms used in the plot. Thus, in real situations, irrespective of the symmetry, the pyramidalization angles and curvatures at conjugated carbon atoms are directly proportional to a high order of accuracy.

Given the applicability of both measures of nonplanarity to the geometry of the carbon atoms of the fullerenes, it is now appropriate to turn to the question of which is most suitable for chemical purposes (while recognizing that either one necessarily involves a simplified model representation). Even in the solid state, C_{60} undergoes the rapid rotation expected of a spherical object, but below 260 K the molecule is known to undergo rapid jumps between equivalent orientations.¹² Thus, deviations from the spherical geometry assumed in the above treatment are evident. The chemistry of the molecule originates primarily from the strain present in the aromatic electronic structure.⁵ An important key to the nature of the electronic structure of the fullerenes is provided by the magnetic properties.¹³ Does C_{60} correspond to a spherical benzene? The ring current contribution to the magnetism of benzene is rather well approximated as a free electron circulation of the π -electrons about the 6-fold axis.¹⁴ The diamagnetism of this circulation makes a large contribution to the magnetic properties as the usual counter-vailing Van Vleck paramagnetism is virtually absent in benzene, because the deviations of the response of the electron density distribution from rotational symmetry are very small. The behavior of C_{60} is entirely distinct from this picture. In 3D analogy with 2D benzene, a large diamagnetism is expected due to the free precession of the 60 π -electrons on the surface of a sphere, but this effect is almost completely canceled by the large Van Vleck paramagnetism.^{15,16} The Van Vleck contribution arises as a result of the deviations of the electronic response from spherical symmetry.^{13,15} Thus, the topology of the molecule is paramount, and hence, C_{60} (and the fullerenes) are best modeled as polyhedra.

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