On the Relationship between the Mean Plane and the Least-Squares Plane of an N-Membered Puckered Ring

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Abstract

The role of a reference plane for the description of puckered ring molecules is discussed. Two such planes, the least-squares plane (LSP) and the mean plane (MP), are presented and compared. A simple way of calculating the LSP that avoids the secular equation is given. Conditions under which the two planes coincide are derived. The advantages of the MP approach are stressed.

This communication investigates the connection between two different reference planes used in the study of puckered N-membered ring molecules. One is the N-atom least-squares plane (LSP) (Schomaker, Waser, Marsh & Bergman, 1959; Blow, 1960; Hamilton, 1961; Rollett, 1965; Scheringer, 1971), the other is the mean plane (MP) of Cremer & Pople (1975a) which was introduced in order to generalize a method first suggested by Kilpatrick, Pitzer & Spitzer (1947).

The geometry of a puckered N-membered ring is defined by $3N-6$ parameters, which can be divided into three sets: (1) the N bond lengths; (2) $N-3$ parameters (*e.g.* internal ring angles) describing, if puckering is reduced, the shape of the planar ring; (3) $N-3$ parameters determining the deviation from planarity and the shape of the puckered ring. It seems natural to use the latter set to describe conformational changes of an N-membered ring. Two different ways of deriving the puckering parameters are possible: first, from the z components of the Cartesian coordinates of the ring atoms provided the planar ring is in the xy plane; secondly, from the dihedral angles of the puckered ring. Since in both cases these parameters are N in number, one has to impose three non-arbitrary conditions in order to reduce z coordinates or dihedral angles to $N-3$ non-arbitrary quantities.

In the first case, this is accomplished by introducing the MP (Cremer & Pople, 1975a). The corresponding equations are exact and hold for any puckered N-membered ring. In the case of the dihedral angles,

an exact method for reducing from N to $N-3$ parameters has not yet been found. Only if an infinitesimally puckered ring is considered can conditions similar to those of the concept of the MP be derived (Rao, Westhof & Sundaralingam, 1981). However, as is shown in the Appendix,† the corresponding $N-3$ parameters become meaningless as soon as a ring with finite puckering is considered. We refrain, therefore, from describing puckering by dihedral angles. Instead we proceed by comparing the MP with the LSP.

Calculation of the N-atom least-squares plane (LSP)

In order to determine the LSP the geometrical center of the ring is chosen as the origin of the Cartesian coordinate system. This implies:

$$(\sum \mathbf{r}_i)/N = 0, \qquad (1)$$

where $\mathbf{r}_i$ is the position vector of the ith atom of the ring. Then the symmetric 3×3 matrix T is introduced with elements

$$T_{11}=\sum x_i^2, \quad T_{22}=\sum y_i^2, \quad T_{33}=\sum z_i^2 \qquad (2)$$

$$T_{12}=\sum x_iy_i, \quad T_{13}=\sum x_iz_i, \quad T_{23}=\sum y_iz_i. \qquad (3)$$

T is closely related to the inertia tensor of the ring. Thus, the eigenvector corresponding to the smallest eigenvalue of T will determine the normal to the LSP and, by convention, this is chosen as the direction of the new z axis. The diagonalization of the matrix T involves the solution of a cubic (secular) equation. This is straightforward using the analytical formulas for the roots of a cubic equation (Abramowitz & Stegun, 1965). If, however, $T_{33} < T_{11}$ and T_{22}, which can easily be achieved by starting from MP coordinates, then

$$\mathbf{z} = \mathbf{R}_x \times \mathbf{R}_y/|\mathbf{R}_x \times \mathbf{R}_y|, \qquad (4)$$

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† The Appendix containing an analysis of the Rao, Westhof & Sundaralingam approach, formulas for the solution of the cubic eigenvalue problem, and two examples have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39312 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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with

$$R_x = \sum x_i r_i \tag{5}$$

$$R_y = \sum y_i r_{i}, \tag{6}$$

is a very good approximation to the normal of the LSP. After transforming to a coordinate system with (4) as the z axis one can again form the vectors (5) and (6) and derive a new z axis, *etc.* For most cases three iterations are sufficient to lead to the LSP within an accuracy of 10^{-4} Å.

If the LSP is the xy plane of the coordinate system the z components will obey the following three conditions:

$$\sum z_i = 0, \tag{7}$$

$$\sum z_i x_i = 0, \tag{8}$$

$$\sum z_i y_i = 0, \tag{9}$$

in view of (1) and the diagonalization of T.

The mean plane (MP) of the ring

One can determine the corners of a regular polygon by

$$x_i^r = r \cos[2\pi(i-1)/N], \tag{10}$$

$$y_i^r = r \sin[2\pi(i-1)/N], \tag{11}$$

where r is the radius of the circumscribed circle of the polygon. The MP is defined as that xy plane for which the z components obey the following three conditions:

$$\sum z_i = 0, \tag{12}$$

$$\sum z_i x_i^r = 0, \tag{13}$$

$$\sum z_i y_i^r = 0. \tag{14}$$

These conditions are closely analogous to (7)–(9) for the LSP. If the projection of a puckered ring onto the LSP is a regular polygon, the two planes must coincide. In fact the two planes coincide in a number of other cases too. Since (8) and (9) hold for the replacements $x_i \to ax_i$, $y_i \to by_i$ for arbitrary constants a and b, the LSP will be invariant to such distortions. If the regular polygon is among the distorted geometries, the LSP and the MP will always coincide. Also, if the projection of an even-membered ring possesses D_{mh} symmetry, the products $x_i z_i$ and $y_i z_i$ will cancel pairwise and the MP and LSP will coincide.

The MP can be calculated as the plane with normal vector

$$z = R_1 \times R_2 / |R_1 \times R_2| \tag{15}$$

where

$$R_1 = \sum x_i^r r_i, \tag{16}$$

$$R_2 = \sum y_i^r r_i. \tag{17}$$

The physical meaning of the puckering coordinates and of the MP becomes obvious when considering the out-of-plane deviations of an N-membered ring for $q_m > 0$ and $\varphi_m = 0$ or 90°. The z displacements generated in this way correspond to the genuine out-of-plane vibrational modes of the N-membered ring, of which there exist just $N-3$. Thus, knowing the puckering coordinates of any puckered ring, one can immediately identify the vibrational modes which transform the ring conformation in question back into the planar ring lying in the MP (Cremer, 1980). Given the z coordinates of the LSP, a similar analysis is not possible.

If one wishes to generate the coordinates for several puckered ring conformers for known values of the N bond lengths, the $N-3$ endocyclic bond angles and the $N-3$ puckering coordinates, one proceeds as follows. Values of φ_m are selected corresponding to the puckered forms to be considered. For each φ_m value, the z coordinates are calculated from

$$z_i = (2/N)^{1/2} \sum_{m=2}^{(N-1)/2} q_m$$

$$\times \cos[\varphi_m + 2\pi m(i-1)/N] \quad \text{for odd } N, \tag{18}$$

$$z_i = (2/N)^{1/2} \sum_{m=2}^{N/2-1} q_m \cos[\varphi_m + 2\pi m(i-1)/N]$$

$$+ (1/N)^{1/2} q_{N/2}(-1)^{i-1} \quad \text{for even } N. \tag{19}$$

Then, the projections of the known bond lengths and bond angles onto the mean plane are calculated leading to a new set of $2N-3$ internal coordinates, from which the x_i, y_i coordinates are derived in the usual way. Several authors (*e.g.* Rao, Westhof & Sundaralingam, 1981) have changed the original approach (Cremer & Pople, 1975*b*) by keeping x_i, y_i coordinates constant rather than recalculating them for each conformer considered. This, of course, leads to unpredictable changes in bond lengths, bond angles *and* puckering parameters. Attempts to study conformational processes like pseudorotation with this undue simplification lead to erroneous results, since the new conformers do not belong to the family of conformers described by the original puckering parameters.

Any conformer generated from the same set of N bond lengths, $N-3$ bond angles and $N-4$ puckering parameters while varying φ_m possesses the same MP. *The MP remains fixed for any conformational change of the ring.* This can easily be verified by comparing the normal of the planar ring and the normal of the MP of an arbitrary nonplanar conformer: They are always parallel, pointing in the same direction. If one considers, however, at the same time the LSP, its normal will in general deviate slightly from that of the MP. In the case of pseudorotation it will precess around the normal of the MP.

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Review of the Preferred Rotational Orientation of the Carboxyl and *tert*-Butyl Groups. Structure of *trans*-4-*tert*-Butyl-1-cyclohexanecarboxylic Acid, $C_{11}H_{20}O_2$

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Abstract

$M_r = 184 \cdot 28$, monoclinic, $P2_1/c$, $a = 12 \cdot 303$ (3), $b = 7 \cdot 843$ (2), $c = 11 \cdot 854$ (3) Å, $\beta = 107 \cdot 84$ (2)°, $V = 1088 \cdot 8$ Å^3, $Z = 4$, $D_x = 1 \cdot 128$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 081$ mm^{-1}, $F(000) = 408$, $T = 110$ K. Final $R = 0 \cdot 044$ for 2395 (out of 3161) observed data. A flattening at the *tert*-butyl side and a puckering at the carboxyl side of the ring are observed. The carbonyl O atom of the equatorial carboxyl group is twisted away from the eclipsed position with an α,β bond in the ring by 20·2°, in agreement with the synperiplanar C_β–C_α–C=O arrangement observed for equatorial as well as axial carboxyl groups in several cyclohexanecarboxylic acids and related compounds. The equatorial *tert*-butyl group is twisted away from the perfectly staggered position by about 4°. The off-staggering of the equatorial *tert*-butyl group in several ring structures is described with a Gaussian distribution function $G(\omega, \sigma)$ with $\langle \omega \rangle = 0°$ and $\sigma \simeq 5°$. The broad distribution implies a negligible barrier to rotation of the *tert*-butyl group or a potential energy well with a 'flat' minimum.

Introduction

To explain pK_a differences between variously substituted cyclohexanecarboxylic acids, preferred conformations of the carboxyl group were proposed (Sicher, Tichý & Sipos, 1966a, b; van Bekkum,

Verkade & Wepster, 1966; van Bekkum, 1970): in equatorial and axial carboxyl groups the synperiplanar arrangement H–C_α–C=O and C_β–C_α–C=O should be preferred, respectively. Leiserowitz & Schmidt (1965), Dunitz & Strickler (1968) and Leiserowitz (1976) pointed out that the synperiplanar C_β–C_α–C=O arrangement seems to be a general feature of the molecular shape of α,β-saturated carboxylic acids, whether the carboxyl group is axial or equatorial. However, only two appropriate structures were used to prove this statement with respect to cyclohexanecarboxylic acids. Several crystal structures that bear on this problem have since been studied by X-ray analysis.

The generally accepted perfectly staggered conformation of *tert*-butylcyclohexane is not confirmed by many empirical force-field calculations. Depending on the force field used, the predicted off-staggering is ±17° (Altona & Sundaralingam, 1970), ±15·2° or ±8·4° (van de Graaf, Baas & Wepster, 1978). A recent MM2 force field (Burkert & Allinger, 1982) found the symmetrical geometry (off-staggering = 0°) to be the most stable one. All calculations show anomalous values for the bond angles, bond lengths and torsion angles at the *tert*-butyl side of the ring.

The aim of this investigation was to study the preferred rotational orientation of the carboxyl and *tert*-butyl group by determining the molecular structure of *trans*-4-*tert*-butyl-1-cyclohexanecarboxylic