match no. 20 pp. 289-292 1986

RESEARCH NOTE:

COMPUTATION OF CARTESIAN COORDINATES OF ATOMS ROTATED AROUND AN ARBITRARY BOND

Ivan P. Bangov
Institute of Organic Chemistry,
Bulgarian Academy of Sciences,
Sofia 1040, Bulgaria

(Received: February 1986)

Abstract
An alternative algorithm for computation of Cartesian coordinates of atoms rotated around an arbitrary bond is suggested.

In many cases, e.g. theoretical conformational investigations, use of lanthanide shift reagents etc. calculation of Cartesian coordinates of atoms and groups rotated around a given bond (rotation bond) is required. If this bond lies on one of the axes of the coordinate set, then the problem is trivial:

$$r'(i) = \hat{R}.r(i) \qquad (1)$$

where $\hat{R}$ is the rotation matrix for a bond lying, say, on the Z axis:

$$\hat{R} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & \sin(\theta) \\ 0 & -\sin(\theta) & \cos(\theta) \end{vmatrix} \qquad (2)$$

Here θ is the angle of rotation, r(i) is the initial, and r'(i) the rotated positions of the i-th atom.

More complicated is the problem when the rotation bond is not collinear to any of the coordinate axes. In this case the following orthogonal transformation should be carried out:

$$r'(i) = (\hat{A}^{-1}.\hat{R} \; . \; \hat{A}).r(i) \qquad (3)$$

where $\hat{A}$ is a transformation from the basic frame (the coordinate system that the initial coordinates are obtained in, through any of the existing methods[1-8]) to a frame (x',y',z') whose Z' axis is chosen to be collinear to the rotation bond, and $\hat{A}^{-1}$ is the inverse of $\hat{A}$, coinciding with its transposed in our case of orthogonal transformation. From the Euclidean analytical geometry it is known that the $\hat{A}$ matrix entries are direction cosines of the new coordinate axes with respect to the old ones. Usually they are represented as cosine and sine functions of the Euler angles. In many cases the determination of these angles is unpractical.

Furthermore, an alternative algorithm for evaluation of the $\hat{A}$ matrix elements and hence, for computation of the Cartesian coordinates of rotating atoms and groups is suggested.

Consider the molecular fragment (rotating methyl group) presented in FIGURE 1, where the methyl group is to be rotated around bond a.

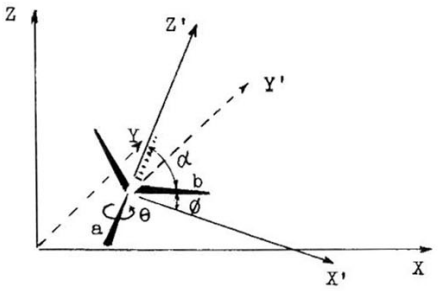

FIGURE 1

Let **b** be a C-H bond of the methyl group. The unit vectors of bonds **a** and **b** are denoted as: r^a and r^b. We place Z' axis of the new coordinate system to coincide with the r^a vector, whence the components $x_i^a(i=1, 3)$ equal a_{3i} entries of the matrix $\hat{A}$. Consequently, one needs the three X' axis components. They could be obtained from the following set of equations:

$$\begin{aligned} (X' \,.\, Z') &= (X' \,.\, r^a) = 0 \\ (X' \,.\, r^b) &= \cos(\emptyset) \\ (X' \,.\, X') &= 1 \end{aligned} \qquad (4)$$

the first and the third one expressing that the axes in the new coordinate system are orthonormal, and the second equation defining the angle between the rotated bond (r^b in our case) and the X' axis. This angle is automatically obtained as $\emptyset = 90^o - \alpha = 90^o - \arccos(r^a.r^b)$ (see FIGURE 1). Thus the X' axis is fixed in the plane determined by $r^a(Z')$ and r^b vectors. From Equations(4) the following expressions for the X' components are derived:

$$x_2' = a_{12} = \frac{(-B \pm \sqrt{B^2 - 4.A.C})}{2.A}$$

$$x_1' = a_{11} = F0 + a_{12}.F1$$

$$x_3' = a_{13} = F2 + a_{12}.F3$$

where

$$A = 1 + F1^2 + F3^2$$

$$B = 2.(F0.F1 + F2.F3)$$

$$C = F2^2 + F0^2 + 1$$

and

$$F0 = (\cos(\phi).x_3^a)/(x_1^b.x_3^a - x_3^b.x_1^a)$$
$$F1 = (x_3^b.x_2^a - x_2^b.x_3^a)/(x_1^b.x_3^a - x_3^b.x_1^a)$$
$$F2 = (-x_1^a.\cos(\phi))/(x_1^b.x_3^a - x_3^b.x_1^a)$$
$$F3=(x_1^a.(x_2^b.x_3^a-x_2^b.x_3^a)-x_2^a.(x_1^b.x_3^a-x_3^b.x_1^a))/(x_3^a.(x_1^b.x_3^a-x_3^b.x_1^a))$$

The components of the Y' axis in the new coordinate system are determined as a vector product of X' and Z' axes:

$$a_{21} = y_i = (X' \times Z')_i$$

Thus, after substituting the a_{ij} entries with their values and performing the transformation (3) the rotated position r'(i) is obtained.

The algorithm is incorporated in CRDN program written in FORTRAN IV. After calculating the unit vectors of the bonds in the starting position of the molecule, the rotation and rotated bonds as well as the step of rotation and lower and upper limits of the angle of rotation are fed into the computer, and the Cartesian coordinates of the rotated atoms are calculated. The program allows to five rotations to be carried out simultaneously.

References

1. H.Eyring, Phys.Rev.,39,746(1932).
2. T.Shimanuchi, and S.Mizushima, J.Chem.Phys.,23,707(1955).
3. P.L.Cullouph and P.E.McMahon, Trans.Faraday Soc.,60,2093 (1964).
4. H.B.Thompson, J.Chem.Phys.,47,3407(1967).
5. R.L.Hilderbrand, J.Chem.Phys.,51,1654(1969).
6. H.B.Thompson, J.Chem.Phys.,53,3034(1970).
7. C.R.Eddy, J.Chem.Phys.,38,1032(1963).
8. H.Essen, J.Comp.Chem.,4,136(1983).