Numerical Study of Tetrahedral Bond Angles

Igor Novak

Department of Chemistry, National University of Singapore, Singapore 119260, Singapore

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The numerical study of tetrahedral coordination has been performed for several possible symmetries. The extreme values for the sum of tetrahedral bond angles was calculated and used to estimate relative stabilities on the basis of VSEPR model.

INTRODUCTION

The tetrahedral or pseudotetrahedral coordination is very important and widespread in chemistry in general and in organic chemistry in particular. In organic molecules, carbon atoms assume tetrahedral coordination provided that carbon is bonded only via single bonds. A possible descriptor of this coordination is the sum $S = \sum\Theta_{ij}$ of six bond angles (Θ_{ij}) subtended by the four vertexes at tetrahedral center. This descriptor serves several purposes, e.g. the calculation of all bond angles if only a few of them have been determined experimentally.[1] Also, it can be used as a basic criterion for checking consistency of experimental and theoretical molecular structures.[2] In the framework of VSEPR model[3] the most probable geometry is the one which maximizes the distances between valence shell electron pairs. In the case of our tetrahedral coordination this implies the maximization of *S* function. We have decided to investigate numerically the boundaries which geometry itself imposes on the *S*.

Changing the magnitude of one of the angles in tetrahedron affects all others, and this purely geometrical constraint is given by the master-equation[4] below (subscripts refer to vertexes):

$$D = \begin{vmatrix} 1 & \cos\Theta_{12} & \cos\Theta_{13} & \cos\Theta_{14} \\ \cos\Theta_{12} & 1 & \cos\Theta_{23} & \cos\Theta_{24} \\ \cos\Theta_{13} & \cos\Theta_{23} & 1 & \cos\Theta_{34} \\ \cos\Theta_{14} & \cos\Theta_{24} & \cos\Theta_{34} & 1 \end{vmatrix} = 0 \quad (1)$$

METHODOLOGY

The global minima or maxima for *S* function cannot be found analytically so a numerical approach was used. We used Mathematica software[5] and standard numerical methods (expressed in Fortan 90 code) to find global minima.[6−8] During the calculations the bond angles were varied $0° < \Theta_{ij} < 360°$, and the angle increments during the numerical search for boundaries of the *S* were 0.01°.

RESULTS

Out of six Θ_{ij} angles only five can be selected independently while the remaining one is then uniquely determined by (1). We shall examine the sets of angles which lead to different spatial (point group) symmetries for each possible case.

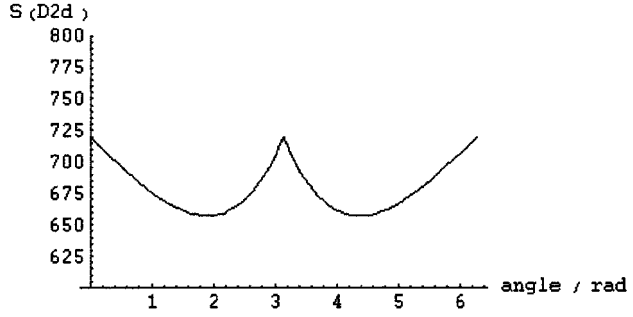

Figure 1.

•When all six angles are equal the coordination has T_d symmetry with $S = 656.83°$.

•With two sets of unequal bond angles there are two possible symmetries: D_{2d} and C_{3v}.

***D*$_{2d}$ Symmetry.** The master equation (angular determinant) becomes

$$\begin{vmatrix} 1 & x & y & y \\ x & 1 & y & y \\ y & y & 1 & x \\ y & y & x & 1 \end{vmatrix} = 0$$

where $\cos\Theta_{12} = \cos\Theta_{34} = x$; $\cos\Theta_{23} = \cos\Theta_{24} = \cos\Theta_{13} = \cos\Theta_{14} = y$ and $S = 2 \text{ arc } \cos(x) + 4 \text{ arc } \cos(y)$. Factorization of the determinant gives the meaningful relationship $y = -(x+1)/2$. Meaningful relationship arises from the constraint that determinantal elements must be real and not constant. Only for T_d symmetry the elements can have constant values.

The plot of angle (Θ_{ij}) vs *S* is shown, and the graph clearly indicates the presence of a global minimum (Figure 1). The minimum has the value $S = 656.83°$ which was established by using Mathematica minimization routine ("FindMinimum").

***C*$_{3v}$ Symmetry.** The angular determinant for this symmetry can be written as

$$\begin{vmatrix} 1 & x & x & x \\ x & 1 & y & y \\ x & y & 1 & y \\ x & y & y & 1 \end{vmatrix} = 0$$

where $x = \cos\Theta_{12} = \cos\Theta_{13} = \cos\Theta_{14}$; $y = \cos\Theta_{23} = \cos\Theta_{24} = \cos\Theta_{34}$, and $S = 3 \text{ arc } \cos(x) + 3 \text{ arc } \cos(y)$.

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Chart 1. Example of Numerical Optimization Code: C_{3v} Symmetry

```
!!c3v symmetry
program tetra
implicit none
  integer :: i
  real :: s, a, x, y
  real, parameter  :: pi = 3.14159265358979323846

s=20

do i=9000,12000

x=i/100
y=acos((3*cos(x*pi/180)**2-1)/2)*180./pi

if ((y-x)==0) then
cycle
end if
if (y<90 .or. y>120) then
cycle
end if

a=3*x+3*y
if (a > s) then
  s=a
end if

end do
write (*,*) "max=", s
stop
end program tetra
```

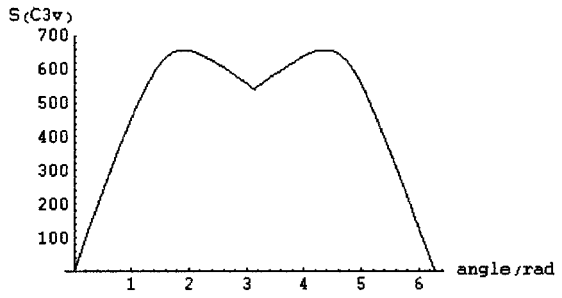

Figure 2.

Expansion and factorization of the determinant gives the sole physically meaningful relationship as $y = (3x^2-1)/2$.

The angular plot is shown below and indicates the existence of global maximum which occurs at $S = 656.83°$ as was established using numerical analysis with Fortran 90 program (see Chart 1 and Figure 2).

•When three sets of unequal angles exist two possible symmetries can be envisaged: C_{2v} and D_2.

***C_{2v}* Symmetry.** The angular determinant can be written as

$$\begin{vmatrix} 1 & x & y & y \\ x & 1 & y & y \\ y & y & 1 & z \\ y & y & z & 1 \end{vmatrix} = 0$$

where $x = \cos \Theta_{12}$; $y = \cos \Theta_{13} = \cos \Theta_{23} = \cos \Theta_{14} = \cos \Theta_{24}$; and $z = \cos \Theta_{34}$. Expansion and factorization of determinant gives $(x-1)(z-1)(x+1-4y^2+z+xz) = 0$ and $z = (4y^2-x-1)/(1+x)$ with $S = \text{arc cos}(x) + 4 \text{ arc cos}(y) + \text{arc cos}(z)$. As 3-D plot indicates there are no global minima or maxima on S surface (Figure 3).

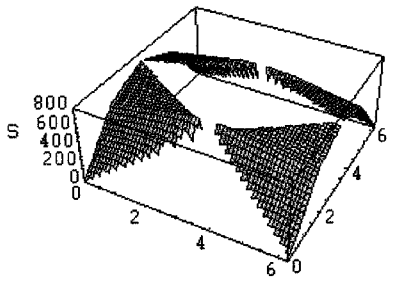

Figure 3.

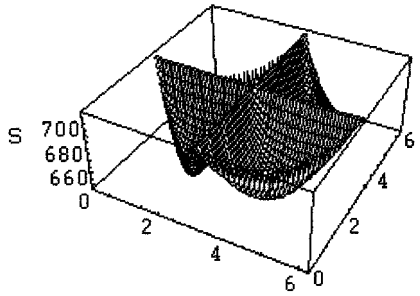

Figure 4.

***D_2* Symmetry.** The angular determinant is

$$\begin{vmatrix} 1 & x & y & z \\ x & 1 & z & y \\ y & z & 1 & x \\ z & y & x & 1 \end{vmatrix} = 0$$

where $\cos \Theta_{12} = \cos \Theta_{34} = x$; $\cos \Theta_{24} = \cos \Theta_{13} = y$; $\cos \Theta_{14} = \cos \Theta_{23} = z$; and $S = 2 \text{ arc cos}(x) + 2 \text{ arc cos}(y) + 2 \text{ arc cos}(z)$. From the determinant $z = -1 - x - y$. The three-dimensional plot of S vs angles shows a minimum at $S = 658.83°$ (Figure 4).

•With four different sets of angles the possible symmetry is C_s.

***C_s* Symmetry.** The angular determinant is

$$\begin{vmatrix} 1 & x & y & y \\ x & 1 & z & z \\ y & z & 1 & w \\ y & z & w & 1 \end{vmatrix} = 0$$

where $x = \cos \Theta_{12}$; $y = \cos \Theta_{13} = \cos \Theta_{14}$; $z = \cos \Theta_{23} = \cos \Theta_{24}$; $w = \cos \Theta_{34}$; and $S = \text{arc cos}(x) + 2 \text{ arc cos}(y) + 2 \text{ arc cos}(z) + \text{arc cos}(w)$. Factorization and expansion gives $w = (1-x^2-2y^2+4xyz-2z^2)/(x^2-1)$. The numerical analysis of S shows that there are no global minima or maxima.

•In the final case when all angles are different the only possible symmetry is C_1.

***C_1* Symmetry.** The angular determinant is

$$\begin{vmatrix} 1 & a & b & c \\ a & 1 & d & f \\ b & d & 1 & e \\ c & f & e & 1 \end{vmatrix} = 0$$

where $a = \cos \Theta_{12}$; $b = \cos \Theta_{13}$; $c = \cos \Theta_{14}$; $d = \cos \Theta_{23}$; $e = \cos \Theta_{34}$; and $f = \cos \Theta_{24}$. This determinant cannot be factorized and gives the polynomial $1 - a^2 - b^2 - c^2 + 2abd - d^2 + c^2d^2 + 2bce - 2acde - e^2 + a^2e^2 + 2acf - 2bcdf - 2abef + 2def - f^2 + b^2f^2 = 0$, while $S = \text{arc cos}(a) + \text{arc cos}(b) + \text{arc cos}(c) + \text{arc cos}(d) + \text{arc cos}(e) + \text{arc}$

cos(f). The physically meaningful solution for f is $f = [bcd+abe-de-ac+(a^2+b^2-1-2abd+d^2)^{1/2}(b^2+c^2-1-2bce+e^2)^{1/2}]$. The numerical study has shown the existence of a maximum $S = 656.83°$.

CONCLUSION

The results are interesting because they indicate relative stabilities of different molecular structures assuming VSEPR model to be valid. Thus for instance relative stabilities decrease in the order $D_{2d} = D_2 > T_d > C_{3v} = C_1$ based on the assertion that maximization of separation between bonding electron pairs reflected in maximization of S leads to improved stability.

Furthermore, the knowledge of the boundaries on S can help in random search methods which are routinely employed in molecular modeling.[9] By utilizing a combined S/VSEPR approach a good initial guess can be made for geometry during the optimization calculations and thus make the calculations more efficient. This approach may be useful for large molecules where such a guess can speed up the convergence.

REFERENCES AND NOTES

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