

# A NEW TYPE OF DIHEDRAL ANGLE FOR THE DESCRIPTION OF BIOMOLECULAR STRUCTURES\*

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## ABSTRACT

In addition to the conventional dihedral angle associated with a sequence of four atoms, a new type of dihedral angle, also associated with four atoms P, Q, R, S, is defined as the angle between the planes containing P, R, S and Q, R, S, when P and Q are both attached to the same atom R. The notation  $\xi$  (P, Q; RS) is adopted for this angle. It is pointed out that the conformational energy of a biomolecule may also contain contributions due to the distortions produced by the changes in rotation angles of the type defined here.

THE use of dihedral angles for the specification of the backbone conformation of neighbouring peptide units was first enunciated by Ramachandran, Sasisekharan and Ramakrishnan<sup>1</sup> in 1963. These angles have been standardized in the rules formulated by the International Union of Pure and Applied Biophysics<sup>2</sup>. According to these rules, a general dihedral angle associated with four atoms A, B, C, D as in Fig. 1 (a) is given by the angle between the two planes containing the atoms A, B, C and B, C, D respectively, the sign of the angle being considered to be positive if the latter plane is obtained from the former by a clockwise direction looking from B to C. The *cis*-convention is used for  $\theta = 0$ , i.e., the torsion angle  $\theta$  is taken to be zero when the atoms A and D in the sequence A—B—C—D are *cis* to each other.

According to the international rules, the terms dihedral angle, rotation angle, torsion angle, are all applicable for the angle  $\theta$  as defined above. It is the purpose of this note to indicate that another type of dihedral angle can be defined for a set of four atoms P, Q, R, S, which are connected by bonds as in Fig. 1(b), which is different from the connectivity adopted in Fig. 1(a). Here the two atoms P and Q are both attached to the atom R which in its turn is connected to an atom S by the bond RS. The relevant angle  $\theta$  is indicated in the figure both in magnitude and sign, and it is the angle between the planes containing P, R, S and Q, R, S respectively. We may define  $\theta$  to be zero in the imaginary situation (as far as

normal organic molecules are concerned) when Q lies in the plane PRS and on the same side of RS as P (P and Q are *cis*) and its sense to be positive if the angle of rotation about RS, looking from R to S, is clockwise for going from the plane containing P to the plane containing Q.

The definitions of the two types of dihedral angles are particularly clear from the Newman projections shown in Figs. 2 (a) and 2 (b). In order to distinguish between the two types, it is suggested that the former may be called 'torsion angle' (symbol  $\chi$ ) and the latter 'rotation angle' (symbol  $\xi$ ). Where the precise nature of the angle is not essential to be defined, both of them could be denoted by the term 'dihedral angle' (symbol  $\theta$ ). If the atoms concerned have to be specified, the detailed form of the torsion angle may be denoted by symbols of the form  $\chi$  (A—B—C—D),  $\chi$  (A, B, C, D) or even briefly as  $\chi$  (A, D). (The symbol  $\chi$  agrees with that used for side-chain torsion angles in the IUPAB rules<sup>2</sup>). Under similar circumstances, the rotation angle may be denoted by  $\xi$  (P, Q; RS) or simply  $\xi$  (P, Q) when the axis of rotation is not in doubt.

The use of the two types of dihedral angles for the specification of the full three-dimensional structure of a molecule may be illustrated by the example of ethane, whose atoms are numbered as in Fig. 3 (a), and shown in a Newman projection in Fig. 3 (b), corresponding to the staggered conformation. Apart from the seven bond lengths and the six bond angles (three at C<sub>1</sub> and three at C<sub>2</sub>) that are normally defined, it is necessary to define five dihedral angles to obtain the total of 18 internal parameters that are required for specifying the conformation of the molecule.

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Using the definitions mentioned above, these are most conveniently represented by the following set:

$$\begin{aligned} \chi(3, 1, 2, 6) \\ \xi(3, 4; 12) \quad \xi(3, 5; 12) \\ \xi(6, 7; 21) \quad \xi(6, 8; 21) \end{aligned}$$

In this set, only one torsion angle is adopted for the rotation about the bond  $C_1-C_2$ , which is the only bond in this molecule that does not have a terminal atom at either end. In the same way, it can be shown that, in a general molecule, having  $N$  atoms, the number of bonds ( $b$ 's) necessary to be included in the list of parameters is  $(N-1)$ , which is readily seen by converting the graph representing the connectivity of the atoms in the molecule into a 'tree'. (See for example the case of cyclohexane shown in Fig. 4). So also the minimum number of bond angles ( $\tau$ 's) required is  $(N-2)$ . As regards the remaining  $(N-3)$  dihedral angles, the minimum number of torsion angles ( $\chi$ 's) that is required is  $n$ , where  $n$  is the number of non-terminal bonds in the tree. The remaining parameters required can all be specified as rotation angles ( $\xi$ 's), whose number is obviously  $(N-n-3)$ .

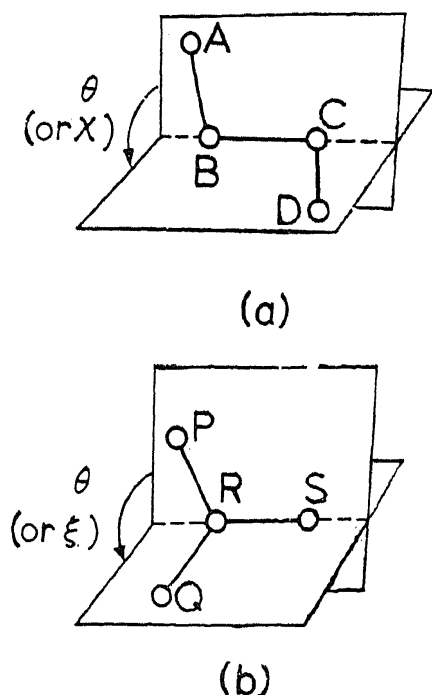


FIG. 1. Diagram showing the definitions of the two types of dihedral angles; (a) Torsion angle  $\chi$  and (b) Rotation angle  $\xi$ .

The above list of internal parameters are those that are required for the complete specification of the three-dimensional structure of the molecule concerned. Actually many more angles can be defined in the molecule—for example  $\chi(C_1, C_2, C_3, C_4)$ ,  $\chi(C_2, C_3, C_4, C_5)$ , or  $\xi(H_{11}, H_{12}; C_3C_4)$  in Fig. 4—which may be required for calculating the total energy of the molecule. The details of these aspects as well as the proof of

the statements made in the previous paragraph will be discussed in a separate communication.

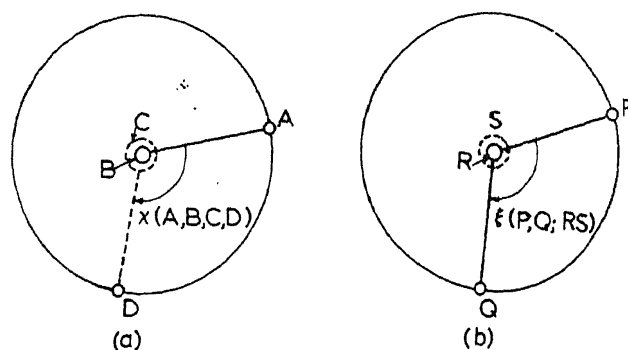


FIG. 2. Newman projections of the conformation of the atoms used in the definition of (a)  $\chi(A, B, C, D)$  and (b)  $\xi(P, Q; RS)$ .

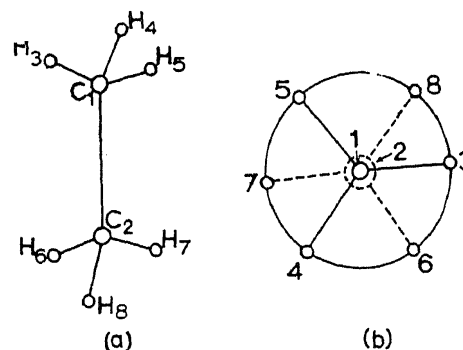


FIG. 3. (a) Perspective diagram of the ethane molecule,  $C_2H_6$ . (b) Newman projection of the atoms contained in the molecule.

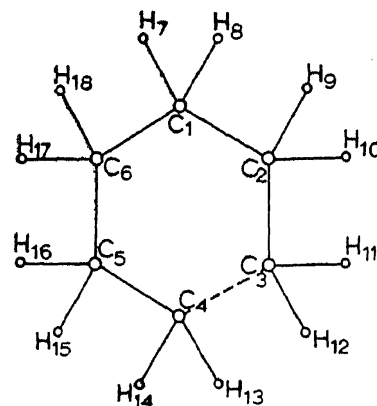


FIG. 4. Schematic diagram of the atoms  $C_1$  to  $C_6$  and  $H_7$  to  $H_{18}$  of the molecule cyclohexane, showing their connectivities. The bond between  $C_1$  and  $C_4$ , shown by dotted lines, has been removed to convert the corresponding graph into a 'tree'.

The fact that the new type of dihedral angle ( $\xi$ ) is required in practical examples is illustrated by the case of the non-planar peptide unit<sup>3</sup> proposed from the author's laboratory. Denoting the atoms in a single peptide unit by the symbols  $C_1, C', O, N, H, C_2$ , the angle  $\theta_N$ , defined therein to indicate the non-planarity of the three bonds meeting at the nitrogen atom, can be described in terms of the rotation angle  $\xi(C_2, H; NC')$ . (See Ref. 3 for diagrams). The relation between  $\xi$  and  $\theta_N$  is

$$\theta_N = 180^\circ - \xi$$

where  $\xi = 180^\circ$  defines the planarity of the peptide unit at the nitrogen atom. This illustrates the great importance of the newly defined dihedral angle for biopolymer conformation. Calculations are under way to work out the contribution to the energies of molecules of interest in biology, associated with both the dihedral angles of the type  $\xi$  and of the type  $\xi'$ .

ACKNOWLEDGEMENTS

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THE ROLE OF 'COSMOLOGICAL CONSTANT' AND f-GRAVITY IN REMOVING GRAVITATIONAL SINGULARITIES

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ABSTRACT

In Trautman's recent model of a universe with  $10^{80}$  spin-aligned neutrons, the usual space-time singularity, which is an inherent feature of isotropic general relativistic cosmologies, and the occurrence of which was hitherto considered inevitable in gravitational collapse, is averted by incorporating torsion effects in the usual Einstein field equations through the Einstein-Cartan gravitational theory. Also in another recent paper Salam *et al.* have investigated the effect of taking f-gravity into account in Trautman's model. However, the severe difficulty of finding a suitable mechanism for aligning perfectly all the nuclear spins of the  $10^{80}$  collapsing hadrons still persists. We suggest an alternative way which does not suffer from this drawback by invoking a "cosmological" constant  $\Lambda$  suitably defined to incorporate short-range f-gravity. It is shown that the singularity is then avoided and the results obtained by the above authors can be reproduced.

It is generally accepted, especially after the work of Penrose and Hawking<sup>1</sup>, that gravitational collapse inescapably leads to space-time singularities. The singularity theorems imply the inevitability of unlimited collapse to a singular state. It was also known from the much earlier work of Oppenheimer and Snyder<sup>2</sup> that the spherically symmetric gravitational collapse of a dust cloud gives rise to a similar singularity. The occurrence of such singularities is an inherent feature of Einstein's general relativity. Again, the usual isotropic evolutionary models of the universe (Robertson-Walker models) are singular, *i.e.*, at some instant of time they pass through a singular state (interpreted sometimes as the 'initial' state in big-bang models) when matter is collapsed to a physically meaningless infinite density. Modified versions of general relativity such as the Brans-Dicke theory also predict such singularities.

However, Trautman<sup>3</sup> has recently indicated that such singularities may be avoided by directly including the influence of spin on the space-time geometry, *i.e.*, by incorporating the effects of

Cartan's torsion in the Einstein-Cartan theory of gravitation, which is a generalization of Einstein's general relativity. This theory which essentially involves the addition of torsion terms to the usual Einstein equations was originated by Cartan<sup>4</sup> and independently worked out by Sciama<sup>5</sup> and Kibble<sup>6</sup>. Here the geometry of space-time is determined by a metric tensor and linear connection fields which are independently varied in the usual Palatini form of the action integral. In the absence of sources the connection reduces to the ordinary Christoffel symbol but with sources included the resulting equations imply an additional torsion term apart from the Riemannian connection. Unlike Einstein's theory the torsion tensor  $\Omega_{\rho}^{\mu}$  is not required to vanish but is related to the density  $S_{\nu\rho}^{\mu}$  of an intrinsic angular momentum source. The field equations then become<sup>6,7</sup>:

$$R_{\mu\nu} - \frac{1}{2} g_{\mu\nu} g^{\rho\sigma} R_{\rho\sigma} = 8\pi G c^{-4} T_{\mu\nu}, \quad (1)$$

$$\Omega_{\nu\rho}^{\mu} + \delta_{\nu}^{\mu} \Omega_{\sigma\rho}^{\sigma} - \delta_{\rho}^{\mu} \Omega_{\sigma\nu}^{\sigma} = 8\pi G c^{-4} S_{\nu\rho}^{\mu}. \quad (2)$$

Here  $R_{\mu\nu\rho\sigma}$  is the curvature tensor formed from the connection,  $R_{\mu\nu} = g^{\rho\sigma} R_{\rho\mu\nu\sigma}$ ,  $g_{\mu\nu}$  is the metric