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

G. N. RAMACHANDRAN** AND A. S. KOLASKAR

*Molecular Biophysics Unit***

Indian Institute of Science, Bangalore-560012, India

AND

RAMESH NARAYAN

Materials Science Division, National Aeronautical Laboratory, Bangalore-560017, India

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 ξ (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[1] in 1963. These angles have been standardized in the rules formulated by the International Union of Pure and Applied Biophysics[2]. 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 θ 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 θ 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 θ 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 θ 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 χ) and the latter 'rotation angle' (symbol ξ). 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 θ). If the atoms concerned have to be specified, the detailed form of the torsion angle may be denoted by symbols of the form χ (A—B—C—D), χ (A, B, C, D) or even briefly as χ (A, D). (The symbol χ agrees with that used for side-chain torsion angles in the IUPAB rules[2]). Under similar circumstances, the rotation angle may be denoted by ξ (P, Q; RS) or simply ξ (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_1 and three at C_2) 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.

* Contribution No. 45 from the Molecular Biophysics Unit.

** Address to which reprint requests are to be sent.

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

χ (3, 1, 2, 6)
ξ (3, 4 ; 12) ξ (3, 5 ; 12)
ξ (6, 7 ; 21) ξ (6, 8 ; 21)

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 (r's) required is (N-2). As regards the remaining (N-3) dihedral angles, the minimum number of torsion angles (χ'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 (ξ's), whose number is obviously (N-n-3).

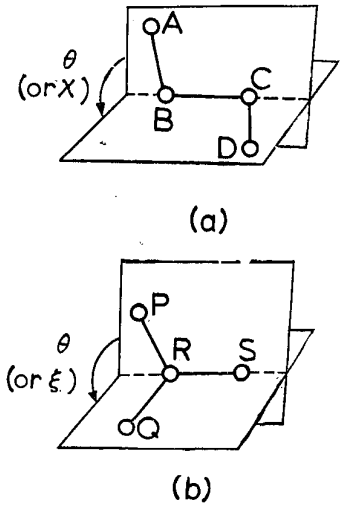

FIG. 1. Diagram showing the definitions of the two types of dihedral angles; (a) Torsion angle χ and (b) Rotation angle ξ.

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 χ (C_1, C_2, C_3, C_4), χ (C_2, C_3, C_4, C_5), or ξ (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.

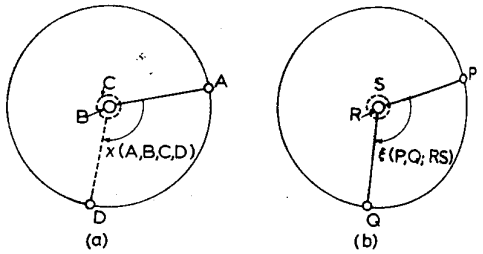

FIG. 2. Newman projections of the conformation of the atoms used in the definition of (a) χ (A, B, C, D) and (b) ξ (P, Q ; RS).

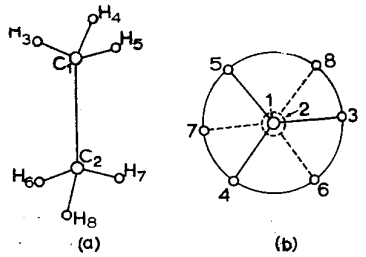

FIG. 3. (a) Perspective diagram of the ethane molecule, C_2H_6. (b) Newman projection of the atoms contained in the molecule.

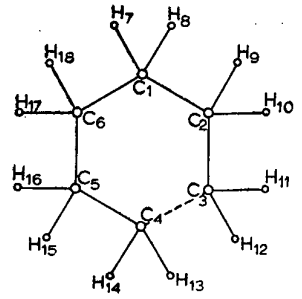

FIG. 4. Schematic diagram of the atoms C_1 to C_6 and H_7 to H_{18} of the molecule cyclohexane, showing their connectivities. The bond between C_3 and C_4, shown by dotted lines, has been removed to convert the corresponding graph into a 'tree'.

The fact that the new type of dihedral angle (ξ) is required in practical examples is illustrated by the case of the non-planar peptide unit[3] 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 θ_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 ξ (C_2, H ; NC′). (*See* Ref. 3 for diagrams). The relation between ξ and θ_N is

$$\theta_N = 180° - \xi$$

where $\xi = 180°$ 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 χ and of the type ξ.

ACKNOWLEDGEMENTS

We wish to acknowledge the support from U.S. Public Health Service Grant AM-15964. One of us (R. N.) is grateful to the National Council of Educational Research and Training, India, for a scholarship.

1. Ramachandran, G. N., Sasisekharan, V. and Ramakrishnan, C., *J. Mol. Biol.*, 1963, 7, 95.
2. IUPAC-IUB, *Commission on Biochemical Nomenclature, Biochemistry,* 1970, 9, 3471.
3. Ramachandran, G. N., Lakshminarayanan, A. V. and Kolaskar, A. S., *Biochim. Biophys. Acta,* 1973, 303, 8.