A New Type of Representation of Dipeptide Conformation

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The possibility of representing the conformations of a pair of peptide units in terms of two parameters, namely angle (ν) between the two peptide planes and the virtual-bond angle δ ($C_{(\alpha)t-1}$, $C_{(\alpha)t}$, $C_{(\alpha)t+1}$), and its usefulness in recognizing unfavourable conformations, is discussed. To exemplify the concept, the local conformations in lysozyme have been plotted in the (ν, δ) plane.

The representation of a pair of peptide units in terms of the dihedral angles ϕ (the rotation around the bond N– $C_{(\alpha)}$) and ψ (around $C_{(\alpha)}$ –C) is fundamental (Ramachandran *et al.*, 1963). Recently some new parameters to represent the chain folding in proteins have been suggested from this laboratory (Srinivasan *et al.*, 1975; Balasubramanian & Srinivasan, 1976). In the present communication, the possibility of representing a pair of peptide units in terms of the angle between the two peptide planes and the angle between the virtual bonds connecting the $C_{(\alpha)}$ atoms is discussed, with special reference to its utility in recognizing unfavourable or non-allowed conformations of a pair of peptide units in the polypeptide chain of protein molecules.

For all practical purposes the peptide units in protein molecules can be considered to be planar, and the angle between the planes of the adjacent peptide units (ν) can be easily calculated (Balasubramanian & Srinivasan, 1976). In a peptide unit, the two $C_{(\alpha)}$ atoms can be assumed to be connected by a virtual bond, and the virtual-bond angle between pair of adjacent peptide units (δ) can also be readily calculated (Balasubramanian, 1976). The values of ν and δ for Pauling–Corey peptide units (Pauling & Corey, 1951) have been shown as equi-value contours in the (ϕ, ψ) plane (Fig. 1). In Fig. 1 the —.—.— contours enclose the area where there are no observed conformations (Pohl, 1971, and personal communication). They can be fittingly called ‘excluded area’ in the (ϕ, ψ) plane. The shape and position of the ‘exclusion’ curve, when compared with the equi- ν and equi- δ contours, immediately suggest that (ν, δ) representation of a pair of peptide units would be interesting and useful.

It is seen from Fig. 1 that the excluded conformations have broadly two characteristics, with

regard to their values of ν and δ : (1) ν lies between -20° and -40° while δ is above 110° ; (2) ν lies between -130° and -180° and also between $+130^\circ$ and $+180^\circ$ while δ is below 85° .

It is readily seen that such a simple compartmentalization of the excluded conformations in the (ν, δ) plane would be quite useful in eliminating impossible conformations of a pair of peptide units in a protein molecule.

In other words, even in the early stages of the refinement of the protein structures, the (ν, δ) values for each pair of peptide units can be calculated, and special attention may be given to (1) those pairs whose ν value is lying between -20° and $+40^\circ$ and δ value is above 110° , and (2) those pairs whose ν value exceeds 130° (ignoring the sign) and δ value is below 85° , and these conformations may be suitably adjusted for further refinements.

The conditions are seen to be very simple and can be easily incorporated in a refinement procedure like that of Diamond (1971).

Here it may be remarked that, although (ν, δ) combination may serve such a purpose, it should be remembered that the (ν, δ) value cannot uniquely specify a particular conformation, in contrast with the (ϕ, ψ) values, which uniquely specify a conformation. For example, the $\nu = 60^\circ$ contour crosses the $\delta = 100^\circ$ contour at two places in the region of $\phi \sim 120^\circ$ and $\psi \sim 0^\circ$.

By taking lysozyme (Blake *et al.*, 1967) as an example, the conformations of pairs of peptide units have been plotted in the (ν, δ) plane and are shown in Fig. 2. In Fig. 2 the rectangular areas of ‘excluded conformations’ are shown hatched.

First, it may be noticed that, as expected, no observed point falls in the hatched regions.

At this stage it may be noted that some of the combinations of ν and δ do not exist for a pair of peptide units. This is clear from Fig. 1. where,

Fig. 1. *Equi- ν , equi- δ and 'exclusion' contours in the (ϕ, ψ) plane*

—, ν contours; ----, δ contours; ·-·-·, 'exclusion' contours.

Fig. 2. *Plot of the conformations of pairs of peptide units of lysozyme in the (ν, δ) plane*

The hatched rectangles (■) correspond to 'excluded conformations'.

for example, the combination of $\nu = 0^\circ$ and $\delta = 80^\circ$ cannot be found. But this has not been explicitly shown in the (ν, δ) plane of Fig. 2, since the peptide units may not always have Pauling-Corey dimensions and the borders in the (ν, δ) plane may not be precisely defined. But, in spite of this, the rectangular hatched regions in the (ν, δ) plane can well be taken as reasonable

boundaries for excluding a conformation in a refinement procedure.

Secondly, a few observations on the distribution of conformations of pairs of peptide units of lysozyme in the (ϕ, ψ) plane may be made.

Conformations having positive ν values are more clustered than those with negative ν values. Those with positive ν values in general correspond to

α -helical region, whereas those with negative ν values in general correspond to extended conformations.

There is a peculiar inverted U-shaped distribution of points (marked as $\cap$ in Fig. 2). On examination, all the points were found to occur in the bridge region of the (ϕ, ψ) map (Ramachandran & Sasisekharan, 1968) having ϕ values around -120° and ψ values around 0° , and this arises because of the degeneracy of the (ν, δ) representation mentioned above.

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