

19.7. NMR SPECTROSCOPY

(Wüthrich & Wagner, 1975) was a genuine surprise for the following reasons. In the refined X-ray crystal structure of BPTI, the aromatic rings of phenylalanine and tyrosine are among the side chains with the smallest temperature factors. For each ring, the relative values of the B factors increase toward the periphery, so that the largest positional uncertainty is indicated for carbon atom 4 on the symmetry axis through the $C^\beta-C^1$ bond, rather than for the carbon atoms 2, 3, 5 and 6 (Fig. 19.7.5.1), which undergo extensive movements during the ring flips. Theoretical studies then showed that the crystallographic B factors sample multiple rotation states about the $C^\alpha-C^\beta$ bond, whereas the ring flips about the $C^\beta-C^1$ bond seen by NMR are very rapid 180° rotations connecting two indistinguishable equilibrium orientations of the ring. The B factors do not manifest these rotational motions because the populations of all non-equilibrium rotational states about the $C^\beta-C^1$ bond are vanishingly small. The ring-flip phenomenon is now a well established feature of globular proteins, manifesting ubiquitous low-frequency internal motions with activation energies of $60\text{--}100\text{ kJ mol}^{-1}$, amplitudes of $\gtrsim 1.0\text{ \AA}$ and activation volumes of about 50 \AA^3 (Wagner, 1980), and involving concerted displacement of numerous groups of atoms (Fig. 19.7.5.1).

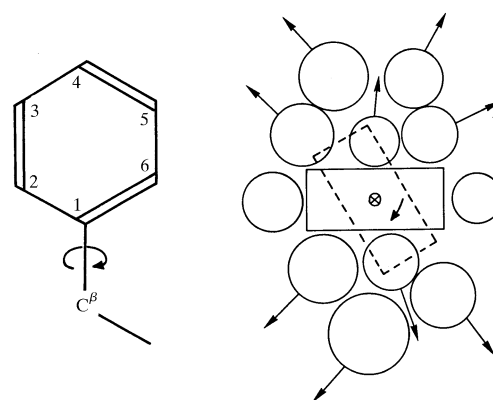


Fig. 19.7.5.1. 180° ring flips of tyrosine and phenylalanine about the $C^\beta-C^1$ bond. On the left, the atom numbering is given and the χ^2 rotation axis is identified with an arrow. The drawing on the right presents a view along the $C^\beta-C^1$ bond of a flipping ring in the interior of a protein, where the broken lines indicate a transient orientation of the ring plane during the flip. The circles represent atom groups near the ring, and arrows indicate movements of atom groups during the ring flip (Wüthrich, 1986).

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19. OTHER EXPERIMENTAL TECHNIQUES

19.2 (cont.)

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