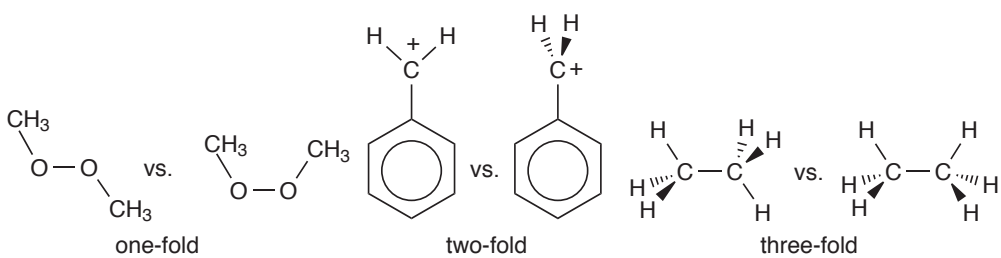
INTERPRETING CONFORMATIONAL PREFERENCES

Rotation about single bonds is periodic, retracing itself every 360°, and any function that seeks to describe the energy of internal rotation must also repeat itself every 360°. In practice, the energy function, $E^{torsion}$, is written as a combination of simpler functions, V_n, in the torsion angle ω, each of which repeats n times in a 360° interval.

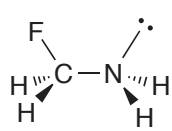
$$E^{torsion}(\omega) = V_1(\omega) + V_2(\omega) + V_3(\omega)...$$

The first three terms, V_1, V_2, and V_3 repeat every 360°, 180°, and 120°, respectively, and are referred to as one-fold, two-fold, and three-fold potentials.*

Separation into distinct n-fold potentials is a useful concept because each can be associated with a particular chemical phenomenon. For example, a one-fold potential describes the different energies of *anti* (COOC=180°) and *syn* (COOC=0°) conformers of dimethylperoxide, while a two-fold potential describes the different energies of planar and perpendicular conformers of benzyl cation. Three-fold potentials, which are more familiar to chemists, describe the difference between staggered and eclipsed conformers in molecules like ethane.

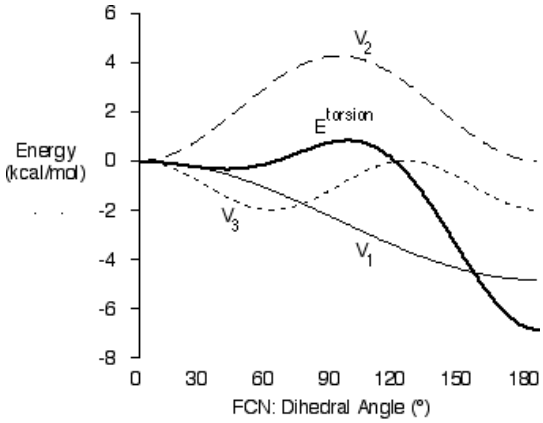


While rotation in some molecules might be adequately described using only one of the components or a combination of two components, other molecules require more complex combination. This is illustrated by fluoromethylamine.

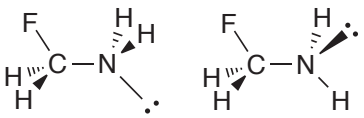


FCN: = 0°

* The torsional potential in most organic molecules will be adequately described in terms of one, two and three-fold components, and only rarely will higher-order terms be needed.



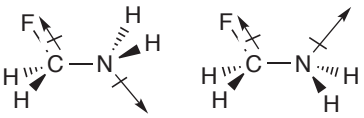
The heavy solid line describes $E^{torsion}$ for rotation about the CN bond, while the light solid line, the dashed line and the dotted line correspond to the one-fold, two-fold and three-fold components, respectively. There are two distinct minima.



FCN: = 180° FCN: ≈ 45°

The lower (global) minimum arises when the CF bond and the nitrogen lone pair are *anti*, while the higher and much more shallow minimum is close to a *gauche* structure, FCN: dihedral angle of ~45°. Also, note that one of the two energy maxima is close to an eclipsed structure, with the FCCN: dihedral angle of ~115°.

The behavior of $E^{torsion}$ becomes clear when it is resolved into its components. The one-fold term reflects a clear and very strong preference for the CF bond and the nitrogen lone pair to be *anti* and not *syn*. This preference might be electrostatic since the *anti* structure arranges the dipoles associated with the CF bond and nitrogen lone pair in opposite directions.

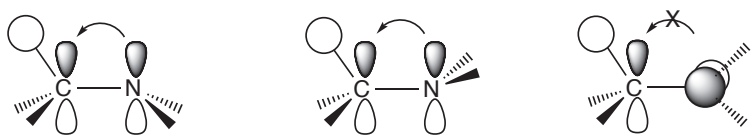


FCN: = 180°
dipoles subtract

FCN: = 0°
dipoles add

The three-fold term reflects the preference for staggered over eclipsed structures, and contributes less to the variation in $E^{torsion}$ than either of the one-fold or two-fold terms.

What is most interesting, and perhaps not have been easily anticipated without this type of analysis, is the large contribution made by the two-fold potential, which reflects a strong preference for a planar arrangement of FCN:. This can be attributed to stabilization resulting from donation of the lone pair orbital on nitrogen into low-energy unfilled molecular orbital associated with the CF bond, requiring that the molecule adopts either a *syn* planar or *anti* planar conformation and not a perpendicular conformation.



syn planar *anti* planar *perpendicular*

Note that the terms that contribute to $E^{torsion}$ are completely independent of each other, and each may be treated as one part of a larger picture. Thus, the observation that electron donation from the nitrogen lone pair into the empty orbital associated with the CF bond is optimal when the two groups are planar is independent of the observation that *cis* coplanar structure is destabilized, relative to the *anti* structure, by dipole-dipole interactions.