steric effect

The effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of *substituents* having different steric requirements. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a *transition state* (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). (The adjective 'steric' is not to be confused with stereochemical.)

Steric effects arise from contributions ascribed to *strain* as the sum of (1) non-bonded repulsions, (2) bond angle strain and (3) bond stretches or compressions.

For the purpose of *correlation analysis* or *linear free-energy relations* various scales of steric parameters have been proposed, notably *A values,* Taft's E_S and Charton's ν scales.

In a reactant molecule RY and an appropriate reference molecule R^oY, the 'primary steric effect' of R is the direct result of differences in compressions which occur because R differs from R^o in the vicinity of the reaction centre Y. A 'secondary steric effect' involves the differential moderation of electron delocalization by non-bonded compressions.

Some authors make a distinction between 'steric' effects attributed to van der Waals repulsions alone, and 'strain' effects, attributed to deviations of bond angles from 'ideal' values.

See *Taft equation, van der Waals forces.*

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