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PYRAMIDAL INVERSION BARRIERS: THE SIGNIFICANCE OF GROUND STATE GEOMETRY

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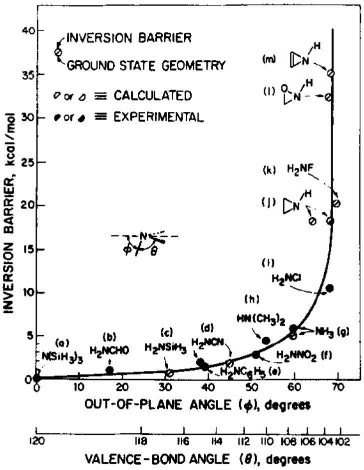
We wish to present an empirical scheme which provides a convenient method for correlating inversion barriers at nitrogen with ground state geometries.

It is generally recognized that the magnitude of the barrier to inversion in pyramidal molecules is, at least in part, a function of ground state valence-bond angles (1). Structural features such as the presence of conjugating substituents, which effect an increase in these bond angles, will also tend to decrease the inversion barrier, whereas factors such as the incorporation of the inversion center in a small ring system, which effect a decrease in the valence-bond angles, will tend to increase the magnitude of this barrier. This relationship is displayed in Figure 1, a plot of nitrogen inversion barrier vs. the out-of-plane angle, φ, in the pyramidal ground state. For compounds of the type A_2NX, where A_2 may represent the termini of a ring system, φ is defined as the angle between the extension of the N-X bond axis and the bisector of the ANA angle. The angle φ is a convenient measure of the "pyramidality" of a tri-coordinate system, since it increases with this property and a value of 0° corresponds to planarity. The valence-bond angles of the acyclic amines under consideration may be treated approximately as equal (i.e., C_{3v} symmetry), and in this case φ is a simple, non-linear function of the valence bond angle, θ. Values of θ derived in this manner are included with given φ values on the abscissa scale of Figure 1. The selection of data (2) for this plot is limited to systems in which the requisite information on both barrier height and geometry is available from experimental or theoretical studies. Moreover, calculated values are restricted to those obtained by non-empirical LCAO-MO-SCF methods which give reliable geometries as well as barriers.

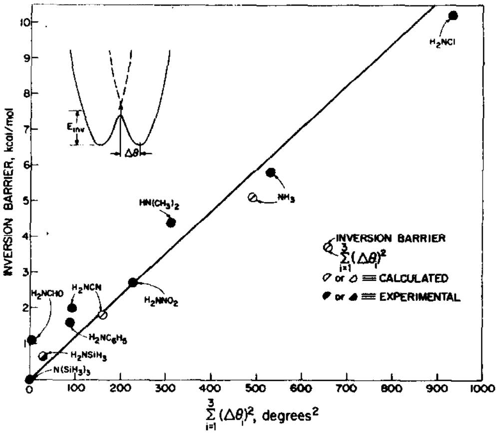
Figure 1



As a convenience in discussion, Figure 1 may be divided into two distinct regions. The first of these encompasses molecules with inversion barriers of less than about 10 kcal/mol. In this region, small variations in E_{inv} are accompanied by large changes in φ. As indicated in Figure 2 (3), the barrier height (E_{inv}) within this region is roughly a linear function of $\sum_{i=1}^{3} (\Delta\theta_i)^2$, the sum of the squares of the deformations which occur in each of the three valence-bond angles in going from the ground state to planarity (4). Accordingly, the relation between inversion barrier and extent of angular distortion in this region may be described, to a first approximation, as harmonic (equation 1). The existence of such a harmonic relation may also be inferred, for a three-fold rotor, from examination of the simplified model for the inversion process described by Kincaid and Henriques (5), and implies that for molecules in this region, E_{inv} is largely a function of ground state geometry (inset, Figure 2). Despite the expected variation in the effective angle-bending force constant, k_θ, among the variety of compounds plotted in Figure 2, and despite the anharmonicity in the potential functions of the real inversion process, the value for k_θ of 0.023 kcal/mol-degree^2 derived from the slope is in remarkably good agreement with the corresponding value for ammonia, 0.022 kcal/mol-degree^2 (6), a typical compound in this region.

$$E_{inv} = (k_\theta/2) \sum_{i=1}^{3} (\Delta\theta_i)^2 \qquad \underline{\text{eq. 1}}$$

Figure 2



For molecules belonging to the second region of Figure 1, with barriers above the knee at *ca.* 10 kcal/mol, large changes in E_{inv} are accompanied by negligible changes in φ, *i.e.*, ground state geometries are substantially independent of the corresponding inversion barriers. This difference in behavior between the two regions may be rationalized as follows. Successive incorporation of ligands which favor greater p-character in the bonding orbitals of the inversion center tends to induce greater pyramidality in the ground state and thus raises the inversion barrier; however, as the limiting pyramidal geometry (7) is approached, further incorporation of such ligands serves mainly to increase the relative stability of this limiting structure. As observed in the second region of Figure 1, an increase in E_{inv} is thus effected without accompanying changes in θ, *i.e.*, θ approaches a limiting value of *ca.* 102°, and further increases in barrier height are effectively a function of the angle-bending force constant. A striking example of the insensitivity of ground state geometry to inversion barrier is found in the symmetrically substituted phosphines: the bond angles in trifluorophosphine (8) and trisilylphosphine (9) are found to be identical ($\theta = 97^\circ$) within experimental error, despite the fact that a huge difference (greater than 50 kcal/mol) is expected (10) in the pyramidal inversion barriers. Phosphines may be assumed to exhibit behavior similar to that shown in Figure 1, but the position (E_{inv} and θ) of the corresponding knee is unknown.

It is apparent that nitrogen systems with θ_{av}, the averaged valence-bond angles (4), greater than *ca.* 104° (out-of-plane angles smaller than *ca.* 65°) have inversion barriers which may be conveniently estimated (Figure 1) from ground state geometries. This empirical relation may thus be employed to supplement existing theoretical and experimental methods for the evaluation of low inversion barriers (1).

The same relationship also indicates that molecules whose gas phase geometries have θ_{av} greater than *ca.* 110° (φ less than *ca.* 55°) may suffer significant pyramidal deformation at a low cost in energy (less than 5 kcal/mol). For example, the reported (11) value of $\varphi = 32^\circ$ for dimethylaminodifluorophosphine allows an estimate (Figure 1) of 1.5 kcal/mol for E_{inv}. It also follows that these are the molecules most likely to have their pyramidality in the crystalline state determined by lattice packing forces; thus, dimethylaminodifluorophosphine is planar at N in the crystalline state (12). Similarly, in formamide, the molecule has been shown to be more pyramidal in the gas phase (2b) than in the solid phase (13), and N-methylacetanilide, which is planar in the solid phase (14), appears to be pyramidal in the gas phase (15). This type of behavior is reminiscent of the phase-dependent geometry of biphenyl, a molecule which is planar in the crystalline state (16), but which is twisted in the gas phase, with a dihedral angle between the phenyl planes of 45° (17). The difference in energy between the two forms of biphenyl has been estimated to be less than 1 kcal/mol (18).

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