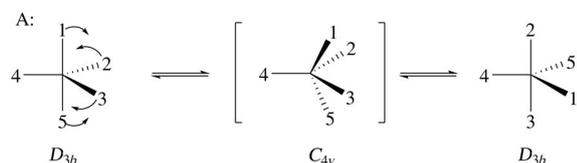


Stereomutation in Trigonal-Bipyramidal Systems: A Unified Picture

Christina Moberg*

fluxionality · phosphorus · pseudorotation · trigonal bipyramids · turnstile rotation

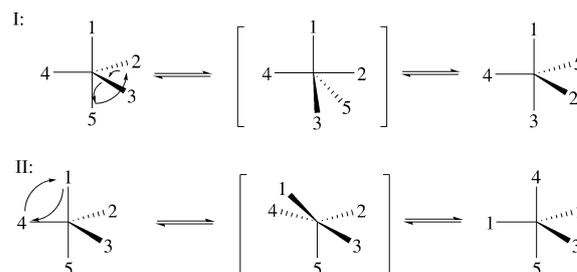
The mechanism responsible for interconversion of axial and equatorial ligands in pentavalent bipyramidal structures has intrigued scientists ever since the discovery of the fluxional behavior of PF_5 in solution.^[1] Numerous trigonal-bipyramidal structures with P, Si, and transition metals as central atoms are now known to undergo stereomutations in the same way as PF_5 . In 1960 Berry proposed a mechanism for the rearrangement by which the D_{3h} structures (for the case of five identical ligands) interconvert via a square-pyramidal C_{4v} transition state, and with at least C_{2v} symmetry maintained throughout the entire process (Scheme 1).^[2] Four out of the five substituents are involved in the rearrangement, the fifth group serving as the pivot. The Berry pseudorotation (BPR) mechanism later also gained firm experimental support.^[3] That MX_5 structures representing gradual deformations from D_{3h} to C_{4v} symmetry fall along the Berry coordinate provides further credibility to the mechanism.^[4]



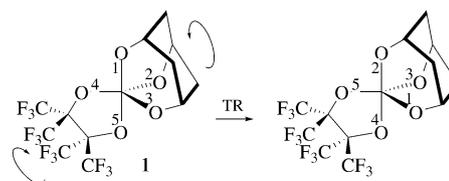
Scheme 1. Berry pseudorotation, with ligand 4 serving as pivot.

Muetterties later identified additional permutation mechanisms, two of which proceed via planar transition states and are therefore highly unlikely.^[5] The experimentally most likely alternatives to BPR are those shown in Scheme 2. They both proceed via C_1 - or C_3 -symmetric transition states.

Yet another mechanism was suggested by Ugi et al., who found that Berry's pseudorotation mechanism was unfeasible for the bridged system he studied (Scheme 3, **1**). Based on group theory arguments, he proposed a turnstile rotation (TR) mechanism, whereby three of the five groups rotate by 60° relative to the remaining two groups.^[6] Ugi's turnstile



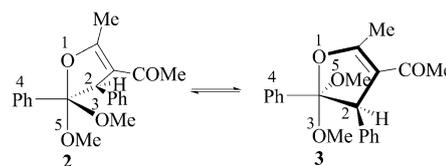
Scheme 2. Mechanisms for isomerizations suggested by Muetterties.



Scheme 3. Ugi's turnstile rotation (TR) mechanism.

rotation exchanges apical and equatorial substituents in a pairwise manner, and is also in agreement with experimental data, but unlike BPR, TR involves an external rotation, and the transition state has lower symmetry. Ugi concluded that BPR might be the preferred exchange mechanism in some systems, whereas TR is favored in cyclic molecules as well as in some other systems.

Studies of bridged structures have provided additional information on trigonal-bipyramidal stereomutations. Gorenstein and Westheimer studied the interconversion of **2** and **3** (Scheme 4).^[7] They noted that the process resembles Muetterties' mechanism I (Scheme 2), in which one axial



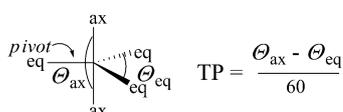
Scheme 4. Interconversion of **2** and **3** can occur via Muetterties' mechanism I but was suggested to proceed by four consecutive Berry pseudorotations.

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and one equatorial position are fixed while the remaining three rotate. However, they suggested an alternative mechanism, consisting of four consecutive Berry pseudorotations.

This suggestion has gained support from a recent report by Couzijn, Lammertsma, and co-workers, who studied the different mechanisms theoretically.^[8] The authors described the geometry around the five-coordinate atoms using internal coordinates, by which any external reorientations could be neglected. A crucial parameter that defines the motion along the Berry coordinate is the topology parameter, TP, defined in such a way that TP = 1 for an ideal trigonal bipyramid and TP = 0 for the square pyramid (Scheme 5). For BPR, TP decreases linearly along the reaction coordinate from 1 to 0 as the transition structure is reached, then increases to 1. The same general mechanism was found for [Fe(CO)₅] and PF₄Cl, although the latter can undergo two types of rearrangements, one of which is non-degenerate.



Scheme 5. Definition of the topology parameter TP.

The authors also computed the stereomutation of Ugi's structure **1**. They found a single V-shaped graph for the topology parameter, that is, the same topology as found for PF₅, albeit comprising less symmetrical structures. The permutational and topological equivalence of the two mechanisms has been pointed out previously,^[9] but has now been convincingly demonstrated. The previously experimentally determined rather high energy barrier for stereomutation of **1** was shown to originate from torsion of the central bond of the five-membered ring; instead the barrier for rearrangement was shown to be exceedingly low owing to relief of strain in the transition state. The authors thus concluded that the BPR and TR mechanisms merely describe alternative model motions for the same general mechanism.

An analogous analysis of Muetterties' mechanism I resulted in a double V-shaped curve for the topology parameter (from 1 via 0, 1, and 0 to 1), corresponding to two consecutive

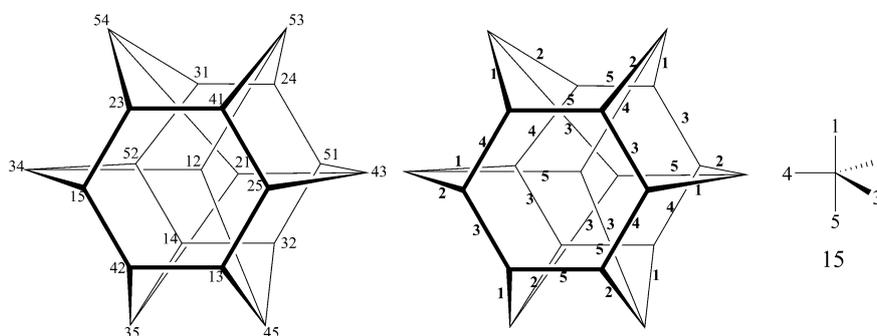
BPRs, although with a single energy barrier. Muetterties' mechanism II was shown to correspond to three consecutive BPRs, with a triple V-shaped curve for the topology parameter, again with a single energy barrier (or a barrier with a shallow minimum).

How do these new results cope with the suggestion by Gorenstein and Westheimer? To answer this question it is instructive to use graph theory. Mislow illustrated all possible interconversions by using a Desargues–Levi graph, with each of the 20 vertices representing each of the 20 permutational isomers of a trigonal-bipyramidal system, and the edges representing the pivots for the actual transformations (Scheme 6).^[10] As each bipyramidal structure has three equatorial substituents that can serve as pivots, three permutations leading to three different isomers are in principle possible. The number of edges that need to be traveled along in going from one isomer to another equals the number of Berry pseudorotations needed for the transformation, provided that the intermediates have sterically and electronically viable structures. The energy is minimized when the most electronegative groups occupy apical positions, and rearrangements via such intermediates are therefore favored.

Muetterties' mechanism I corresponds to a path from 15 to 13 (see Scheme 2 and Scheme 6), and thus comprises two BPRs (15 to 13 via 42), corresponding to the double V-shape curve of the topology parameter.^[8] The interconversion of **2** and **3** also corresponds to a transformation of 15 to 13. However, the path via isomer 42 is in this particular case energetically unfeasible since this isomer is destabilized owing to three electronegative elements in equatorial positions, and the route via 23–41–25 is therefore preferred. The interpretation of the transformation as a sequence of four BPR by Gorenstein and Westheimer^[7] has gained support from the present study.^[8]

Muetterties' mechanism II (Scheme 2) comprises a transformation of 15 to 45, and thus corresponds to three BPRs (via 42 and 13; Scheme 6), in line with the change of TP along the reaction coordinate, albeit with a single energy barrier.

In conclusion, Couzijn, Lammertsma, and co-workers have demonstrated that the Berry pseudorotation and the Ugi turnstile mechanisms are equivalent. They seem different because although one equatorial substituent necessarily has to remain equatorial, all five substituents are affected in the



Scheme 6. Desargues–Levi graph with vertices representing the isomers (left) and edges showing the pivots (middle). The isomers are labeled after the apical substituents in such a manner that the numbers of equatorial substituents increase in clockwise sequence when viewed from the first apical substituent (right).

latter. The two mechanisms suggested by Muetterties have different energy profiles, but the topology is the same as that for pseudorotation. The authors finally suggest that Muetterties' mechanism I should be named turnstile rotation as this mechanism, in contrast to that suggested by Ugi, represents the movement of a true turnstile. The authors have convincingly demonstrated that the Berry pseudorotation is the fundamental mechanism by which interconversion of penta-valent isomers proceed.

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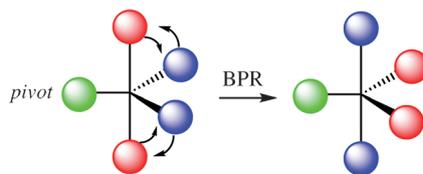
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Highlights

Pseudorotation

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Same difference: Berry pseudorotation (BPR) and Ugi turnstile rotation, which are generally treated as two distinctly different mechanisms for rearrangement of trigonal-bipyramidal structures, have been shown to be equivalent. Alternative mechanisms consist of sequences of pseudorotations proceeding in a single step.