

# Berry Pseudorotation and Turnstile Rotation

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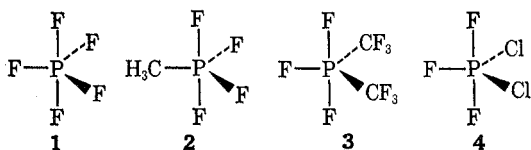
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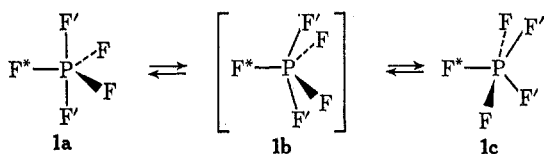
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Trigonal-bipyramidal structures are indicated for PF<sub>5</sub> (1) and CH<sub>3</sub>PF<sub>4</sub> (2) by electron diffraction data,<sup>2,3</sup> for (CF<sub>3</sub>)<sub>2</sub>PF<sub>3</sub> (3) by ir and Raman spectra,<sup>4</sup> and for PCl<sub>2</sub>F<sub>3</sub> (4) by chlorine nuclear quadrupole resonance data.<sup>5</sup>



There are differences in the apical and equatorial F-P bond lengths in molecules 1-4.<sup>2,3</sup> However, in spite of the nonequivalence of the two positions in the trigonal bipyramid, these compounds show only one <sup>19</sup>F nmr signal at temperatures above 25°; this implies very rapid interchange of apical and equatorial fluorine atoms.<sup>6,7</sup> When Berry observed positional exchange of the fluorine atoms in phosphorus pentafluoride (1), he suggested that this exchange follows a pathway now known as the Berry pseudorotation (BPR) mechanism (1a → 1c).<sup>6</sup>



Berry postulated that positional exchange in trigonal-bipyramidal pentacoordinate (TBP) compounds occurs by pairwise exchange of apical and equatorial ligands. Of the latter, one plays the role of a "pivot," e.g., F\* of 1a (any of the equatorial F of 1 can, of course, act as the pivot), and does not participate in the positional exchange. The originally apical fluorines undergo an angular bending displacement (F'PF' angle: 180° → 120°) in a plane including F\* and the formerly apical F'. The initially equatorial fluorines participate in a simultaneous bending displacement (FPF angle: 120° → 180°) in the original equatorial plane. Concurrent

with this, the bond distances adjust to the new geometry. A C<sub>4v</sub> transition state is passed.

With PF<sub>5</sub> the effect of BPR is that the whole molecule has seemingly been rotated (see 1a → 1c), although the displacements that constitute BPR, as it is defined, do not involve any rotational motion, hence the name pseudorotation.<sup>8</sup> It is interesting to note that, of all conceivable mechanisms (M1-M7) by which regular (see below) positional exchange of pentacoordinate D<sub>3h</sub> TBP molecules might occur, BPR (M6) is the only one not involving internal rotation of some part of the molecule relative to another part.

It is important to differentiate between two types of polytopal isomerizations: regular and irregular. Regular processes are those positional exchanges that occur by skeletal rearrangement without breaking and re-forming bonds, conserving neighborhood relations as in the closely related processes of interconversion of conformers. Irregular polytopal rearrangements occur with bond fission and re-formation involving intermediates which differ in coordination number compared to the reactants or products. Examples of this type are found among phosphorus compounds where the rearrangement involves fission of a P-ligand bond to give a tetravalent intermediate. Irregular rearrangements may also involve substitution of a ligand in a pentacoordinate compound, via a hexacoordinate intermediate or transition state.<sup>9</sup> If the distinction between these regular and irregular processes is not rigorously observed, erroneous mechanistic conclusions invariably result. The isomerizations which have hitherto been interpreted by BPR are, with very few exceptions,<sup>9,10</sup> regular processes. Thus mechanistic alternatives to BPR considered for these processes must be regular.

Further important aspects of pentatopal isomerization processes and their interpretation employing BPR are illustrated by the following three examples.

(8) The term pseudorotation was originally invoked to describe the rapid up-and-down motion of the carbon atoms in cyclopentane, and this meaning has been extended to include puckering in all ring compounds. As many chemists prefer this nomenclature for puckering, we use the symbolism BPR to mean the positional exchange, as advanced by Berry,<sup>6</sup> observed in pentacoordinate phosphorus compounds. J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947).

(9) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsois, and I. Ugi, *Angew. Chem.*, in press.

(10) (a) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *ibid.*, **82**, 741 (1970); *Angew. Chem., Int. Ed., Engl.*, **9**, 703 (1970). (b) The authors reported on the TR concept at the following: Thirteenth Conference on Reaction Mechanisms, Santa Cruz, Calif., June 23-26, 1970 (F. R.); Euchem Conference on Heterocyclic Chemistry, Conglows, Ireland, July 6-10, 1970 (I. U.); Symposium on Chirality, Elmau, Germany, Oct 18-22, 1970 (I. U.).

(1) Postdoctoral research associate in the Department of Chemistry of the University of Southern California, 1969-1970; member of the Wissenschaftliches Hauptlaboratorium der Farbenfabriken Bayer, A.G., 509 Leverkusen.

(2) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

(3) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965).

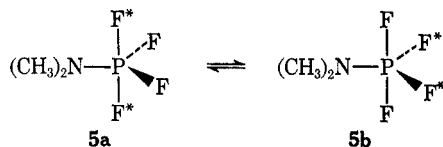
(4) J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).

(5) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *Inorg. Chem.*, **3**, 1748 (1964).

(6) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

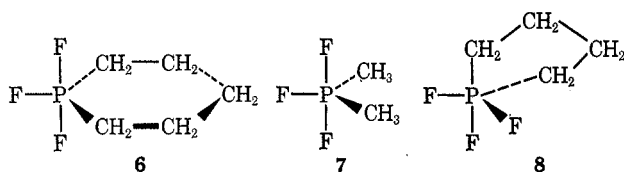
(7) Review article: R. Schmutzler, *Angew. Chem.*, **77**, 530 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 496 (1965).

Whitesides and Mitchell<sup>11</sup> did an ingenious study on the isomerization of pentacoordinate phosphorus compounds. These authors analyzed the temperature dependence of the <sup>31</sup>P nmr spectrum of **5**, and were able to show the conversion **5a** ⇌ **5b**. At low temperatures



(< -100°) structure **5** is frozen; the dimethylamino group and two of the fluorines occupy equatorial positions, and two of the P-F bonds are apical, without any exchange of the equatorial and apical fluorines. Above -50° all four fluorines become completely equivalent, but there is an intermediate temperature range in which the equatorial pair of fluorines (F) replaces the apical pair of fluorines (F\*) and vice versa in a single concerted step. This result was, with good justification, considered by the authors as proof that none of the previously published ("non-Berry") alternatives (see below) to the BPR mechanism of pentatopal rearrangements could be responsible for the F exchange of **5**. A BPR of **5** with (CH<sub>3</sub>)<sub>2</sub>N as a pivot produces a partial or coupled F exchange **5a** → **5b** involving the pairwise exchanging of F and F\*. Using one of the equatorial fluorines as a pivot would lead to species violating the polarity rule.<sup>12,13</sup> The complete magnetic equivalence of all four <sup>19</sup>F of **5**, as observed at -50°, can be achieved by BPR only if an equatorial fluorine is used as a pivot, *i.e.*, only if the polarity rule is violated. According to the polarity rule,<sup>12,13</sup> in TBP molecules with different ligands, the more electronegative ligands occupy apical positions and the less electronegative ligands occupy the equatorial positions.

At temperatures as high as +100°, the <sup>19</sup>F nmr of **6** and **7**<sup>13c</sup> show two distinguishable fluorine atoms in the signal ratio 2:1. In these cases no BPR can be expected, as this would involve an intermediate exchange of an apical P-F bond by a P-C bond and an equatorial P-C bond by a P-F bond, which would constitute a



(11) G. M. Whitesides, and H. G. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969).

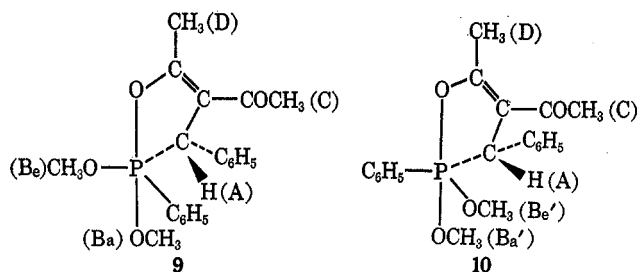
(12) (a) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970); (b) R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962).

(13) (a) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

(13c) NOTE ADDED IN PROOF. Recently, some fluorophosphoranes including P(CH<sub>3</sub>)<sub>2</sub>F<sub>3</sub> (**7**) have been observed to undergo a temperature and concentration dependent rearrangement. These are postulated to proceed intermolecularly *via* a fluorine bridged dimer. This falls under the purview of irregular rearrangement and thus does not affect the discussion at hand: T. A. Furtch, D. S. Dierdorf, and A. H. Cowley, *J. Amer. Chem. Soc.*, **92**, 5759 (1970); H. Dreeskamp and K. Hildenbrand, *Z. Naturforsch. B*, **26**, 269 (1971).

considerable energy barrier determined by the polarity rule.<sup>12,13</sup>

The fluorine atoms of **8** are not distinguishable above -70°. In **8**, the five-membered ring would be highly strained with two equatorial P-C bonds and a C-P-C bond angle of 120°. Here, ring strain forces one of the P-C bonds into the apical position. This should lower the polarity difference of the exchange products, but for the BPR of **8** it might also involve a considerable ring strain barrier, as has been indicated by Muetterties, *et al.*<sup>13a</sup> Furthermore, in **6-8** the CH bonds introduce considerable steric hindrance on the pathway to the positional exchange transition state.



The temperature dependence of the nmr spectra of equilibrium mixtures of **9** and **10** has been considered as particularly convincing evidence for BPR.<sup>14,15</sup> At -25° the nmr spectra of **9** and **10** show two doublets with different coupling constants for A. This is due to P-H coupling and to the fact that in **9** the two phenyls are in a trans relation and in **10** in a cis relation. An analogous situation exists for the equatorial methoxyls (B<sub>e</sub> and B<sub>e'</sub>) as well as the apical methoxyls (B<sub>a</sub> and B<sub>a'</sub>) in **9** and **10**. There are two separate singlets for the acetyl groups (C) of **9** and **10**, whereas only one peak is observed for the methyl group (D). At 25° the chemical shift differences between protons A and protons C, and between B<sub>e</sub> and B<sub>e'</sub>, for the two diastereomers **9** and **10** begin to vanish. At 52° there is only one signal each for A and C, and the signals for B and B' begin to coalesce. At 104° there is only one sharp doublet for A, two sharp doublets (superimposed to a pseudotriplet) for B and B', and a sharp singlet for C.

This implies that at -25° the interconversion **9** ⇌ **10** is slow. At 25° the rate of this reaction is such as to begin to influence the nmr spectrum, but the apical and equatorial methoxyls are still distinguishable. Above 52° the equilibrium **9** ⇌ **10** is so fast that there is no distinction between axial and equatorial for the protons of A, C, and D, whereas B and B' (but not B<sub>a</sub>, B<sub>e</sub>, B<sub>a'</sub>, and B<sub>e'</sub>) are still distinguishable.

The above data have been interpreted in terms of a sequence of four BPR,<sup>14,15</sup> but it should be noted that this involves intermediates with apical P-C bonds. The interconversion of **9** and **10** corresponds to a con-

(14) (a) F. Ramirez, *Trans. N. Y. Acad. Sci.*, **30**, 411 (1968); (b) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **90**, 1275 (1968); (c) review article: F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

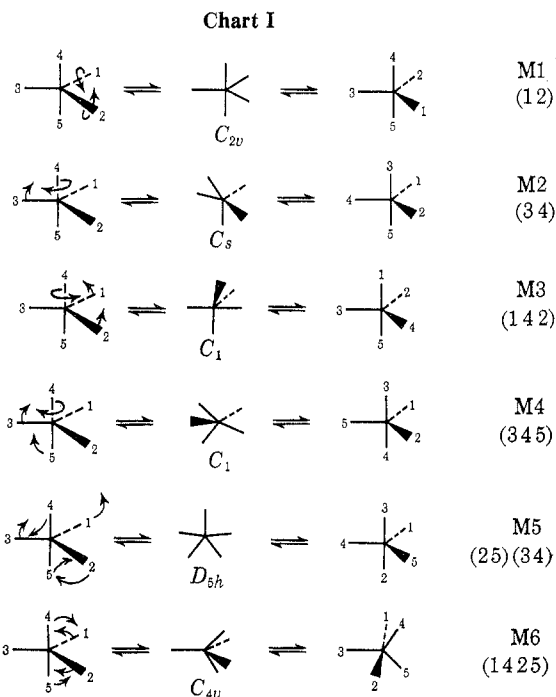
(15) (a) D. Gorenstein and F. H. Westheimer, *Proc. Nat. Acad. Sci. U. S. A.*, **58**, 1747 (1967); (b) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970); (c) review article: F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

figurational inversion of the pentacoordinate chiral center or an exchange of the equatorial phenyl and methoxyl.

These examples illustrate the concept of BPR mechanism and the isomerization processes which call for an interpretation by this or alternate regular mechanisms.

### Muetterties' Alternative Mechanisms

Recently, Muetterties<sup>16</sup> set out to symbolize all of the conceivable mechanisms and symmetries of intermediate states for the isomerization of trigonal-bipyramidal pentacoordinate compounds (see Chart I).



With the ligands symbolized by numbers, the mechanisms can be simply characterized by permutations of these numbers. The cyclic permutation (345) corresponds to the statement, "3 replaces 4, 4 replaces 5, and 5 replaces 3," and represents mechanism M4. (A more formal treatment of pentatopal isomerization by permutations is given below.) Muetterties' mechanistic alternatives M1–M5 to BPR (M6) have been discarded, as they were all found to be in disagreement with pertinent experimental evidence. In particular, all of them are eliminated by the Whitesides–Mitchell experiment.<sup>11</sup>

### The Turnstile Rotation (TR) Mechanism and Its Relation to BPR

We submit a further, physically possible mechanism for pentatopal isomerizations, the turnstile rotation (TR) mechanism.<sup>10b, 17, 18</sup> In contrast to BPR, TR is

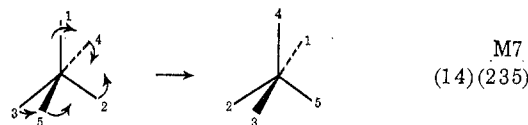
(16) (a) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969); (b) E. L. Muetterties, *ibid.*, **91**, 4115 (1969).

(17) F. Ramirez, I. Ugi, S. Pfohl, E. A. Tsolis, J. F. Pilot, C. P. Smith, D. Marquarding, P. Gillespie, and P. Hoffman, *Phosphorus*, in press.

(18) I. Ugi, F. Ramirez, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, **82**, 766 (1970); *Angew. Chem., Int. Ed., Engl.*, **9**, 725 (1970).

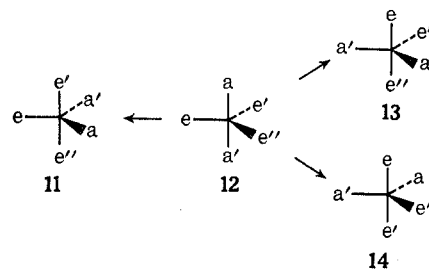
the rearrangement of a pentacoordinate molecule by internal rotation.

This mechanism, M7, not considered by Muetterties, corresponds to an internal rotation of one apical and one equatorial ligand rotating as a pair *vs.* the oppositely rotating trio of the three remaining ligands. The rotation resembles that of a turnstile. Process M7 may



be described as a combination of rotations about an approximate local  $C_2$  axis for the pair of ligands and an approximate  $C_3$  local axis for the trio, and it may be represented by the permutation (14)(235). The relative internal rotation is  $180^\circ \pm 120^\circ$ , that is,  $60^\circ$  or  $-300^\circ$ . Alternately, this may be considered as the equivalent pair rotation by  $36^\circ$  counterclockwise *vs.* the trio rotation by  $24^\circ$  clockwise.

The TR has some characteristic features in common with the BPR mechanism. (1) Both mechanisms can, in an idealized case (where no intermolecular exchange of angular momentum takes place), occur with conservation of angular momentum, a feature not present in the alternatives. (2) A TR process, as BPR, exchanges apical and equatorial ligands pairwise, in agreement with the Whitesides–Mitchell experiment.<sup>11</sup> (3) Each BPR has four equivalent TR, as is illustrated by the TBP molecule **12**. A BPR of **12** with e as the pivot



leading to **11** is represented by the permutation cycle (ae''a'e'). The same result **12** → **11** can be achieved by any of the four TR processes represented by: (ee'a)-(a'e''), (ee'a')(ae''), (ee''a)(a'e'), (ee''a')(ae'). Analogously, **12** → **13** and **12** → **14** may each be achieved by any of four equivalent TR processes. These TR processes contain the following common feature: their "trios" all contain the pivot e of the corresponding BPR, and the angular direction of the "trio" rotation is such that e replaces the other originally equatorial ligand. Due to this correspondence, the same Ramirez–Lauterbur,<sup>19</sup> Prelog,<sup>20</sup> or Mislow<sup>21</sup> graphs can be used for this mechanism.

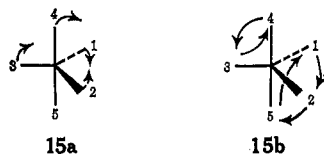
(19) (a) P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968); (b) F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970).

(20) (a) J. D. Dunitz and V. Prelog, *Angew. Chem.*, **80**, 700 (1968); (b) see also M. Gielen, M. De Clerq, and J. Nasielski, *J. Organometal. Chem.*, **18**, 217 (1969).

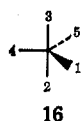
(21) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969).

A sequence of five BPR with five different "pivots" is required for the configurational inversion of a trigonal bipyramid with five different ligands. To achieve the identical result, one must apply five TR processes as well. However, there are  $4^5 = 1024$  different TR pathways to inversion for each BPR pathway!

As a model concept of the TR one can visualize it to begin as a combination of three motions, illustrated by **15a** and **15b**. Two equatorial bonds (1 and 2 of **15a**)



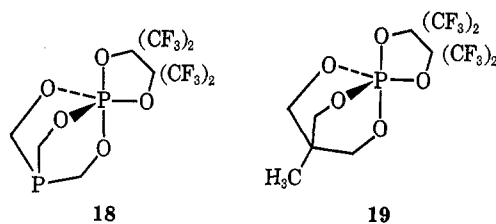
undergo a relative bending motion such that one initially equatorial bond angle finally becomes  $\sim 90^\circ$ . At the same time, a pair of ligands (3 and 4 in **15a**) tilt by approximately  $9^\circ$ . Superimposed upon the above motions is the incipient internal rotation of the pair (3 and 4) vs. the trio (1, 2, and 5) according to **15b**. This overall motion leads to the TR barrier situation **16a,b** (*vide infra*) after the relative internal rotation of  $30^\circ$ , and from there by further analogous  $30^\circ$  rotation to **16**. In



the barrier situation, the pair has an approximate  $C_2$  and the trio a  $C_3$  local skeletal symmetry. The TR process can also, in approximation, be considered as a combination of local  $C_2$  and  $C_3$  operations.

Although the final results of BPR and TR are essentially equal, there are fundamental differences between them. All of the differences relate to the fact that BPR is a process *not involving any sort of internal rotation about an axis through the central atom* and the TR is an internal rotation process, resulting in two mechanistic pathways proceeding through entirely different sets of states differing in geometry, symmetry, and potential energy described in detail below.

The observed rapid positional exchange<sup>17</sup> in **18** and **19** is particularly illustrative of the TR concept. If, for



the sake of discussion, one forces molecules **18** and **19** through a positional exchange by the BPR mechanism, *this would involve a simultaneous relative internal rotation of the bicyclic vs. the five-membered cyclic moiety which is a TR process* or, at best, a BPR + TR process. This result is a consequence of the molecular topology of the two molecular structures. In the following sections, some further criteria are discussed which, in suitably

chosen model cases, allow one to distinguish which of the alternative mechanisms is the valid interpretation of a given set of data.

### Calculated Energies of BPR and TR Models

It is understood that the total or binding energy data concerning those geometric configurations of some model species involved in positional exchange processes of pentacoordinate phosphorus compounds do not provide a fully adequate basis for the comparison of BPR and TR processes. However, it is of interest to examine the proposed reaction paths with respect to their energetic barriers. Our calculations have been carried out in the CNDO/2 approximation.<sup>22-26</sup> Recent applications<sup>27</sup> of this method, employed in an analogous effort to determine energetic barriers in mechanistic pathways, demonstrate the usefulness and feasibility of this type of MO calculation. Details of this method and its capabilities may be found in the original papers and in a recent review by Jaffé.<sup>26b</sup> Calculation data assuming the experimentally determined  $D_{3h}$  skeleton of the trigonal-bipyramidal pentacoordinate phosphorus compounds have yielded results in good agreement with published data concerning bond lengths.<sup>2,3</sup> In these cases optimizing the molecular structure involved adjusting only the P-ligand bond lengths. In each case the equilibrium structure was determined within  $\pm 0.01$  Å. This produced bond lengths that were uniformly greater than electron diffraction data<sup>2,3</sup> by approximately 5%. Molecular energies calculated along the reaction pathway required optimization of bond angle and distance. While the absolute values of their resulting energies contain uncertainties, the comparison of the trends in the two mechanisms is realistic. The fact that the energy barriers to both pseudorotation and turnstile rotation are reasonably low and within 5–10 kcal/mole of each other indicates that neither of the mechanisms is impossible from quantum mechanical considerations. Further, sets of binding energy data of pertinent species give some substance to ideas concerning reaction coordinate diagrams for the two processes under consideration.

For **1a** and the hypothetical model compound **20** the ground-state binding energies (kilocalories/mole) shown were obtained. The higher stability of **20a** relative to **20b** and **20c** is in accord with the polarity rule. It must be observed that **20c** is slightly more stable than **20b**, not in accordance with the polarity rule.<sup>12,13</sup> Although this discrepancy may be attributed to some program insensitivity, one must include the possibility that the polarity rule has some limitations that should be ex-

(22) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 5129 (1965).

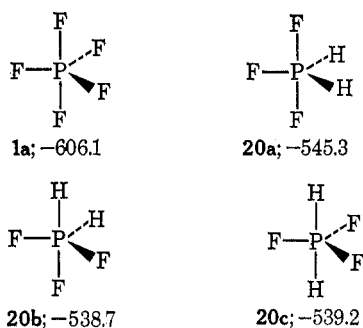
(23) J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965).

(24) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

(25) P. Gillespie and I. Ugi, unpublished results.

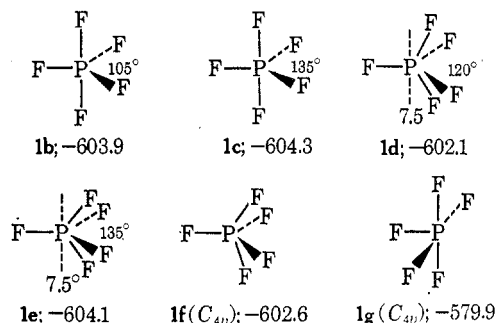
(26) (a) Review article: J. A. Pople, *Accounts Chem. Res.*, **3**, 217 (1970); (b) review article: H. H. Jaffé, *ibid.*, **2**, 136 (1969).

(27) C. S. Cheung, R. A. Beaudet, and G. A. Segal, *J. Amer. Chem. Soc.*, **92**, 4158 (1970).



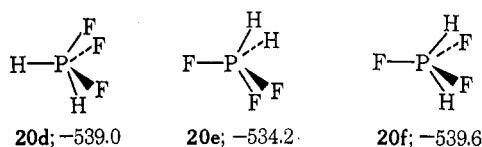
plored. It is conceivable that the polarity rule must be restated in some more precisely defined terms.

The model species, **1** and **20**, are of interest relative to BPR. The binding energies (kilocalories/mole) of the species **1b-1g** are as follows.

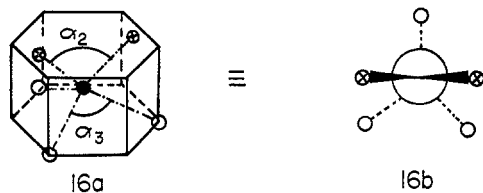


One can conclude the following from models **1a-1g**. (1) During BPR the apical and equatorial ligands move synchronously, approximately *via* **1e** and **1f** over a low energy barrier. (2) BPR *via* an "octahedron with a missing vertex," a geometry where four ligands and the phosphorus are coplanar, **1g**, invokes a high energy barrier relative to other BPR pathways. (3) The apical bonds of **1a** are "stiffer" relative to bending compared to the equatorial bonds.

Figure 1 illustrates an approximate reaction coordinate diagram for  $\text{PF}_5$  BPR. It is of further interest to note that the various BPR barrier states (containing a  $105^\circ$ - $150^\circ$ - $C_{4v}$  skeleton) of **20d-20f** differ considerably in energy.



The staggered barrier situation **16** of a TR process can be visualized by using either model **16a**, a regular hexagonal prism, as a "steric reference system" or simply model **16b**. Species **16** ( $\equiv 30^\circ$ -TR) is "halfway"



between two eclipsed TR species, **17** ( $\equiv 0^\circ$ -TR), from which they result due to a  $\pm 30^\circ$  relative rotation of the

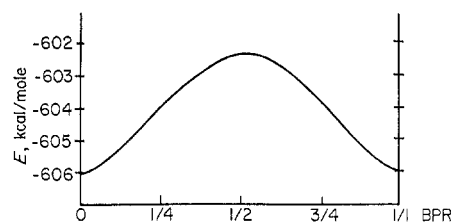
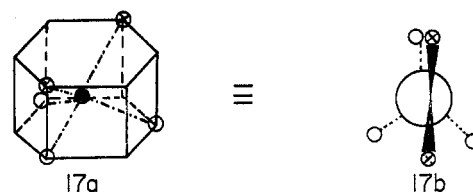


Figure 1.

Table I  
Binding Energies (kilocalories/mole) of  $\text{PF}_5$

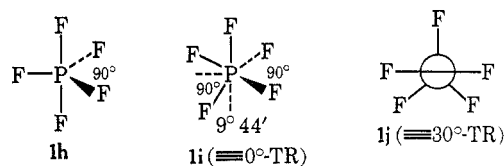
$\alpha_3$	$\alpha_2$			
	$80^\circ$	$85^\circ$	$90^\circ$	$95^\circ$
$85^\circ$		-591.4	-591.3	-589.5
$90^\circ$	-594.0	-595.5	-595.0	-592.5
$95^\circ$	-596.0	-597.0	-595.9	-592.8
$100^\circ$		-594.4	-592.3	-588.1

pair ( $\otimes$ ) *vs.* the trio ( $\circ$ ) of **16**. The dependence of the binding energy upon the pair angle  $\alpha_2$  and the trio angle  $\alpha_3$  in  $\text{PF}_5$  (**1**), arranged in a staggered state of type **16**, is illustrated by Table I. The idealized BPR and TR



intermediates are different by a displacement greater than the amplitudes of the zero point bending vibrations given by ref 2 as the F-P-F angles for **1f** are  $105^\circ$  and  $150^\circ$  while the angles for **16b** are  $\sim 90^\circ$ . It should be pointed out that motions other than those presented might be operating in certain cases, as the nature of the saddle point between **1f** and **16b** is not known. According to Table I,  $\alpha_2 \simeq 85^\circ$  and  $\alpha_3 \simeq 95^\circ$  provides the lowest barrier for a TR process of  $\text{PF}_5$ . One notes that the energy of **16** does not seem to be very sensitive to  $\alpha_2$  and  $\alpha_3$ .

Species **1i** and **1j** are illustrative of a TR process of  $\text{PF}_5$  with  $\alpha_2 = \alpha_3 = 90^\circ$ . Nuclear spherical coordinates



of some  $\text{PF}_5$  species undergoing TR rotation were obtained from linear combinations of the spherical coordinate sets of **1i** and **1j** (dotted line of Figure 2) and **1a** and **1j** (solid line of Figure 2).

The solid line in Figure 2 represents a turnstile process beginning with the compression of an equatorial F-P-F angle (see **1h**); at the same time the remaining equatorial F and an apical F form a pair which is synchronously tilting (see **1i**) and rotating relative to the trio about an axis common to the pair and trio until the staggered turnstile species **1j** is reached. The tran-

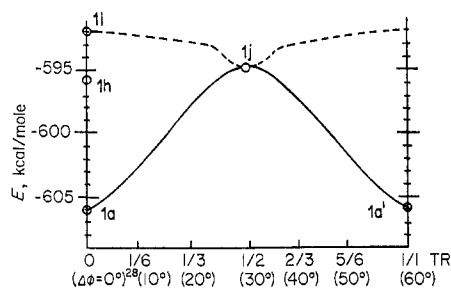


Figure 2.

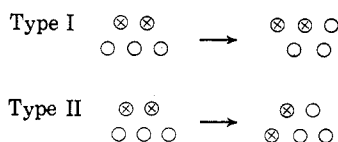
Table II

Species; number (binding energy)	$\phi_1$ $\theta_1$	$\phi_2$ $\theta_2$	$\phi_3$ $\theta_3$	$\phi_4$ $\theta_4$	$\phi_5$ $\theta_5$
<b>1a</b> ; ligands 1, 2, 3 are equatorial, 4 and 5 are apical (-606.1 kcal/mole)	71° 34'	-71° 34'	180°	0°	180°
One-third of the way from <b>1a</b> to <b>1j</b> ; 1/6-TR or 10°-TR (-603.5 kcal/mole)	57° 43'	77° 42'	180°	0°	170°
Two-thirds of the way from <b>1a</b> to <b>1j</b> ; 2/6-TR or 20°-TR (-599.1 kcal/mole)	43° 51'	-83° 51'	180°	0°	160°
<b>1j</b> ; barrier configuration; 3/6-TR or 30°-TR (-595.0 kcal/mole)	30°	-90°	180°	0°	150°
	125° 16'	125° 16'	45°	45°	125° 16'

sition of **1j** into **1a'**, a TBP  $\text{PF}_5$  molecule with two exchanged pairs of apical and equatorial F-ligand bonds, proceeds analogously to a reversal of the process **1a**  $\rightarrow$  **1j**. This process is further illustrated by  $\phi$ , the azimuth, and  $\theta$ , the zenith distance coordinates, of the five F atoms of some representative model species (Table II,  $r_{\text{PF}} = 1.73 \text{ \AA}$ ).

It is interesting to note that in  $\text{PF}_5$  there is a geometric situation halfway between two eclipsed turnstile species which is energetically quite favorable (-600.3 kcal/mole). This means that there are energetically favorable pathways by which a turnstile species with a certain pair and trio can switch over to another turnstile species with a different pair and trio; here one of the trio ligands undergoes a displacement such that it now forms a new trio with the previous pair, leaving the two remaining ligands of the previous trio to form a new pair. This geometric configuration corresponds to the following situation in  $\text{PF}_5$ :  $\phi_1 = 45^\circ$ ,  $\theta_1 = 94^\circ 52'$ ;  $\phi_2 = -67^\circ 31'$ ,  $\theta_2 = 90^\circ$ ;  $\phi_3 = 180^\circ$ ,  $\theta_3 = 85^\circ 08'$ ;  $\phi_4 = -135^\circ$ ,  $\theta_4 = 4^\circ 52'$ ;  $\phi_5 = 180^\circ$ ,  $\theta_5 = 175^\circ 08'$ .

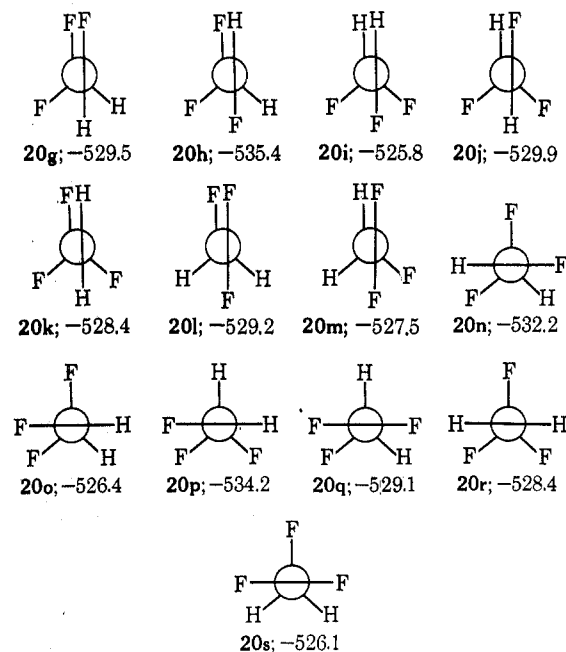
Two general types, I and II, of switches are possible (initial pair ligands =  $\otimes$ , initial trio ligands =  $\circ$ ).



There can be a variety of switches between TR species (e.g., (0°-TR)  $\rightarrow$  (0°-TR)', (0°-TR)  $\rightarrow$  (30°-TR)', (30°-TR)  $\rightarrow$  (0°-TR)', (30°-TR)  $\rightarrow$  (30°-TR)', etc.) by certain pathways, while certain other switch pathways

are forbidden by high barriers, e.g., for  $\text{PF}_5$  the (30°-TR)  $\rightarrow$  (30°-TR)' by switch I via **1g**.

Further, the energies of species **20g-20m** associated with the TR ( $\alpha_2 = \alpha_3 = 90^\circ$ ) of  $\text{PH}_2\text{F}_3$  show that only one of the eclipsed turnstile species, **20h**, is of relatively low energy. Incidentally, **20h** results from **20a**, the low-energy isomer of **20**, by deformation of an equatorial F-P-H angle to  $90^\circ$ , forming an H-F-F trio and tilting the remaining H-F pair by  $9^\circ 44'$  (see **20a**  $\rightarrow$  **20h**). The lowest energy staggered (barrier) turnstile species **20n** and **20p** also have an H-F pair and an H-F-F trio. Therefore, it is to be expected that positional exchange of **20** by a TR mechanism will involve the above-mentioned species.

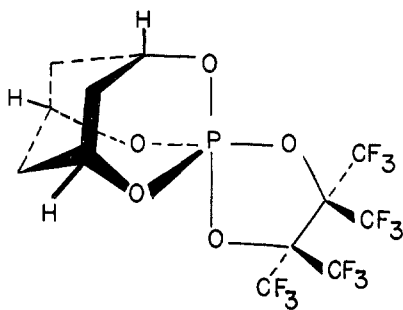


The present binding energy data indicate that, for the model compounds  $\text{PF}_5$  (**1**) and  $\text{PH}_2\text{F}_3$  (**20**), positional exchange can occur equally well by the TR or the BPR mechanisms. The differences in the calculated barriers are within the range of error of the present method of calculation. We turn, therefore, to empirical data in an effort to decide which of these two mechanisms explains permutational isomerizations of trigonal-bipyramidal molecules more satisfactorily.

### Permutational Isomerization of a Polycyclic Oxyphosphorane Derived from a Phosphatrioxadamantane<sup>18</sup>

The substance **21** is a highly stable crystalline oxyphosphorane until a decomposition temperature of  $175^\circ$  is reached. In methylene chloride solution, at  $30^\circ$ , there is a  $^{31}\text{P}$  nmr signal (a quartet) at +41.7 ppm vs.  $\text{H}_3\text{PO}_4$  as 0. The  $^{19}\text{F}$  nmr spectrum shows one doublet at -9.5 ppm vs.  $\text{CF}_3\text{COOH}$  as 0. The  $^1\text{H}$  nmr spectrum in  $\text{CDCl}_3$  solution at  $30^\circ$  shows one doublet due to the three methine protons at 5.00 ppm (vs. TMS = 10), with  $J_{\text{HCOF}} = 28 \text{ Hz}$ . The methylene protons gave one doublet at 7.20 and another at 8.26 ppm, due, respectively to the equatorial and axial cyclohexane

hydrogens;  $J_{\text{HCH}} = 15$  Hz. From the  $^{19}\text{F}$  and the  $^1\text{H}$  nmr data it appears that there is permutational isomerization in **21**. Solvent-dependent  $^{31}\text{P}$  nmr data indicate that this isomerization occurs without bond breaking and re-formation. The  $^{19}\text{F}$  variable temperature spectrum was examined in vinyl chloride and down to  $-75^\circ$  yielded a doublet 649 Hz downfield from the reference  $\text{CF}_3\text{COOC}_2\text{H}_5$ . Visible broadening is detected at  $-90^\circ$  and reaches a maximum at  $t_c \cong -122^\circ$ . Sharpening of the signal occurs at  $-140^\circ$  and continues to  $-150^\circ$ , with the signal at 575 Hz.



21

An examination of molecular models reveals that permutational isomerization of **21** by BPR must traverse a prohibitively high energy barrier. The experimental facts, however, are nicely explained by the TR mechanism. A reasonable facsimile of the TR barrier configuration is shown in Figure 3.<sup>28</sup> It is interesting to note that the structure of **21** already places it close to a TR barrier configuration. An approximately  $9^\circ$  bending (see the motion of ligands 3 and 4 in **15a**) of the two P-O bonds of the five-membered ring is all that remains to make **21** a TR species.

### Formalistic Considerations

Let us define a class of molecules,  $C_5$  ( $= A, \dots, E, \dots, Z$ ), characterized by a skeleton with five positions,  $S$  ( $= S_1, \dots, S_5$ ), occupied by a set of five ligands,  $L$  ( $= L_1, \dots, L_5$ ). We recommend the assignment of the ligand indices according to the sequence rule<sup>29</sup> and the assignment of the skeletal indices according to procedures outlined elsewhere.<sup>10</sup> The skeletal indices of **22** correspond to the latter assignment. Molecules belonging to this class may be described by indicating the distribution of the set of ligands  $L$  on the skeleton  $S$ , e.g., by mapping the ligand indices  $l = 1, \dots, 5$ , onto the skeletal indices  $s = 1, \dots, 5$ .

The description of molecules by a double numbering and mapping process has the advantage that one may carry out ligand permutations and skeletal operations separately. This is necessary if skeletal symmetries and permutational equivalence of some of the ligands must be considered simultaneously. It is a formalistic convenience to introduce the concept of the reference isomer<sup>10</sup>  $E$  of a given class of isomers. The reference

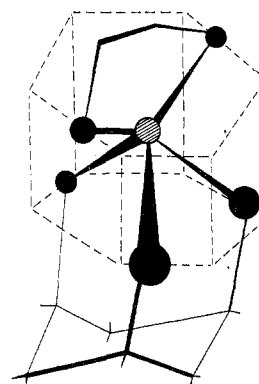


Figure 3.

isomer is that isomer in which the ligand indices match the skeletal indices, i.e., the isomer in which the ligand with index  $i$  is attached to the skeletal position with index  $i$ . The reference isomer corresponds to a mapping of the set of ligand indices onto the set of skeletal indices such that numerically equal indices are together according to the matrix representation

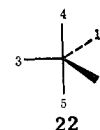
$$\begin{pmatrix} l \\ s \end{pmatrix}_E = \begin{Bmatrix} 1 & 2 & 3 & 4 & 5 \\ 1 & 2 & 3 & 4 & 5 \end{Bmatrix}$$

the reference matrix of the class  $C_5$  of permutation isomers.

The isomers  $M$  of  $E$  which belong to  $C_5$  are obtained from  $E$  by permutations,  $P_l$ , of the ligands or permutations,  $P_s$ , of the skeletal positions, respectively, represented by eq 1. Thus we call these the permutational

$$\begin{pmatrix} l \\ s \end{pmatrix}_M = P_l \begin{pmatrix} l \\ s \end{pmatrix}_E = P_s \begin{pmatrix} l \\ s \end{pmatrix}_E \quad (1)$$

isomers of  $E$ .  $P_l$  and  $P_s$  belong to  $S_5$ , the full permutation group on five letters which has  $5!$  elements. The reference matrix  $\begin{pmatrix} l \\ s \end{pmatrix}_E$  ( $R_E$ ) has, within the set  $M$  of "isomeric matrices," the unique property that the ligand and skeletal indices are contravariant variables with regard to  $R$  which does not generally hold for other matrices of  $M$ . This means that applying the permutation operator  $P$  upon the ligand indices of  $R_E$  has the same result as applying its inverse operator  $P^{-1}$  upon the skeletal indices of  $R$ , where  $P^{-1} \cdot P = e$ . If all ligands of  $L$  are distinguishable and the skeleton  $S$  does not have any symmetry equivalent skeletal positions, the number of different  $R$  mappings and therefore isomers in  $C_5$  is  $5!$ . If, however, some of the skeletal positions of  $S$  are symmetry equivalent, then some of the  $R$  mappings become equivalent, as do the molecules which they represent. In the case of a TBP penta-coordinate skeleton **22** with a  $D_{3h}$  symmetry all  $R$  map-



22

(28) If the  $Z$  axis is conceived as the "TR axis," then the relative change,  $\Delta\phi$ , in the azimuth coordinates of the pair and trio ligands can be used as the reaction coordinate.

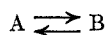
(29) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem.*, **78**, 413 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

pings which differ only by the permutations (123),

(132), (12)(45), (13)(45), and (23)(45) of the skeletal indices  $s$  or corresponding permutations of the ligand indices are equivalent. The number of possible isomers is reduced to  $\binom{5}{2} = 5!/(2!3!) = 10$  pairs of antipodes.

Further, if some of the ligands of L are equal, those R mappings become equivalent and are interconvertible by permutations of equivalent ligands. With properly defined numbers for ligands and skeletal positions and suitably chosen  $l$  or  $s$  permutations it is possible to use the above concept for designing an effective nomenclature system for permutational isomers.<sup>10</sup> We call these properly chosen permutations for the representation of the isomers *descriptors*.<sup>10</sup> It can be shown<sup>10,30</sup> that these descriptors represent a mathematically well-founded nomenclature system, less arbitrary than any prior naming attempt.

Let us assume that a molecule A, represented by the descriptor  $P$ , is isomerized to molecule B, represented by  $Q$ , and vice versa.



The mathematical description of the process for A and B, respectively, is achieved as follows.

$$\begin{pmatrix} l \\ s \end{pmatrix}_A = P_i \begin{pmatrix} l \\ s \end{pmatrix}_E \quad (2)$$

$$\begin{pmatrix} l \\ s \end{pmatrix}_B = Q_i \begin{pmatrix} l \\ s \end{pmatrix}_E \quad (3)$$

We obtain eq 4 (for the equilibrium) by solving (2) and (3) for  $R_E$  and then equating them. Equation 4 is

$$P^{-1} \begin{pmatrix} l \\ s \end{pmatrix}_A = Q^{-1} \begin{pmatrix} l \\ s \end{pmatrix}_B \quad (4)$$

transformed into eq 5 by applying  $Q_i$  (by multiplication with  $Q$ ).

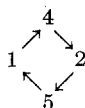
$$\begin{pmatrix} l \\ s \end{pmatrix}_B = Q_i P_i^{-1} \begin{pmatrix} l \\ s \end{pmatrix}_A \quad (5)$$

$$P_i^{-1} \cdot P_i = Q_i^{-1} \cdot Q_i = e \quad (6)$$

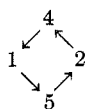
where  $P_i^{-1}$  and  $Q_i^{-1}$  are the inverted permutation operators and  $e$  is the identity operator.<sup>31</sup> Since  $P_i$  and

(30) (a) E. Ruch, W. Hässelbarth, and B. Richter, *Theor. Chim. Acta*, **19**, 288 (1970); (b) E. Ruch, lectures delivered in Zurich and at the University of Southern California, 1969.

(31)  $P^{-1} \cdot P = e$  reads: first apply the permutation  $P$  to a given set of numbers, then apply  $P^{-1}$  to the resulting set of numbers; as a result, you obtain the initial set of numbers. This is illustrated by the following example. Let  $P$  be the permutation operator (1425) which replaces 4 by 1 (or maps 1 onto 4), 5 by 2, and 1 by 5 according to



Then  $P^{-1} = (5241) = (1524)$  represents



$Q_i$  belong to the group  $S_5$ , the permutation operator  $I_i = Q_i \cdot P_i^{-1}$  (where  $I$  is the descriptor representing an isomerization) also belongs to  $S_5$ .

By utilizing the foregoing formalisms we are able to establish that the various mechanistic types of interconversions of the permutational isomers of the class of molecules possessing a skeleton with five ligand positions can be classified by partitioning the group  $S_5$  into its distinct classes of conjugate elements

$$S_5 = (P_1, P_2, P_3, P_{2+2}, P_4, P_{2+3}, P_5)$$

$$P_1 = \{e\}$$

$$P_2 = \{(12), (13), \dots, (45)\}$$

$$P_3 = \{(123), (124), \dots, (354)\}$$

$$P_{2+2} = \{(12)(34), (12)(35), \dots, (25)(34)\}$$

$$P_4 = \{(1234), (1235), \dots, (2543)\}$$

$$P_{2+3} = \{(12)(345), (13)(245), \dots, (45)(243)\}$$

$$P_5 = \{(12345), (13245), \dots, (15432)\}$$

If these permutations represent isomerization processes of pentacoordinate molecules with five different ligands and a skeleton devoid of any symmetry, each permutation refers to a different process and the classes  $P_1 \dots P_5$  of  $S_5$  refer to types of mechanisms. However, if the pentacoordinate skeleton has some symmetry, *e.g.*, a  $D_{3h}$  TBP symmetry, or some of the ligands are equivalent, then some of the mechanisms within a class  $P_x$  of  $S_5$  have common features and belong to subclasses within  $P_x$  and can be collectively called "a mechanism."

Mechanisms M1 and M2 are represented by subclasses of class  $P_2$ , M3 and M4 by subclasses of class  $P_3$ , M5 by  $P_{2+2}$ , and mechanism M6, the BPR, is represented by the alternating permutations  $P_{4a}$  of class  $P_4$ .<sup>32</sup> The latter are cycles of four elements in which the indices of the apical and equatorial ligands alternate and from which the index of the "pivot" is excluded. The permutations of the subclass  $P_{4a}$  are mutually conjugate.

The TR process is represented by those permutations of class  $P_{2+3}$  containing one apical and one equatorial ligand in a cycle of two and the remaining ligands in a cycle of three elements. M7 represents one possible permutation by this mechanism.

As one can immediately see, the result of applying the turnstile mechanism twice  $[(14)(235)][(14)(235)] = (253)$  corresponds to Muetterties' mechanism M3. Three applications of the turnstile,  $[(14)(235)]^3 = (14)$ , yield the result of Muetterties' mechanism M2.

Since molecules are not held rigidly in any certain spatial orientation, the rotation of some part of the molecule can be described only with reference to some other part of the molecule. Therefore the isolated "tritopal" and "ditopal" internal rotations like M2 and

and "undoes" what  $P$  has just accomplished. The operator  $P = (12345)$  transforms the set  $Z = \{12345\}$  into  $Z' = \{54312\}$  and  $P^{-1}$  transforms  $Z'$  into  $Z$ .

(32) Since a permutation cycle of one element, *e.g.*, (1), does not affect a given set of numbers, the permutation (1)(2345) is equivalent to (2345); therefore, class  $P_4$  also means  $P_{1+4}$ .



M3 as described by Muetterties cannot be considered individually, but correspond indeed to (TR)<sup>2</sup> and (TR)<sup>3</sup>.

### Conclusions

Considering all aspects of BPR and TR presented in the foregoing, we conclude that both mechanisms and even a superposition of the two are possible for the explanation of positional exchange in trigonal-bipyramidal pentacoordinate molecules, not just the BPR as hitherto claimed. We assume that for some acyclic molecules, like **1**, **2**, and **5**, BPR might even be the preferred exchange mechanism, while in other acyclic molecules,

*e.g.*, **4** and **20**, where BPR invariably leads to disfavored isomers, *e.g.*, **20b** or **20c**, a TR or a multiple TR (M2 or M3) or a TR with a "switch" is favored.

*Cyclic pentacoordinate compounds with a trigonal-bipyramid D<sub>3h</sub> skeleton cannot undergo positional exchange unless a TR is involved.*

The considerations developed herein lead us to further state that TR may explain positional exchange in trigonal-bipyramidal compounds of pentacoordinate central atoms other than phosphorus as well.<sup>33</sup>

(33) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).