and 2.19 (1) Å in $Zn(N_2H_4)_2(NCS)_2$,[25] 2.07 (1) Å in $[OC(NH_2)NHNH_2]ZnCl_2$,[26] 2.179 (7) and 2.206 (7) Å in $[Zn(N_2H_4)_3][(CH_3COO)_2]_n$,[27] and 2.099 (4) in $Zn[C_7H_6N_2O]_2 \cdot 2H_2O$.[28]

All three ethylenediamine chelate rings have the *gauche* configuration with the angles between the planes CCN(1) and N(primary)CC respectively 37.5, 33.4, and 43.6°, and all have the k conformation as in the case of $Cu(tren)(NCS)_2$[5] and of the isomorphous series $M(Me_6\text{-}tren)Br_2$.[9] The asymmetry of the ethylenediamine moiety with respect to the coordination plane can most conveniently be expressed by the angle between the coordination plane defined by the metal atom and the two nitrogen atoms and the plane defined by the two nitrogen atoms and the midpoint of the carbon–carbon bond. These angles are 3.2, 3.4, and 4.9° for N(2), N(3), and N(4) chelate rings, respectively. The corresponding values in $Cu(tren)(NCS)_2$[5] are 5.6, −0.6, and 7.3°, in $Ni(tren)(NCS)_2$[2] 15.6, 25.5, and 19.3°, and 8.3° in $Co(Me_6tren)Br_2$.[7] The observed differences between lengths of chemically identical bonds in the tren molecule are possibly significant (maximum difference, 4.5σ), but we can suggest no explanation for these small differences.

The Zn–N–C (thiocyanate) angle is 166.6° and agrees with the values reported in the literature: 161.2° in $Zn(N_2H_4)_2(NCS)_2$,[27] 163.3° in $Cu(tren)(NCS)_2$.[5] In Table III are compared bond distances and angles of the thiocyanate groups found in the present work and in $Cu(tren)(NCS)_2$.[5] The C–S distances in the thiocyanate groups have been corrected for anisotropic thermal vibration effects assuming the S atom riding on the carbon atom, and the values are reported in brackets. As in the case of $Cu(tren)(NCS)_2$ the bond distances within the two thiocyanate ions are not significantly different, even though one is bonded to zinc and the other is unbonded and their infrared spectra are clearly different.[1]

Table III. Bond Lengths in Thiocyanate

		Zn(tren)	Cu(tren)
C–S, Å	Bonded	1.628 (5) [1.644]	1.612 (5)
	Unbonded	1.561 (8) [1.625]	1.624 (5)
N–C, Å	Bonded	1.135 (7)	1.142 (7)
	Unbonded	1.140 (12)	1.168 (7)
N–C–S, deg	Bonded	178.5 (0.5)	177.4 (0.5)
	Unbonded	176.1 (0.8)	178.4 (0.5)

A comparison of the general arrangement of the ions in $Zn(tren)(NCS)_2$ and in $Cu(tren)(NCS)_2$ and the hydrogen-bond network are shown in Figure 1. A list of short contacts, some of which can be considered as hydrogen bonds, is reported in Table IV. In brackets are given the H—N···atom angles.

Table IV. Short Contact Distances (Å)

N(2)–S(2)	3.604	[16.5][e]
N(2)–S(1)[a]	3.538	[61.6]
N(3)–N(6)[b]	2.962	[11.8]
N(3)–S(2)[c]	3.432	[35.5]
N(4)–S(1)[d]	3.646	[13.7]
N(4)–N(6)	3.091	[56.4]

[a] $x + 1/2, y, 1/2 - z$. [b] $x, 1/2 - y, 1/2 + z$. [c] $x - 1/2, 1/2 - y, z$. [d] $x, 1/2 - y, z - 1/2$. [e] H–N···atom angles in degrees.

Acknowledgment. This work was supported in part by the National Science Foundation under Research Grants GP-4446 and GP-5795.

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(25) A. Ferrari, A. Braibanti, G. Bigliardi, and A. Lanfredi, *Acta Cryst.*, **18**, 367 (1965).

(26) M. Nardelli, G. Gasparri, P. Boldrini, and G. Battistini, *ibid.*, **19**, 491 (1965).

(27) A. Ferrari, A. Braibanti, G. Bigliardi, and A. Lanfredi, *ibid.*, **19**, 548 (1965).

(28) G. Palenik, *ibid.*, **17**, 696 (1964).

Topological Representation of Stereoisomerism. II. The Five-Atom Family[1]

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Contribution from Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08650. *Received January 18, 1969*

Abstract: Polytopal[1] rearrangements for the five-atom family are compared by topological or matrix presentation to delineate mechanistic differences subject to experimental test in molecular species.

Stereoisomerization through polytopal[1] rearrangements is examined here on a topological basis in an attempt to identify substantive mechanistic differences for experimental tests. The topological approach and definitions were presented in the first paper of this series[1] and a later note.[2] The following discussion is limited to the five-atom family which includes five-coordinate complexes, polyhedral boranes, and metal clusters. Polytopal isomerism in this family has been extensively described in the literature, and there are pertinent general articles[3,4] and reviews.[5–7]

Polytopal Isomerism

The mechanism of intramolecular rearrangements has been generally discussed in terms of the Berry[3]

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(1) Part I: E. L. Muetterties, *J. Am. Chem. Soc.*, **91**, 1636 (1969).

(2) E. L. Muetterties and A. T. Storr, *ibid.*, **91**, 3098 (1969).

(3) S. Berry, *J. Chem. Phys.*, **32**, 923 (1960).

(4) E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967); **4**, 769 (1965).

(5) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(6) F. W. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(7) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, Chapter III.

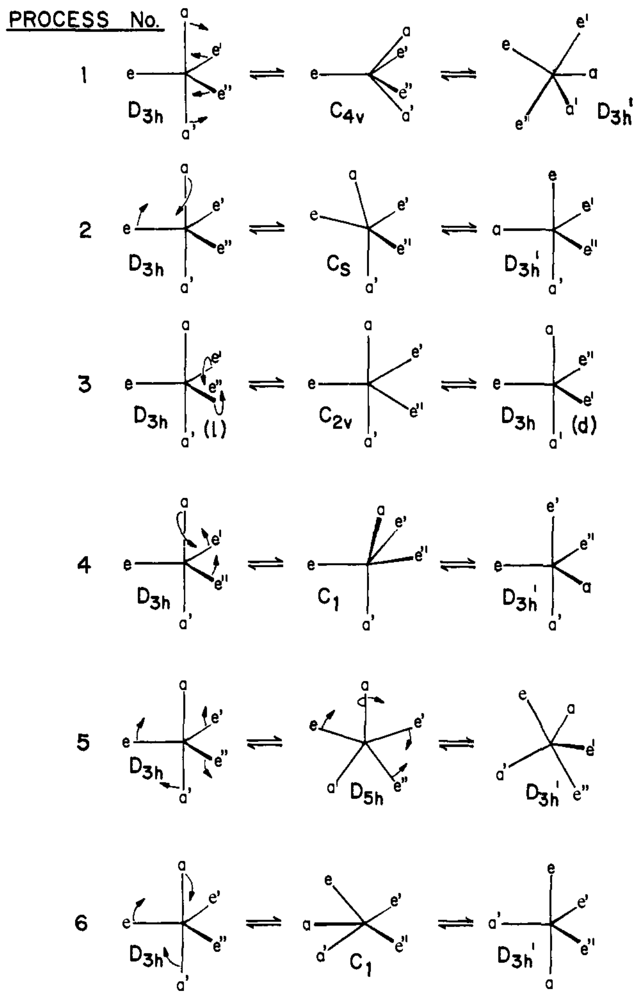

Figure 1. Possible intramolecular (polytopal[1]) rearrangements for a trigonal bipyramid.

mechanism,[8] outlined as process 1 in Figure 1. This rearrangement comprises traverse of trigonal-bipyramidal and square-pyramidal forms. Alternatives have not been seriously considered with but few exceptions.[9,10] Five alternative mechanisms will be considered here for the general and special ML_5 or M_5 cases in the context of stereoisomerization in a reference trigonal-bipyramidal form. These alternatives are schematically represented in Figure 1. The six processes are: (1) the Berry mechanism, D_{3h}-C_{4v}; (2) permutation of one axial and one equatorial positions—C_s or C_1 intermediate; (3) permutation of two equatorial positions (concerted)—C_{2v} transition state; (4) a twist permuting one axial and two equatorial positions—C_s or C_1 intermediate; (5) coplanar pentagonal intermediate; (6) a twist permuting two axial and one equatorial positions—C_1 intermediate.

Processes 3 and 5 involve coplanar intermediates or transition states which unequivocally should be the highest energy states for most molecular species in the five-atom family. The most symmetrical process and the one that appears to involve the minimal change in shape parameters is process 1. However, if ligand atoms differ significantly in size, then processes such as 2, 4, or 6 may effectively compete with 1.

As in paper I,[1] the general case is hypothetical and is defined as an ML_x or M_x aggregate with identical vertex atoms which are distinguishable by labeling. Isomer notations follow the earlier procedure[1] of specifying the axial substituents by numbers or letters and enantiomer notations as 12 and $\overline{12}$.

General Case: ML_5 or M_5

The trigonal-bipyramidal set of isomers for the general case numbers 20, and these are related by a group of permutations that are even–odd. Hence, set closure requires a polytopal rearrangement of such transpositional character.[2] For the processes of Figure 1, graph analysis established the stereochemical matrices (Tables I–III) and the group elements outlined below. Element definitions[1] are: c_E the minimal chain for A to $\bar{A}$ traverse, $\mathcal{C}_E$ the minimal cycle for A to $\bar{A}$ to A traverse, and subcycles, C, A to A circuits not passing through $\bar{A}$. The tables are symmetrical about the diagonal, and the number entries represent the minimum number of steps required for traverse from an isomer in the vertical column to one in the horizontal column.

Process 1. (1) The class is closed, $I_A\delta_A = I_B\delta_B$ $(20 \times 3 = 30 \times 2)$, where I is the number of isomers and δ is the isomer connectivity.[1] Process permutations are even–odd. (2) c_E is of order five (12-fold degeneracy), $\mathcal{C}_E$ is ten, and the one subcycle, C, is of order six.

Process 2. (1) The class is open ($I_A\delta_A = 20 \times 6$ and $I_B\delta_B = 120 \times 2$) but is closed for the trigonal-bipyramidal set (even–odd permutations). (2) c_E is of order three (20-fold degeneracy), C_E is six, and there are subcycles of order four (alternating chirality) and of order five.

Process 3. (1) The class is open ($I_A\delta_A = 20 \times 3$ and $I_B\delta_B = 60 \times 2$). (2) c_E is first order and this is the only element of the stereochemical class.

Process 4. (1) The class is open ($I_A\delta_A = 20 \times 6$ and $I_B\delta_B = 120 \times 2$). The trigonal-bipyramidal set is also open since the process involves only even permutations. (2) The class is represented by two disjoint and isomorphic groups. Enantiomers stand in a one-to-one relationship in these groups. Only one of the groups is displayed in Table III. (3) Neither group possesses the elements c_E and $\mathcal{C}_E$; *i.e.*, racemization cannot occur through this process. There are subcycles of order three and four.

Process 5. (1) The class is closed ($I_A\delta_A = 20 \times 6$ and $I_B\delta_B = 12 \times 10$) and process permutations are even–odd. (2) Any trigonal-bipyramidal stereoisomer can rearrange to *any* other stereoisomer in this group in one step.

Process 6. (1) This process is indistinguishable from process 4.

From the standpoint of experimental tests on ML_5 or an M_5 aggregate[11] in which the five vertex atoms are distinguishable, there are certain outstanding distinctions among the various processes: (A) racemization cannot occur *via* process 4 or 6, (B) racemization *only* can occur in process 3, (C) in process 5, one step

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[8] E. Teller and J. A. Wheeler, *Phys. Rev.*, **53**, 778 (1938), noted the close relationship of the trigonal bipyramid and square pyramid in a consideration of exchange of nuclear constituents through rotation.

[9] W. Mahler and E. L. Muetterties, *Inorg. Chem.*, **4**, 1520 (1965).

[10] G. M. Whitesides and W. M. Bunting, *J. Am. Chem. Soc.*, **89**, 6801 (1967).

[11] *E.g.*, a polyhedral carborane of the type $BHBClB(CH_3)CHC(CH_3)$.

Table I. ML_5—Process 1

R^1	12	23	34	45	13	14	15	24	25	35	$\overline{12}$	$\overline{23}$	$\overline{34}$	$\overline{45}$	$\overline{13}$	$\overline{14}$	$\overline{15}$	$\overline{24}$	$\overline{25}$	$\overline{35}$
12	E	2	4	4	3	2	3	3	2	1	5	3	1	1	2	3	2	2	3	4
23	2	E	2	4	3	4	1	3	2	3	3	5	3	1	2	1	4	2	3	2
34	4	2	E	2	3	2	1	3	4	3	1	3	5	3	2	3	4	2	1	2
45	4	4	2	E	1	2	3	3	2	3	1	1	3	5	4	3	2	2	3	2
13	3	3	3	1	E	3	2	4	1	2	2	2	2	4	5	2	3	1	4	3
14	2	4	2	2	3	E	3	3	4	1	3	1	3	3	2	5	2	2	1	4
15	3	1	1	3	2	3	E	4	3	2	2	4	4	2	3	2	5	1	2	3
24	3	3	3	3	4	3	4	E	3	4	2	2	2	2	1	2	1	5	2	1
25	2	2	4	2	1	4	3	3	E	3	3	3	1	3	4	1	2	2	5	2
35	1	3	3	3	2	1	2	4	3	E	4	2	2	2	3	4	3	1	2	5
$\overline{12}$	5	3	1	1	2	3	2	2	3	4	E	2	4	4	3	2	3	3	2	1
$\overline{23}$	3	5	3	1	2	1	4	2	3	2	2	E	2	4	3	4	1	3	2	3
$\overline{34}$	1	3	5	3	2	3	4	2	1	2	4	2	E	2	3	2	1	3	4	3
$\overline{45}$	1	1	3	5	4	3	2	2	3	2	4	4	2	E	1	2	3	3	2	3
$\overline{13}$	2	2	2	4	5	2	3	1	4	3	3	3	3	1	E	3	2	4	1	2
$\overline{14}$	3	1	3	3	2	5	2	2	1	4	2	4	2	2	3	E	3	3	4	1
$\overline{15}$	2	4	4	2	3	2	5	1	2	3	3	1	1	3	2	3	E	4	3	2
$\overline{24}$	2	2	2	2	1	2	1	5	2	1	3	3	3	3	4	3	4	E	3	4
$\overline{25}$	3	3	1	3	4	1	2	2	5	2	2	2	4	2	1	4	3	3	E	3
$\overline{35}$	4	2	2	2	3	4	3	1	2	5	1	3	3	3	2	1	2	4	3	E

Table II. ML_5—Process 2

R^2	12	23	34	45	13	14	15	24	25	35	$\overline{12}$	$\overline{23}$	$\overline{34}$	$\overline{45}$	$\overline{13}$	$\overline{14}$	$\overline{15}$	$\overline{24}$	$\overline{25}$	$\overline{35}$
12	E	2	2	2	1	2	1	1	2	3	3	1	3	3	2	1	2	2	1	2
23	2	E	2	2	1	2	3	1	2	1	1	3	1	3	2	3	2	2	1	2
34	2	2	E	2	1	2	3	1	2	1	3	1	3	1	2	1	2	2	3	2
45	2	2	2	E	3	2	1	1	2	1	3	3	1	3	2	1	2	2	1	2
13	1	1	1	3	E	1	2	2	3	2	2	2	2	2	3	2	1	3	2	1
14	2	2	2	2	1	E	1	1	2	3	1	2	1	1	2	3	2	3	3	2
15	1	3	3	1	2	1	E	2	1	2	2	2	2	2	1	2	3	3	2	1
24	1	1	1	1	2	1	2	E	1	2	2	2	2	2	3	2	3	3	2	3
25	2	2	2	2	3	2	1	1	E	1	1	1	3	1	2	3	2	2	3	2
35	3	1	1	1	2	3	2	2	1	E	2	2	2	2	1	2	1	3	2	3
$\overline{12}$	3	1	3	3	2	1	2	2	1	2	E	2	2	2	1	2	1	1	2	3
$\overline{23}$	1	3	1	3	2	2	2	2	1	2	2	E	2	2	1	2	3	1	2	1
$\overline{34}$	3	1	3	1	2	1	2	2	3	2	2	2	E	2	1	2	3	1	2	1
$\overline{45}$	3	3	1	3	2	1	2	2	1	2	2	2	2	E	3	2	1	1	2	1
$\overline{13}$	2	2	2	2	3	2	1	3	2	1	1	1	1	3	E	1	2	2	3	2
$\overline{14}$	1	3	1	1	2	3	2	2	3	2	2	2	2	2	1	E	1	1	2	3
$\overline{15}$	2	2	2	2	1	2	3	3	2	1	1	3	3	1	2	1	E	2	1	2
$\overline{24}$	2	2	2	2	3	3	3	3	2	3	1	1	1	1	2	1	2	E	1	2
$\overline{25}$	1	1	3	1	2	3	2	2	3	2	2	2	2	2	3	2	1	1	E	1
$\overline{35}$	2	2	2	2	1	2	1	3	2	3	3	1	1	1	2	3	2	2	1	E

Table III. ML_5—Processes 4 and 6

R^4, R^6	12	25	$\overline{15}$	$\overline{24}$	$\overline{13}$	23	14	$\overline{35}$	45	34
12	E	1	1	1	1	1	1	2	2	2
25	1	E	1	1	2	1	2	1	1	2
$\overline{15}$	1	1	E	2	1	2	1	1	1	2
$\overline{24}$	1	1	2	E	2	1	1	2	1	1
$\overline{13}$	1	2	1	2	E	1	1	1	2	1
23	1	1	2	1	1	E	2	1	2	1
14	1	2	1	1	1	2	E	2	1	1
$\overline{35}$	2	1	1	2	1	1	2	E	1	1
45	2	1	1	1	2	2	1	1	E	1
34	2	2	2	1	1	1	1	1	1	E

suffices to convert any stereoisomer to any other stereoisomer in the trigonal-bipyramidal set.

Further discrimination of greater subtlety may be operationally realized if the molecular aggregate under study isomerizes at a rate that can be followed by nmr. The discrimination would be based on line-shape analysis of the transitional region. Alternative topological representations of process 1 have been published by Lauterbur and Ramirez,[12] Dunitz and Prelog,[13] and Muetterties.[2,14]

The foregoing implicitly assumed that for a given class the rates associated with the unique one-step chains do not vary significantly. If there are gross differences in individual rates, distinguishing features of the individual process may be lost or may be accentuated. Qualitatively, the effect of electronic and steric factors may be anticipated.[4]

Specific Cases: Nonchelate Structures

MA_4B. In trigonal-bipyramidal form, there are two isomers: the unique ligand is either at the axial or equatorial position. The stereochemical classes for processes 1–6 are closed with the exception of the trivial process 3 and isomerization comprises one step.

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(12) P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968).

(13) J. D. Dunitz and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **7**, 725 (1968).

(14) E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 5097 (1968).

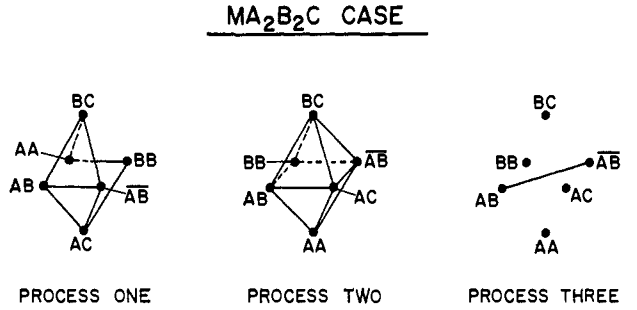
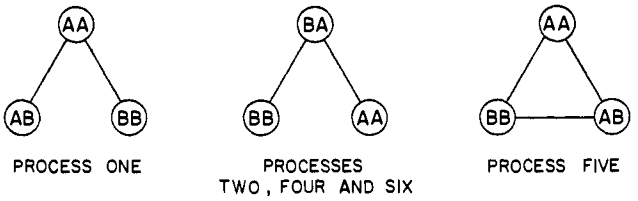


Figure 2. Topological representations for an MA_2B_2C complex or an $M_2M'_2M''$ cluster for three distinct rearrangements.

MA_3B_2. This case has three isomers: AA, BB, and AB (axial labeling). For process 3, all three isomers are mechanistically isolated, the remaining classes are closed, and the topological representations are



Thus there are four operationally distinct classes.

MA_2B_2C. This case has six isomers: AA, BB, BC, AC, AB, and $\overline{AB}$. Topological representations for three classes are given in Figure 2, and group elements are readily discerned therefrom. Through process 5, any isomer can be converted to any other in one step. Processes 4 and 6 yield isomer connectivities of three, four, and five; representation by a noninterpenetrating three-dimensional figure is not possible. The stereochemical matrix is the same for both processes (Table IV).

Table IV. MA_2B_2C—Processes 4 and 6

R^4, R^6	AA	BB	BC	AC	AB	$\overline{AB}$
AA	E	2	2	1	1	1
BB	2	E	1	2	1	1
BC	2	1	E	1	1	1
AC	1	2	1	E	1	1
AB	1	1	1	1	E	1
$\overline{AB}$	1	1	1	1	1	E

MA_3BC. There are four stereoisomers: BC, AA, AC, and AB. Stereochemical class representations based on a tetrahedron are given in Figure 3, and all elements are evident. In process 3 no isomerization can occur. There are four distinct groups out of the six classes.

MA_2BCD. The ten stereoisomers for this case are AA, BC, BD, CD, AD, $\overline{AD}$, AB, $\overline{AB}$, AC, and $\overline{AC}$. Process 3 only allows the interconversion of enantiomers. In process 5 each isomer has a connectivity of nine, and hence any isomerization is minimally one step. Processes 1 and 2 and also the stereochemically identical processes 4 and 6 are most simply represented by Tables V–VII. Process 2 differs from processes 4 and 6 only in the fact that dissymmetric isomers are only five connective, whereas all isomers are six connective in processes 4 and 6.

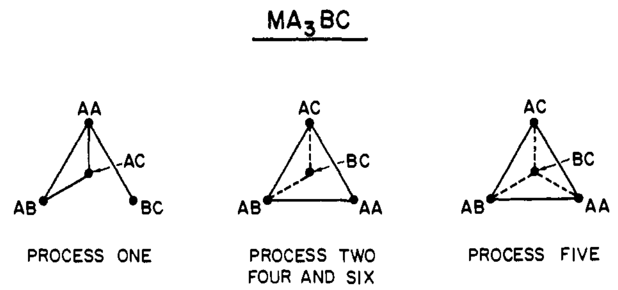


Figure 3. Topological representations in the MA_3BC family.

Chelates

In the following sections, the only limitation placed on each process is that the metal chelate angle not significantly *exceed* 120° in the intermediate or transition state. Obviously, the severe angle diminution encountered in process 5 should greatly elevate the barrier to rearrangement by this route. Ring strain does, in fact, significantly affect barriers to polytopal rearrange-

Table V. MA_2BCD—Process 1

R^1	AA	BC	BD	DC	AD	$\overline{AD}$	AB	$\overline{AB}$	AC	$\overline{AC}$
AA	E	1	1	1	2	2	2	2	2	2
BC	1	E	2	2	1	1	2	2	2	2
BD	1	2	E	2	2	2	2	2	1	1
DC	1	2	2	E	2	2	1	1	2	2
AD	2	1	2	2	E	2	1	2	2	1
$\overline{AD}$	2	1	2	2	2	E	2	1	1	2
AB	2	2	2	1	1	2	E	2	2	1
$\overline{AB}$	2	2	2	1	2	1	2	E	1	2
AC	2	2	1	2	2	1	2	1	E	2
$\overline{AC}$	2	2	1	2	1	2	1	2	2	E

Table VI. MA_2BCD—Process 2

R^2	AA	BC	BD	DC	AD	$\overline{AD}$	AB	$\overline{AB}$	AC	$\overline{AC}$
AA	E	2	2	2	1	1	1	1	1	1
BC	2	E	1	1	2	2	1	1	1	1
BD	2	1	E	1	1	1	1	1	2	2
DC	2	1	1	E	1	1	2	2	1	1
AD	1	2	1	1	E	2	2	1	1	2
$\overline{AD}$	1	2	1	1	2	E	1	2	2	1
AB	1	1	1	2	2	1	E	2	1	2
$\overline{AB}$	1	1	1	2	1	2	2	E	2	1
AC	1	1	2	1	1	2	1	2	E	2
$\overline{AC}$	1	1	2	1	2	1	2	1	2	E

Table VII. MA_2BCD—Processes 4 and 6

R^4, R^6	AA	BC	BD	DC	AD	$\overline{AD}$	AB	$\overline{AB}$	AC	$\overline{AC}$
AA	E	2	2	2	1	1	1	1	1	1
BC	2	E	1	1	2	2	1	1	1	1
BD	2	1	E	1	1	1	1	1	2	2
DC	2	1	1	E	1	1	2	2	1	1
AD	1	2	1	1	E	1	1	2	2	1
$\overline{AD}$	1	2	1	1	1	E	2	1	1	2
AB	1	1	1	2	1	2	E	1	2	1
$\overline{AB}$	1	1	1	2	2	1	1	E	1	2
AC	1	1	2	1	2	1	2	1	E	1
$\overline{AC}$	1	1	2	1	1	2	1	2	1	E

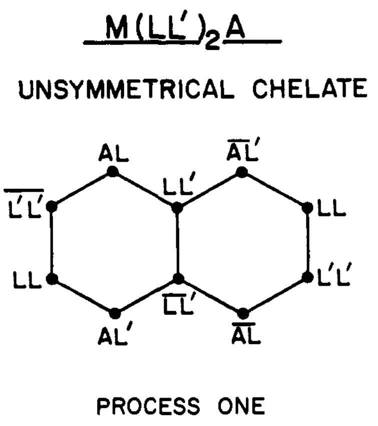
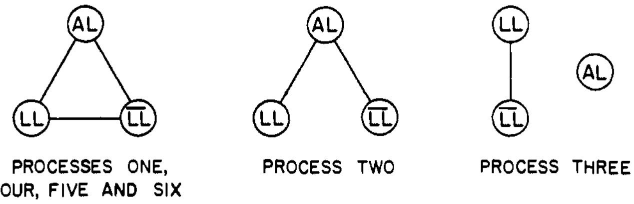


Figure 4. Planar graph for representation of the group defined by the Berry[3] process in M(LL')$_2$A.

ments.[4-6,15] Ring-strain effects have been discussed previously in the context of process 1.[4,6,12]

M(LL)$_2$A: Symmetric Chelate. The three isomers are LL, $\overline{LL}$, and AL. Topological representations for the six processes are



M(LL')$_2$A: Unsymmetric Chelate. Here the ten isomers are LL, $\overline{LL}$, L'L', $\overline{L'L'}$, LL', $\overline{LL}'$, AL', $\overline{AL}'$, AL, and $\overline{AL}$. In process 1 all isomers have connectivities of two except LL' and $\overline{LL}'$ which have connectivities of three. The simplest representation is the planar graph illustrated in Figure 4. In process 3 only interconversion of enantiomers is possible. Process 2 is topologically illustrated in Figure 5. Processes 4 and 6 are identical and define two disjoint and isomorphic groups. A topological representation of one of these groups is illustrated below.

Table VIII. M(LL')$_2$B—Process 1

R^1	AA	AB	$\overline{AB}$	BL	BL'	AL	$\overline{AL}$	AL'	$\overline{AL'}$
AA	E	3	3	1	1	2	2	2	2
AB	3	E	4	2	2	1	3	3	1
$\overline{AB}$	3	4	E	2	2	3	1	1	3
BL	1	2	2	E	2	2	2	1	1
BL'	1	2	2	2	E	1	1	2	2
AL	2	1	3	2	1	E	2	3	1
$\overline{AL}$	2	3	1	2	1	2	E	1	3
AL'	2	3	1	1	2	3	1	E	2
$\overline{AL}'$	2	1	3	1	2	1	3	2	E

Table IX. M(LL')$_2$B—Process 2

R^2	AA	AB	$\overline{AB}$	BL	BL'	AL	$\overline{AL}$	AL'	$\overline{AL'}$
AA	E	1	1	2	2	1	1	1	1
AB	1	E	2	1	1	2	1	1	2
$\overline{AB}$	1	2	E	1	1	1	2	2	1
BL	2	1	1	E	1	1	1	2	2
BL'	2	1	1	1	E	2	2	1	1
AL	1	2	1	1	2	E	2	1	2
$\overline{AL}$	1	1	2	1	2	2	E	2	1
AL'	1	1	2	2	1	1	2	E	2
$\overline{AL}'$	1	2	1	2	1	2	1	2	E

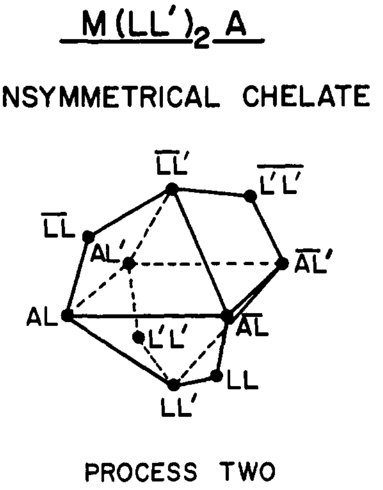


Figure 5. Representation of the group defined by process 2 in M(LL')$_2$A.

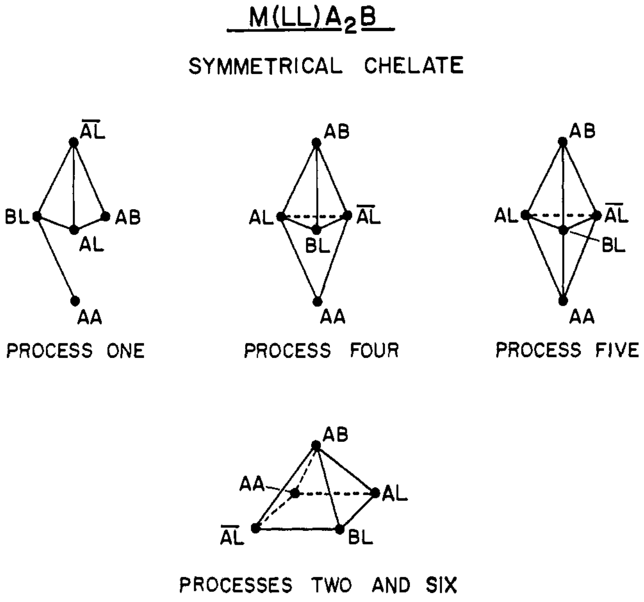


Figure 6. Topological representations for the M(LL)A$_2$B family.

Table X. M(LL')$_2$B—Process 4

R^4	AA	AB	$\overline{AB}$	BL	BL'	AL	$\overline{AL}$	AL'	$\overline{AL'}$
AA	E	2	2	2	2	1	1	1	1
AB	2	E	2	1	1	1	2	2	1
$\overline{AB}$	2	2	E	1	1	2	1	1	2
BL	2	1	1	E	1	1	1	2	2
BL'	2	1	1	1	E	2	2	1	1
AL	1	1	2	1	2	E	1	2	1
$\overline{AL}$	1	2	1	1	2	1	E	1	2
AL'	1	2	1	2	1	2	1	E	1
$\overline{AL'}$	1	1	2	2	1	1	2	1	E

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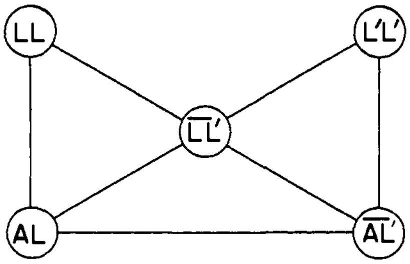
(15) E. L. Muetterties, W. Mahler, and R. S. Schmutzler, *Inorg. Chem.*, 2, 613 (1963).



In process 5, the isomer connectivities are nine and all isomerizations are minimally one step.

Table XI. M(LL')A_2B—Process 5

R^5	AA	AB	$\overline{AB}$	BL	BL'	AL	$\overline{AL}$	AL'	$\overline{AL'}$
AA	E	2	2	1	1	1	1	1	1
AB	2	E	1	1	1	1	1	1	1
$\overline{AB}$	2	1	E	1	1	1	1	1	1
BL	1	1	1	E	1	1	1	1	1
BL'	1	1	1	1	E	1	1	1	1
AL	1	1	1	1	1	E	1	1	1
$\overline{AL}$	1	1	1	1	1	1	E	1	1
AL'	1	1	1	1	1	1	1	E	1
$\overline{AL'}$	1	1	1	1	1	1	1	1	E

Table XII. M(LL')A_2B—Process 6

R^6	AA	AB	$\overline{AB}$	BL	BL'	AL	$\overline{AL}$	AL'	$\overline{AL'}$
AA	E	1	1	2	2	1	1	1	1
AB	1	E	1	1	1	1	2	2	1
$\overline{AB}$	1	1	E	1	1	2	1	1	2
BL	2	1	1	E	1	1	1	2	2
BL'	2	1	1	1	E	2	2	1	1
AL	1	1	2	1	2	E	1	2	1
$\overline{AL}$	1	2	1	1	2	1	E	1	2
AL'	1	2	1	2	1	2	1	E	1
$\overline{AL'}$	1	1	2	2	1	1	2	1	E

Table XIII. M(LL)ABC—Process 1

R^1	AC	BC	AB	CL	$\overline{CL}$	BL	$\overline{BL}$	AL	$\overline{AL}$
AC	E	3	3	2	2	1	1	2	2
BC	3	E	3	2	2	2	2	1	1
AB	3	3	E	1	1	2	2	2	2
CL	2	2	1	E	2	3	1	1	3
$\overline{CL}$	2	2	1	2	E	1	3	3	1
BL	1	2	2	3	1	E	2	3	1
$\overline{BL}$	1	2	2	1	3	2	E	1	3
AL	2	1	2	1	3	3	1	E	2
$\overline{AL}$	2	1	2	3	1	1	3	2	E

Table XIV. M(LL)ABC—Process 2

R^2	AC	BC	AB	CL	$\overline{CL}$	BL	$\overline{BL}$	AL	$\overline{AL}$
AC	E	1	1	1	1	2	2	1	1
BC	1	E	1	1	1	1	1	2	2
AB	1	1	E	2	2	1	1	1	1
CL	1	1	2	E	2	1	2	2	1
$\overline{CL}$	1	1	2	2	E	2	1	1	2
BL	2	1	1	1	2	E	2	1	2
$\overline{BL}$	2	1	1	2	1	2	E	2	1
AL	1	2	1	2	1	1	2	E	2
$\overline{AL}$	1	2	1	1	2	2	1	2	E

Table XV. M(LL)ABC—Process 4

R^4	AC	BC	AB	CL	$\overline{CL}$	BL	$\overline{BL}$	AL	$\overline{AL}$
AC	E	2	2	1	1	2	2	1	1
BC	2	E	2	1	1	1	1	2	2
AB	2	2	E	2	2	1	1	1	1
CL	1	1	2	E	1	2	1	1	2
$\overline{CL}$	1	1	2	1	E	1	2	2	1
BL	2	1	1	2	1	E	1	2	1
$\overline{BL}$	2	1	1	1	2	1	E	1	2
AL	1	2	1	1	2	2	1	E	1
$\overline{AL}$	1	2	1	2	1	1	2	1	E

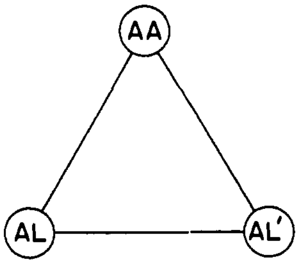
Table XVI. M(LL)ABC—Process 5

R^5	AC	BC	AB	CL	$\overline{CL}$	BL	$\overline{BL}$	AL	$\overline{AL}$
AC	E	2	2	1	1	1	1	1	1
BC	2	E	2	1	1	1	1	1	1
AB	2	2	E	1	1	1	1	1	1
CL	1	1	1	E	1	1	1	1	1
$\overline{CL}$	1	1	1	1	E	1	1	1	1
BL	1	1	1	1	1	E	1	1	1
$\overline{BL}$	1	1	1	1	1	1	E	1	1
AL	1	1	1	1	1	1	1	E	1
$\overline{AL}$	1	1	1	1	1	1	1	1	E

Table XVII. M(LL)ABC—Process 6

R^6	AC	BC	AB	CL	$\overline{CL}$	BL	$\overline{BL}$	AL	$\overline{AL}$
AC	E	1	1	1	1	2	2	1	1
BC	1	E	1	1	1	1	1	2	2
AB	1	1	E	2	2	1	1	1	1
CL	1	1	2	E	1	2	1	1	2
$\overline{CL}$	1	1	2	1	E	1	2	2	1
BL	2	1	1	2	1	E	1	2	1
$\overline{BL}$	2	1	1	1	2	1	E	1	2
AL	1	2	1	1	2	2	1	E	1
$\overline{AL}$	1	2	1	2	1	1	2	1	E

M(LL)A_3 and M(LL')A_3. For the symmetric chelate, there are two stereoisomers, AA and AL. Process 3 does not allow for isomerization, and all other processes comprise closed classes with minimal one-step isomerization. With the unsymmetrical chelate, there are three stereoisomers, AA, AL, and AL'. The topological representation for all but process 3 is



In process 3, all isomers are isolated; no isomerization can occur.

M(LL)A_2B: Symmetric Chelate. The five stereoisomers are AA, AB, BL, AL, and $\overline{AL}$. Topological representations for these processes are given in Figure 6. In process 3, the only step that can take place is interconversion of enantiomers (AL $\rightleftharpoons$ $\overline{AL}$).

M(LL')A_2B: Unsymmetric Chelate. The nine stereoisomers are AA, AB, $\overline{AB}$, BL, BL', AL, $\overline{AL}$, AL', and $\overline{AL'}$. Process 3 is again the most simply structured; enantiomer interconversions are the only allowed steps. The remaining processes are relatively complicated; many have isomers of high connectivity. Although

Table XVIII. M(LL′)ABC—Process 1

R^1	AC	$\overline{\mathrm{AC}}$	BC	$\overline{\mathrm{BC}}$	AB	$\overline{\mathrm{AB}}$	CL	$\overline{\mathrm{CL}}$	CL′	$\overline{\mathrm{CL'}}$	BL	$\overline{\mathrm{BL}}$	BL′	$\overline{\mathrm{BL'}}$	AL	$\overline{\mathrm{AL}}$	AL′	$\overline{\mathrm{AL'}}$
AC	E	5	3	4	3	4	3	2	2	3	4	1	1	4	3	2	2	3
$\overline{\mathrm{AC}}$	5	E	4	3	4	3	2	3	3	2	1	4	4	1	2	3	3	2
BC	3	4	E	5	4	3	2	3	3	2	3	2	2	3	4	1	1	4
$\overline{\mathrm{BC}}$	4	3	5	E	3	4	3	2	2	3	2	3	3	2	1	4	4	1
AB	3	4	4	3	E	5	4	1	1	4	3	2	2	3	2	3	3	2
$\overline{\mathrm{AB}}$	4	3	3	4	5	E	1	4	4	1	2	3	3	2	3	2	2	3
CL	3	2	2	3	4	1	E	5	3	2	3	2	4	1	2	3	1	4
$\overline{\mathrm{CL}}$	2	3	3	2	1	4	5	E	2	3	2	3	1	4	3	2	4	1
CL′	2	3	3	2	1	4	3	2	E	5	4	1	3	2	1	4	2	3
$\overline{\mathrm{CL'}}$	3	2	2	3	4	1	2	3	5	E	1	4	2	3	4	1	3	2
BL	4	1	3	2	3	2	3	2	4	1	E	5	3	2	3	2	4	1
$\overline{\mathrm{BL}}$	1	4	2	3	2	3	2	3	1	4	5	E	2	3	2	3	1	4
BL′	1	4	2	3	2	3	4	1	3	2	3	2	E	5	4	1	3	2
$\overline{\mathrm{BL'}}$	4	1	3	2	3	2	1	4	2	3	2	3	5	E	1	4	2	3
AL	3	2	4	1	2	3	2	3	1	4	3	2	4	1	E	5	3	2
$\overline{\mathrm{AL}}$	2	3	1	4	3	2	3	2	4	1	2	3	1	4	5	E	2	3
AL′	2	3	1	4	3	2	1	4	2	3	4	1	3	2	3	2	E	5
$\overline{\mathrm{AL'}}$	3	2	4	1	2	3	4	1	3	2	1	4	2	3	2	3	5	E

Table XIX. M(LL′)ABC—Process 2

R^2	AC	$\overline{\mathrm{AC}}$	BC	$\overline{\mathrm{BC}}$	AB	$\overline{\mathrm{AB}}$	CL	$\overline{\mathrm{CL}}$	CL′	$\overline{\mathrm{CL'}}$	BL	$\overline{\mathrm{BL}}$	BL′	$\overline{\mathrm{BL'}}$	AL	$\overline{\mathrm{AL}}$	AL′	$\overline{\mathrm{AL'}}$
AC	E	3	3	2	3	2	1	2	2	1	2	2	3	2	1	2	2	1
$\overline{\mathrm{AC}}$	3	E	2	3	2	3	2	1	1	2	2	2	2	3	2	1	1	2
BC	3	2	E	3	2	3	2	1	1	2	1	2	2	1	2	2	3	2
$\overline{\mathrm{BC}}$	2	3	3	E	3	2	1	2	2	1	2	1	1	2	2	2	2	3
AB	3	2	2	3	E	3	2	3	3	2	1	2	2	1	2	1	1	2
$\overline{\mathrm{AB}}$	2	3	3	2	3	E	3	2	2	3	2	1	1	2	1	2	2	1
CL	1	2	2	1	2	3	E	1	3	2	1	2	2	3	2	1	3	2
$\overline{\mathrm{CL}}$	2	1	1	2	3	2	1	E	2	3	2	1	3	2	1	2	2	3
CL′	2	1	1	2	3	2	3	2	E	1	2	3	1	2	3	2	2	1
$\overline{\mathrm{CL'}}$	1	2	2	1	2	3	2	3	1	E	3	2	2	1	2	3	1	2
BL	2	2	1	2	1	2	1	2	2	3	E	1	3	2	1	2	2	3
$\overline{\mathrm{BL}}$	2	2	2	1	2	1	2	1	3	2	1	E	2	3	2	1	3	2
BL′	3	2	2	1	2	1	2	3	1	2	3	2	E	1	2	3	1	2
$\overline{\mathrm{BL'}}$	2	3	1	2	1	2	3	2	2	1	2	3	1	E	3	2	2	1
AL	1	2	2	2	2	1	2	1	3	2	1	2	2	3	E	1	3	2
$\overline{\mathrm{AL}}$	2	1	2	2	1	2	1	2	2	3	2	1	3	2	1	E	2	3
AL′	2	1	3	2	1	2	3	2	2	1	2	3	1	2	3	2	E	1
$\overline{\mathrm{AL'}}$	1	2	2	3	2	1	2	3	1	2	3	2	2	1	2	3	1	E

Table XX. M(LL′)ABC—Process 5

R^5	AC	$\overline{\mathrm{AC}}$	BC	$\overline{\mathrm{BC}}$	AB	$\overline{\mathrm{AB}}$	CL	$\overline{\mathrm{CL}}$	CL′	$\overline{\mathrm{CL'}}$	BL	$\overline{\mathrm{BL}}$	BL′	$\overline{\mathrm{BL'}}$	AL	$\overline{\mathrm{AL}}$	AL′	$\overline{\mathrm{AL'}}$
AC	E	1	2	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1
$\overline{\mathrm{AC}}$	1	E	2	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1
BC	2	2	E	1	2	2	1	1	1	1	1	1	1	1	1	1	1	1
$\overline{\mathrm{BC}}$	2	2	1	E	2	2	1	1	1	1	1	1	1	1	1	1	1	1
AB	2	2	2	2	E	1	1	1	1	1	1	1	1	1	1	1	1	1
$\overline{\mathrm{AB}}$	2	2	2	2	1	E	1	1	1	1	1	1	1	1	1	1	1	1
CL	1	1	1	1	1	1	E	1	1	1	1	1	1	1	1	1	1	1
$\overline{\mathrm{CL}}$	1	1	1	1	1	1	1	E	1	1	1	1	1	1	1	1	1	1
CL′	1	1	1	1	1	1	1	1	E	1	1	1	1	1	1	1	1	1
$\overline{\mathrm{CL'}}$	1	1	1	1	1	1	1	1	1	E	1	1	1	1	1	1	1	1
BL	1	1	1	1	1	1	1	1	1	1	E	1	1	1	1	1	1	1
$\overline{\mathrm{BL}}$	1	1	1	1	1	1	1	1	1	1	1	E	1	1	1	1	1	1
BL′	1	1	1	1	1	1	1	1	1	1	1	1	E	1	1	1	1	1
$\overline{\mathrm{BL'}}$	1	1	1	1	1	1	1	1	1	1	1	1	1	E	1	1	1	1
AL	1	1	1	1	1	1	1	1	1	1	1	1	1	1	E	1	1	1
$\overline{\mathrm{AL}}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	E	1	1
AL′	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	E	1
$\overline{\mathrm{AL'}}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	E

geometrical representations are feasible for some, all five are described by the matrices in Tables VII–XII. All classes are distinct.

M(LL)ABC: Symmetric Chelate. The nine stereoisomers are AC, BC, AB, CL, $\overline{\mathrm{CL}}$, BL, $\overline{\mathrm{BL}}$, AL, and $\overline{\mathrm{AL}}$. For process 3 only racemization can occur. The other processes yield distinct groups. The matrix representations are given in Tables XIII–XVII.

M(LL′)ABC: Unsymmetric Chelate. There are 18 isomers for this case. Process 3 yields an open class wherein only racemization occurs. Processes 4 and 6 each define disjoint groups (enantiomeric in a labeling

Table XXI. M(LL')ABC—Process 4

R^4	AC	$\overline{\mathrm{BC}}$	$\overline{\mathrm{AB}}$	$\overline{\mathrm{CL}}$	CL'	BL	$\overline{\mathrm{BL'}}$	$\overline{\mathrm{AL}}$	AL'
AC	E	2	2	1	1	2	2	1	1
$\overline{\mathrm{BC}}$	2	E	2	1	1	1	1	2	2
$\overline{\mathrm{AB}}$	2	2	E	2	2	1	1	1	1
$\overline{\mathrm{CL}}$	1	1	2	E	1	1	2	1	2
CL'	1	1	2	1	E	2	1	2	1
BL	2	1	1	1	2	E	1	1	2
$\overline{\mathrm{BL'}}$	2	1	1	2	1	1	E	2	1
$\overline{\mathrm{AL}}$	1	2	1	1	2	1	2	E	1
AL'	1	2	1	2	1	2	1	1	E

Table XXII. M(LL')ABC—Process 6

R^6	AC	$\overline{\mathrm{BC}}$	$\overline{\mathrm{AB}}$	$\overline{\mathrm{CL}}$	CL'	BL	$\overline{\mathrm{BL'}}$	$\overline{\mathrm{AL}}$	AL'
AC	E	1	1	1	1	2	2	1	1
$\overline{\mathrm{BC}}$	1	E	1	1	1	1	1	2	2
$\overline{\mathrm{AB}}$	1	1	E	2	2	1	1	1	1
$\overline{\mathrm{CL}}$	1	1	2	E	1	1	2	1	2
CL'	1	1	2	1	E	2	1	2	1
BL	2	1	1	1	2	E	1	1	2
$\overline{\mathrm{BL'}}$	2	1	1	2	1	1	E	2	1
$\overline{\mathrm{AL}}$	1	2	1	1	2	1	2	E	1
AL'	1	2	1	2	1	2	1	1	E

context). The chain c_E is not an element of these groups; racemization cannot occur.

Stereochemical matrices are presented in Tables XVIII–XXII. In processes 4 and 6, only one of the isomorphic groups is tabulated. All classes are distinct.

The Thermal Polymerization of Diphosphine-4

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Abstract: The pyrolysis of diphosphine-4 has been examined in static reactors over the temperature range 300–830°K and reactant pressure range 0.5–10 Torr. Both the loss of diphosphine-4 and the formation of phosphine were observed as a function of time. At the lower temperatures, the formation and subsequent decay of triphosphine-5 was measured, while at the higher temperatures tetraatomic phosphorus was a minor product. The overall reaction is controlled by the nature of the surface, but the role of the surface is not simply to provide catalytic sites. It has been shown by labeling studies that the solid formed on the surface during the reaction is a labile hydride and that this hydride reacts directly with diphosphine-4. In addition, there appears to be a dynamic equilibrium set up between the gas-phase hydrides and the polymeric surface hydride. The entire complex reaction may be explained in terms of two simple generalized reactions.

We have published recently a number of reports on the existence and nature of several hydrides of phosphorus.[3,4] The major part of this work was directed toward identifying and characterizing new hydrides. Pyrolysis of diphosphine-4 at low pressures yielded evidence for diphosphine-2,[3a] a species that was characterized mass spectrometrically.[4] Triphosphine-5 was observed[3b] and, as it was later isolated in the pure state, was characterized more thoroughly.[3d,e] Information on the energetics of these species, obtained mainly by the mass spectrometric method, strongly suggests that the characteristic instability of these hydrides is not due to very weak phosphorus–phosphorus bonds. Rather, the difficulty in isolating higher hydrides of phosphorus lies in the extremely facile condensation reaction which they undergo. This is a particularly rapid reaction in the liquid phase. Consequently, the most characteristic feature of the hydrides with phosphorus–phosphorus bonds is this facile reaction which produces solid hydrides of variable stoichiometry and phosphine.[5] An understanding of this reaction, then, is most pertinent to an understanding of the nature of the phosphorus hydrides.

There were several secondary objectives of this work also. First, we were interested in defining the role of triphosphine-5 as an intermediate in the production and growth of the solid polymeric hydride. Secondly, we wished to test, if possible, the usefulness of the low-pressure pyrolysis technique[3c,d] in making general mechanistic conclusions. Finally, we hoped a kinetic

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[1] Abstracted from the Ph.D. Thesis of R. B. Callen, University of Notre Dame, 1968.

[2] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-657.

[3] (a) T. P. Fehlner, *J. Amer. Chem. Soc.*, 88, 1819 (1966); (b) *ibid.*, 88, 2613 (1966); (c) *ibid.*, 89, 6477 (1967); (d) *ibid.*, **90**, 4817 (1968); (e) *ibid.*, **90**, 6062 (1968).

[4] T. P. Fehlner and R. B. Callen, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, pp 181–190.

[5] A measurement of the molecular weight of this solid in molten red phosphorus yielded a formula of $P_{12}H_6$ as reported by R. Schenk and E. Buck, *Chem. Ber.*, 37, 915 (1904). They suggested that the solid was a low molecular weight polymer. A solid hydride with an empirical formula P_9H_2 formed by heating P_2H was reported by A. Stock, *et al.*, *ibid.*, 42, 2839, 2847 (1909). It was later proposed that the solid, previously characterized as P_2H, was an adsorption complex of diphosphine-4 on a solid with the formula P_6H_2 (L. Hackspill, *Compt. Rend.*, 156, 146 (1913)). Twenty years later, it was postulated that all solid hydrides were "adsorbates" of phosphine on a yellow modification of phosphorus (P. Royen and K. Hill, *Z. Anorg. Allg. Chem.*, **229**, 97, 112 (1936)). Support for this hypothesis resulted from the report by P. Royen, *ibid.*, **229**, 369 (1936), that the yellow solids were amorphous to X-rays. A reexamination of the thermal decomposition of diphosphine-4 has been reported by E. Evers and E. Street, *J. Amer. Chem. Soc.*, 78, 5726 (1956). Their data indicate that a solid roughly of composition P_9H_4 is produced. They conclude that the yellow solids are not "adsorbates" of phosphine on phosphorus and that solids of practically any composition can be produced depending on the conditions.