

Cromer and Waber with anomalous dispersions corrections taken from ref 31.

The triclinic acentric space group $P1$ is evident from the analysis of a Patterson map, where one finds six, rather than three, short Rh-P vectors. The latter are consistent with a nonsymmetrical torsion of the two P_3Rh fragments about the Rh-Rh vector. This pattern has been previously found for other structures of bridged $[(\text{triphos})M]_2$ dications and two BPh_4^- anions, e.g. $[(\text{triphos})Co(\mu-OH)_2Co(\text{triphos})](BPh_4)_2$,³² which is practically isomorphous with **6**. A number of Fourier F_o and ΔF maps allowed the identification of all of the non-hydrogen atoms, including two disordered DMF solvent molecules. Least-squares refinement with the routines of the SHELX76 program package³³ was performed by the full-matrix method, initially with isotropic and then with anisotropic thermal parameters for both Rh and P atoms. The phenyl rings were treated as rigid groups of D_{6h} symmetry with C-C distances fixed at 1.395 Å and calculated hydrogen positions (C-H = 1.08 Å). Physically reasonable temperature factors were refined by assigning population parameters of 0.5 to the atoms of the DMF molecules. The bridging hydrogen ligands could not be clearly located in the final ΔF maps, although some residual electron density of ca. $1 e/\text{\AA}^3$ (slightly above background) appeared in the expected region. As mentioned in the description of the structure, the program HYDEX¹⁰ was used to define good starting positions for the latter H atoms, which were then satisfactorily refined. The final R factor is 0.059 ($R_w = 0.064$). Refinement final coordinates of all non-hydrogen atoms (excluding rigid body atoms)

and of the three bridging hydridic hydrogens are reported in the supplementary material.

Computational Details. All of the MO calculations were of the extended Hückel type³⁴ using a modified version of the Wolfsberg-Helmholz formula. The parameters used for Rh and P atoms are taken from ref 35. Those for the nickel atom are taken from ref 36. The H_{ii} for hydrogen is -13.6 eV, and the Slater exponent is 1.3. The (triphos)Rh fragment was most often simulated with a H_3Rh fragment with Rh-H distances of 1.7 Å and H-Rh-H angles of 90°. In cases where the terminal ligands were taken as PH_3 groups, the Rh-P distance was 2.3 Å. The metal-metal separation was fixed at 2.65 Å.

Registry No. **1**, 100333-94-6; **2**, 104119-27-9; **3**, 104119-31-5; **4**, 104119-29-1; **5**, 104138-93-4; **6**, 105736-79-6; **7**, 104103-50-6; **8**, 104119-23-5; **8a**, 120686-57-9; **9**, 104119-33-7; **10**, 104119-25-7; **10a**, 120686-58-0; $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$, 12081-16-2; $[(\text{triphos})\text{Rh}(\mu-H)_3\text{Rh}(\text{triphos})]$, 120852-80-4; $[(\text{triphos})\text{Rh}(\mu-H)_3\text{Rh}(\text{triphos})]^-$, 120852-81-5; $[(\text{triphos})\text{Rh}(\mu-H)_3\text{Co}(\text{triphos})]$, 120852-82-6; $[(\text{triphos})\text{Rh}(\mu-H)_3\text{Fe}(\text{triphos})]^+$, 120852-83-7; $[(\text{triphos})\text{Rh}(\mu-H)_3\text{Ni}(\text{triphos})]$, 120852-84-8.

Supplementary Material Available: Table SI (complete crystal data), Table SII (listings of thermal parameters), Table SIII (atomic coordinates of rigid body atoms), and Table SIV (calculated coordinates of hydrogen atoms (12 pages); a table of observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page.

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Isomers and Isomerizations in Heteroatomic and Substituted P_7^{3-} and Related Systems

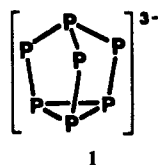
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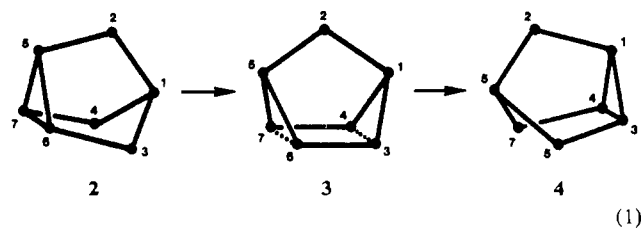
The ion P_7^{3-} is fluxional in solution. Baudler and co-workers have proposed a mechanism for the framework reorganization involved. Isoelectronic and isostructural but heteroatomic systems such as P_6As^{3-} , $As_3S_4^+$, and P_4S_3 are known and present the possibility of positional isomers. If activation barriers to rearrangement are comparable to those in P_7^{3-} , then these heteroatomic systems might undergo isomerization reactions. The various isomers can be conveniently related by reaction graphs derived from the proposed rearrangement mechanism. In reaction graphs vertices represent individual isomers and edges linking the vertices correspond to rearrangement processes. The reaction graph outlines the appropriate cuts through the energy surface along the overall reaction path. Relative energies or stabilities of isomers can be estimated by using the rule of topological charge stabilization. In this paper reaction graphs and relative isomer energies are presented and used to rationalize the existence of known isomers and to predict the existence of others among the binary cluster compounds A_6B , A_5B_2 , and A_4B_3 related to P_7^{3-} .

Introduction

In the crystalline state, the ion P_7^{3-} has the cluster or cage-shaped structure **1**.¹



In solution at 80 °C the ³¹P NMR spectrum shows that all atoms are equivalent; the ion is fluxional.^{2,3} Baudler and co-workers have proposed a mechanism (eq 1) to account for the structural reorganization that takes place. This is a degenerate rearrangement or pseudorotation that restores the original structure but with a new orientation in space. They note the similarity between eq 1 and the degenerate Cope rearrangement



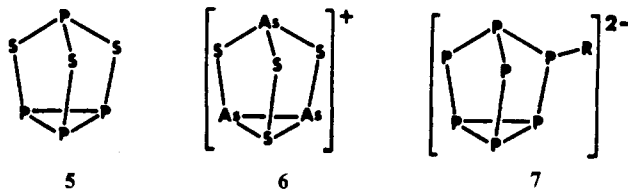
of bullvalene, $C_{10}H_{10}$.^{4,5} The barrier to rearrangement is 10–12 kcal/mol. Böhm and Gleiter have studied this rearrangement with MINDO/3 calculations and rationalized the low activation barrier using qualitative MO theory.⁶ X-ray studies of crystals containing

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As_7^{3-} and Sb_7^{3-} show that these ions have the same structure as P_7^{3-} .^{7,8} It is not known whether As_7^{3-} and Sb_7^{3-} are fluxional in solution. These ions were first reported by Zintl and co-workers, who also reported the formation of Bi_7^{3-} in solution, but no crystalline compound containing this ion has ever been prepared.⁹⁻¹¹ Corbett et al.,⁸ reassessing the report of Zintl and Dullenkopf,¹¹ conjecture that the reported Bi_7^{3-} was probably Bi_4^{2-} , which would be isoelectronic with square-planar Te_4^{2+} , known today but not in Zintl's day.

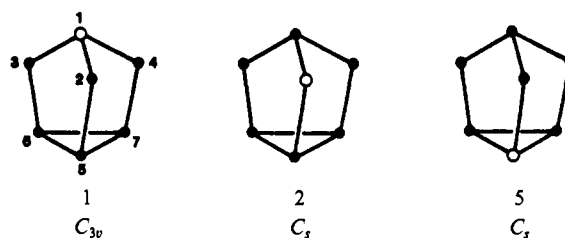
Several isoelectronic and isostructural but heteroatomic species are known (P_4S_3 (5)^{12,13} and $As_3S_4^+$ (6)¹⁴ are examples) as well as substituted forms (P_7R^{2-} (7)).^{15,16} Hönlé and von Schnering¹⁷



have examined the ³¹P NMR spectra of solutions containing $[P_{7-x}As_x]^{3-}$. These spectra can be explained by assuming the presence of P_7^{3-} , P_6As^{3-} , $P_5As_2^{3-}$, $P_4As_3^{3-}$, $P_3As_4^{3-}$, and $P_2As_5^{3-}$. It was not possible to confirm or exclude the possible existence of PA_6^{3-} . NMR intensities indicate a preference for P_6As^{3-} and $P_5As_2^{3-}$.

Heteroatoms and substituents in a fluxional frame create the possibilities of positional isomers and isomerizations. The various isomers can conveniently be related by reaction graphs based on the isomerization mechanism.¹⁸ The reaction graph reveals important connections across the energy surface for the reaction. In reaction graphs, sometimes called rearrangement graphs, vertices or points represent particular isomers and edges or arcs connecting the vertices correspond to rearrangements that carry one isomer into another. Randić, Oakland, and Klein¹⁹ have studied the properties of the rearrangement graph relating the 1680 valence tautomers or permutational isomers of P_7^{3-} . This is a very complicated graph with 1680 vertices and 2520 edges. In our work we are concerned only in rearrangements among positional isomers, chemically distinguishable structures that differ from each other by the location of one or more heteroatoms in a common structural framework. When any consideration of permutations of otherwise identical atoms is omitted, reaction graphs for positional isomers turn out to be simple and conceptually useful. Relative stabilities of isomers can be estimated by the rule of topological charge stabilization.²⁰⁻²⁴ Reaction graphs

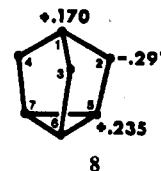
Chart I

Table I. Relative Stabilities of A_6B Isomers

isomer; m	Q_m	E_m
2	-0.291	0
1	+0.170	+0.461
5	+0.235	+0.526

and relative energies of isomers can be used to rationalize the existence of known isomers and to predict the possible existence of others.¹⁹ We have used these ideas in the study of isomers of the *closo*-carboranes.²⁵⁻²⁸ In this paper we will apply them to systems related to P_7^{3-} , As_7^{3-} , and Sb_7^{3-} .

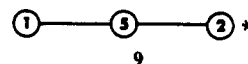
The rule of topological charge stabilization states that different kinds of atoms prefer to occupy those structural locations in which their relative electronegativities match the atomic charges established by topology for the homoatomic reference system.²⁰ For example, the normalized charges for the homoatomic ion P_7^{3-} are shown in 8.^{21,22} The charges are derived from Mulliken net atomic



populations calculated from extended Hückel wave functions. Normalized charges are atomic charges that have been adjusted by an additive constant to sum to zero.²² In P_7^{3-} each of the three different structural locations, apical (1), bridging (2,3,4), and basal triangular (5,6,7), has a different charge. In the case of heteroatomic P_4S_3 (5) the three electronegative sulfurs prefer to occupy the bridging sites that are already negative in the P_7^{3-} reference frame. We have used the rule of topological charge stabilization to account for the arrangement of heteroatoms in a number of chain, planar polycyclic, and cage or cluster-shaped structures.¹⁸

A_6B

Consider P_6As^{3-} and P_6S^{2-} as examples of the P_7^{3-} framework in which a single phosphorus atom has been replaced by a more electronegative heteroatom to form the isostructural, isoelectronic binary system A_6B . Three isomers are possible with the heteroatom located at apical, bridging, or basal-triangular positions 1, 2, or 5 (Chart I). Starting with the heteroatom in all possible positions in 2 on the left-hand side of eq 1, noting where the heteroatom appears in 4 on the right, and relating initial and final structures to the representative 1-, 2-, or 5-isomer produces the reaction graph 9. The vertices are circles that contain the isomer



index 1, 2, or 5. The lines or edges connecting the vertices rep-

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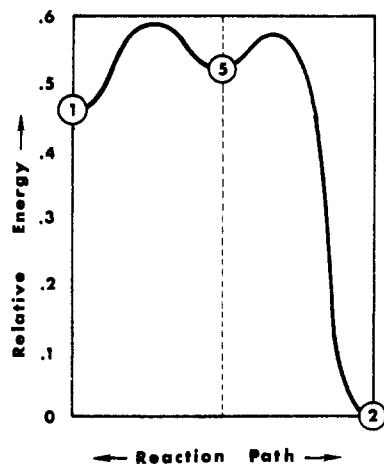
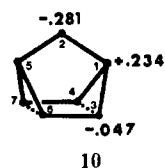


Figure 1. Relative energy as a function of reaction path as specified by the reaction graph 9 for binary clusters A_5B_2 , where B is more electronegative than A. Relative energies of isomers and activation barriers are estimated by the rule of topological charge stabilization.

resent processes that carry one isomer into another following eq 1. For example, if the heteroatom starts at the apex position 1 in structure 2 in eq 1, it ends in structure 4 at a basal position corresponding to a 5-isomer, producing the edge between the positions 1 and 5 in 9. The asterisk by vertex 2 in reaction graph 9 indicates a "loop" or degenerate process involving the 2-isomer. For the heteroatom in position 2 of structure 2, framework reorganization following eq 1 leaves the heteroatom in a bridging position. Although bonds break and new bonds form, the final structure is identical with the initial structure except for orientation in space. The observed tautomerizations of P_7R^{2-} (7) follow this loop.^{15,16}

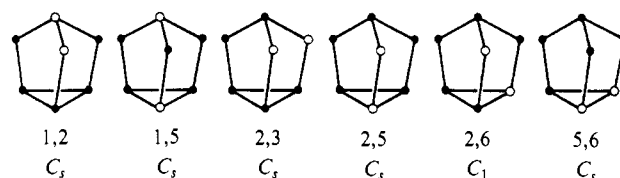
Suppose heteroatom B is more electronegative than A in A_5B_2 . From the rule of topological charge stabilization one would expect B to prefer to occupy one of the negative bridging sites (see 8) rather than an apical or basal position. Here we assume that the energy of the isomer is proportional to the charge Q_m at the replacement site m . Since the lowest energy corresponds to the most negative charge, in this case for $m = 2$, we could set $E_2 = 0$ and express relative energies of other isomers as $E_m = Q_m - Q_2$ and establish the qualitative energy order $E_2 \ll E_1 < E_5$. Values of Q_m and E_m appear in Table I. Figure 1 is a plot of energy as a function of the reaction path specified by the reaction graph 9. In preparing this diagram, we took the relative energies E_m for the individual isomers. We do not know the energies of the activation barriers separating the isomers, but if they are small, e.g. on the order of those for P_7^{3-} rearrangements, then it is likely that 1- and 5-isomers would easily rearrange to form the 2-isomer. From this reasoning we would expect P_6As^{3-} and the unknown P_6S^{2-} to exist only as the 2-isomer.

Normalized charges for the P_7^{3-} transition state 3 of eq 1 appear in 10. These values are based on extended Hückel calculations



with the MINDO/3 optimized structure reported by Böhm and Gleiter.⁶ Our charges are qualitatively similar to theirs. The structure with a heteroatom in position 2 is the transition state for pseudorotation of the 2-isomer, denoted by the asterisk in reaction graph 9. The location of the electronegative heteroatom at the position of greatest negative charge as calculated for the homonuclear frame ensures a low activation barrier for the pseudorotation. Positions 3, 4, 6, and 7 are slightly negative in structure 10. These would be locations of an electronegative heteroatom in the rearrangement of 5- A_5B to the 2-isomer. The heteroatom at the more positive positions 1 and 5 corresponds to

Chart II

Table II. Relative Stabilities of A_5B_2 Isomers

isomer; m,n	$Q_m + Q_n$	$E_{m,n}$	isomer; m,n	$Q_m + Q_n$	$E_{m,n}$
2,3	-0.580	0	2,6	-0.056	+0.526
1,2	-0.121	+0.461	1,5	+0.425	+0.987
2,5	-0.056	+0.526	5,6	+0.470	+1.052

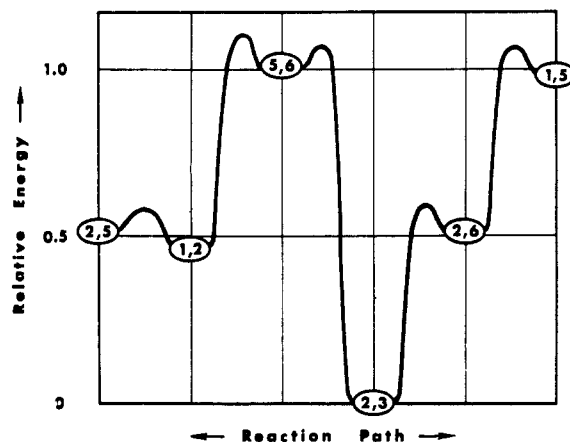
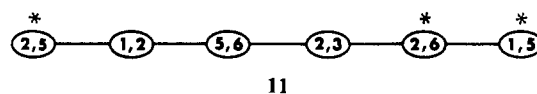


Figure 2. Relative energy as a function of reaction path as specified by the reaction graph 11 for binary clusters A_5B_2 , where B is more electronegative than A.

the transition state for the conversion of the 1- to the 5-isomer.

A_5B_2

Suppose two electronegative heteroatoms B replace two A atoms in the A_7 frame to give A_5B_2 . There are six possible isomers (Chart II). The reaction graph for A_5B_2 isomerizations, when rearrangements by eq 1 are assumed, is given in 11. Again, the



numbers in the ovals denote positions of the two heteroatoms in the structure, edges between vertices correspond to reaction processes following eq 1, and asterisks indicate those isomers for which degenerate rearrangements are possible.

We assume that isomer stabilities are related to the sum of charges Q_m and Q_n of the electronegative heteroatoms at positions m and n . The most stable isomer is that for which both electronegative heteroatoms are located at negative bridging sites, e.g. positions 2 and 3. If we take the energy of the 2,3-isomer, $E_{2,3} = 0$, then relative energies of the isomers are given by $E_{m,n} = Q_m + Q_n - (Q_2 + Q_3)$. The relative energies of the six isomers appear in Table II. The relative energies fall around three values: 0, +0.5, and +1.0. In Figure 2 these relative energies are plotted along the reaction graph 11. For the construction of this figure the activation barriers separating isomers are unknown but are assumed to be small, in analogy with the fluxional behavior of P_7^{3-} . The most stable isomer of binary ions such as $P_5S_2^-$ and $P_5As_2^{3-}$ would be the 2,3-isomer. The 1,5- and 2,6-isomers should readily rearrange to the 2,3-isomer. But the 1,2-isomer might be stabilized from rearrangement to the 2,3-isomer by a barrier at least as high as the energy of the 5,6-isomer, expected to be the least stable of the group of six.

The transition-state energies on opposite sides of a vertex can be compared by using the rule of topological charge stabilization. For example, the transition states on either side of the 5,6-species

Chart III

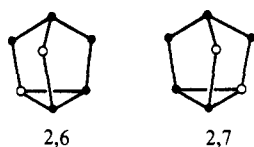
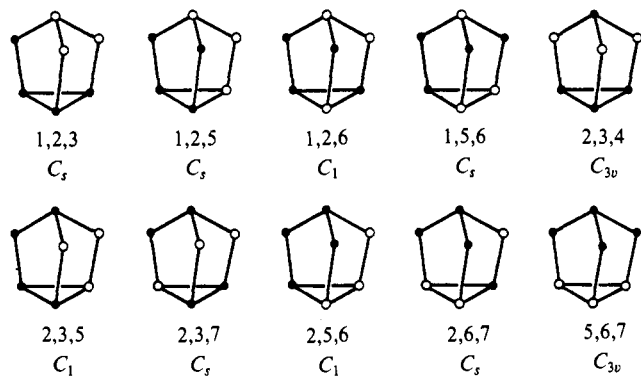
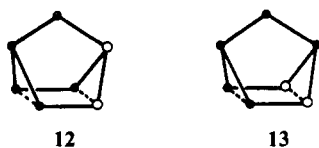


Chart IV

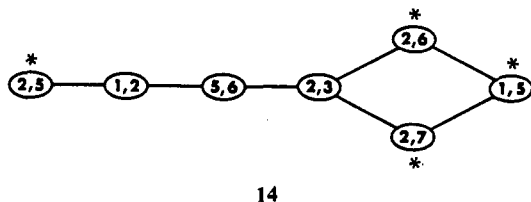


are **12** (between the 1,2- and 5,6-isomers) and **13** (linking the 5,6- to the 2,3-species). In **13** both electronegative heteroatoms occupy



sites that have negative normalized charges in the homoatomic reference structure **10**, while in **12** one heteroatom is in a strongly positive position. Therefore, **13** should be a lower energy transition state than **12**, and this conclusion is reflected in the relative barrier heights drawn schematically in Figure 2.

Of the six possible A_3B_2 isomers, the 2,6-isomer has C_1 symmetry or no symmetry at all. Therefore, the 2,6-species is but one of a pair of optical isomers or enantiomers (Chart III). The reaction graph **14** is a modification of **11** that reflects the difference

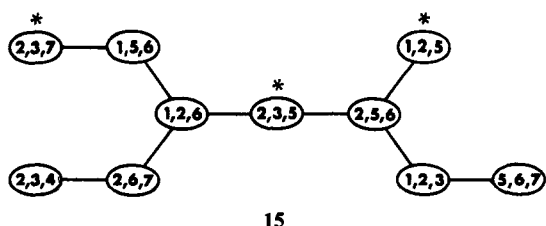


14

between the 2,6- and 2,7-isomers. From relative energy considerations (Figure 2) we concluded that the 2,6-isomer and its 2,7-enantiomer should rearrange easily to the most stable 2,3-isomer. Neither resolution of optical isomers nor stabilization of a racemic mixture is expected.

A_4B_3

The binary compound A_4B_3 with the cage structure **1** or **5** has a total of 10 possible isomers (Chart IV). The reaction graph **15** relates these isomers undergoing interconversion by eq 1.



15

Assuming that the heteroatoms B are more electronegative than A and relating energies to that of the most stable 2,3,4-isomer,

Table III. Relative Stabilities of A_4B_3 Isomers

isomer; l,m,n	$Q_l + Q_m + Q_n$	$E_{l,m,n}$
2,3,4	-0.873	0
1,2,3	-0.412	+0.461
2,3,5; 2,3,7	-0.347	+0.526
1,2,5; 1,2,6	+0.114	+0.987
2,5,6; 2,6,7	+0.179	+1.052
1,5,6	+0.640	+1.518
5,6,7	+0.705	+1.578

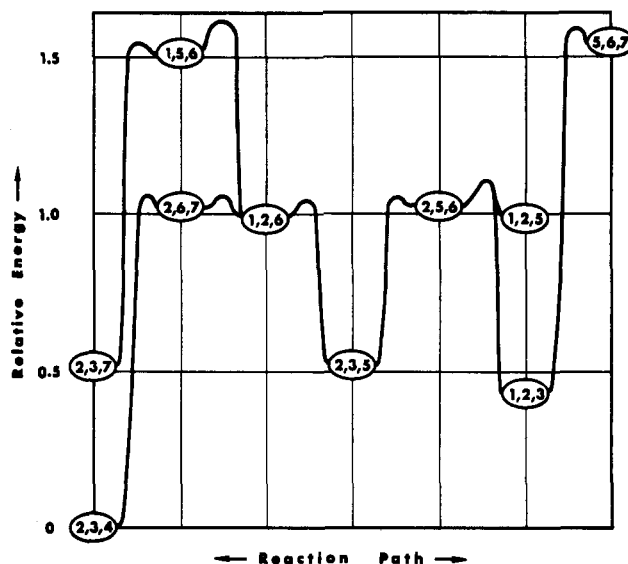
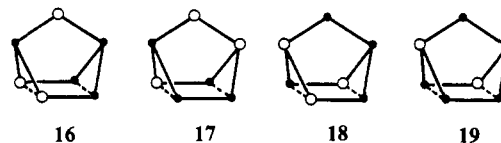


Figure 3. Relative energy of A_4B_3 clusters as a function of reaction path along **14**.

$E_{2,3,4} = 0$; $E_{l,m,n} = Q_l + Q_m + Q_n - (Q_2 + Q_3 + Q_4)$, we get the relative energies listed in Table III. The energies cluster around only four values: 0, +0.5, +1.0, and +1.5. Figure 3 displays these energies along the reaction path specified by the reaction graph **15**. This figure suggests that the isomers 2,3,7, 2,3,5, and 1,2,3 might be metastable because the barriers opposing their rearrangement to the most stable 2,3,4-isomer are at least as high as for higher energy isomers. Therefore, it might be possible to prepare and isolate these as yet unknown isomers.

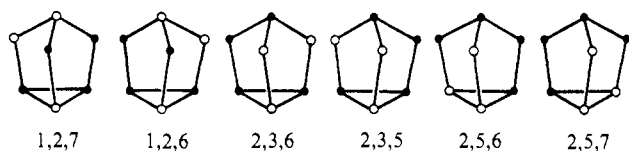
Vertices in reaction graph **15** may be connected by more than one edge because several different isomeric transition states can lead from one positional isomer to another in Figure 3. These multiple edges were suppressed in the construction of **15** and Figure 3. As an example, structures **16–19** can serve as transition



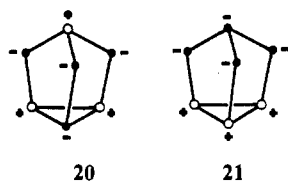
states between isomers 2,6,7 and 1,2,6 in Figure 3. The isomerization should go through the lowest energy transition state and the relative energies can be estimated by the rule of topological charge stabilization. Comparing locations of electronegative heteroatoms in **16–19** with normalized charges for the homoatomic reference **10**, one can see that **16** should be the lowest energy transition state because all three heteroatoms are in sites of negative charge. In contrast, **19** has two heteroatoms in strongly positive positions.

Christian, Gillespie, and Sawyer¹⁴ have determined the X-ray structures of the cations $As_3S_4^+$ (**6**) and $As_3Se_4^+$. Although isoelectronic and isostructural with P_7^{3-} and P_4S_3 , these two cations do not have the arrangement of atoms we expect from the rule of topological charge stabilization. Only two of the three less electronegative As atoms are located at the three basal triangular sites; the third As occupies the slightly less positive apical position. Because apical and basal site charges are similar (+0.170 vs +0.235), the 1,5,6- and 5,6,7-isomers should at least be close in

Chart V



energy. Nature's preference for the 1,5,6-isomer may be due to electrostatic stabilization by separation of like charges. Introduction of heteroatoms of different electronegativity will establish a new pattern of charge. Compare the numbers of neighboring pairs of like charge in isomers 1,5,6 (**20**) and 5,6,7 (**21**). Electrostatic stabilization by charge alternation has recently been reviewed by Klein.²⁹



Among the 10 possible A_4B_3 isomers, there are three of C_1 symmetry, signaling the possible existence of three pairs of optical isomers (Chart V). Figure 4 is the reaction graph for rearrangement of A_4B_3 following eq 1 if the three pairs of optical isomers are included. In Figure 4 the unique structures are located on the central axis of the diagram and enantiomers are paired on either side of the axis. Considering electronegative heteroatoms B once more and going back to relative energies in Figure 3, we predicted 2,3,5 to be metastable. In Figure 4 we see that the optical isomers 2,3,5 and 2,3,6 are directly linked. If rearrangement barriers are low, as they are in P_7^{3-} , we would not expect to be able to separate the optical isomers 2,3,5 and 2,3,6. The 1,2,6-, 1,2,7-isomer pair should readily rearrange to the lower energy 2,3,5-, 2,3,6-isomer pair or through the 2,6,7-isomer to the most stable 2,3,4-isomer. The 2,5,6-, 2,5,7-isomer pair should rearrange easily to isomer 1,2,3 or to the 2,3,5-, 2,3,6-isomer pair. Therefore, we would not expect to be able to resolve any of the three enantiomeric pairs, but one of the pairs, isomers 2,3,5, 2,3,6, might be metastable. If no optical isomers can be resolved, then Figure 4 can be redrawn by merging enantiomers to form a graph isomorphic with **15**.

Conclusions

We have used reaction graphs based on proposed rearrangement mechanisms and relative isomer energies obtained from the rule of topological charge stabilization to reach qualitative conclusions about various isomers, including optical isomers, that might be prepared for binary systems A_6B , A_5B_2 , and A_4B_3 related to P_7^{3-} . For A_6B there could be three different positional isomers. If the heteroatom B is electronegative, it should occupy the 2-position.

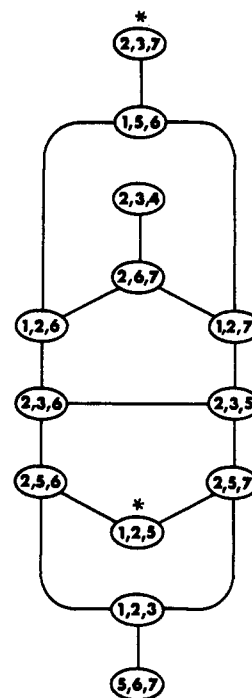


Figure 4. Reaction graph **15** for A_4B_3 clusters as modified to recognize the existence of enantiomers. Unique positional isomers occupy positions on the central axis. Enantiomers are paired on either side of the axis. If paired vertices are merged, the resulting graph is isomorphic with **15**.

A consideration of relative isomer energies and the reaction graph for isomerization suggest that only the 2-isomer is likely to be stable. A_5B_2 , with two electronegative heteroatoms, should have six possible positional isomers. The 2,3-isomer should be the most stable of these, but a higher energy 1,2- A_5B_2 might be stabilized behind a barrier posed by the even higher 5,6-isomer, which lies on the path connecting 1,2- and 2,3-isomers. Although the 2,6-, 2,7-isomer pair are mirror images, we do not expect these optical isomers to be either resolvable into individual isomers or isolable as a racemic mixture. There are 10 possible isomers for A_4B_3 , the most stable of which is the 2,3,4-isomer. The known compound P_4S_3 takes on this arrangement. But the higher energy isomers 2,3,7, 2,3,5, and 1,2,3 might be stabilized from rearrangement to isomer 2,3,4 by the intervention of even higher energy isomers along the route. Three pairs of optical isomers of A_4B_3 are possible. Of these only the 2,3,5-, 2,3,6-isomer pair might be metastable, but a low energy barrier separating the pair should prevent their resolution.

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