

Intramolecular Isomerization and Transformations in Carboranes and Substituted Polyhedral Molecules

Sir:

Nuclear magnetic resonance evidence exists for the transformation of apical $B_{10}H_9OH^{-2}$ to equatorial $B_{10}H_9OH^{-2}$ in aqueous solutions at room temperature.¹ Only the diapically substituted $C_2B_3H_5$ is known, while both the *cis* and *trans* isomers of $C_2B_4H_6$ are known² even though these compounds arise from acetylene (CC bonded) in their preparations. Thus, some experimental background exists which justifies an examination of the pathways and possible generality of intramolecular rearrangements within polyhedral-like molecules in which either there are substituents on the polyhedron or there are atoms substituted for some of those forming the polyhedron.

Polyhedra. (a) $B_5H_5^{-2}$ (D_{3h}).—The conversion of B-B and C-C bonds to B-C bonds in an isomerization process is presumed³ to lead to greater stability. The intermediate of lowest energy probably is closely related in geometry to the tetragonal pyramidal geometry (Fig. 1a) which, however, is unstable in $B_5H_3X_2^{-2}$ or in $C_2B_3H_5$. LCAO calculations⁴ show clearly that the 4-5 isomer is the most stable. In addition we note that the predicted $C_2B_3H_5^{-2}$ of lowest energy has orbital degeneracy in the one-electron LCAO approximation,^{4,5} and hence should not be stable in D_{3h} symmetry. The isomers of different symmetry remain energetically inaccessible.

(b) $B_6H_6^{-2}$ (O_h).—The *trans* form of $C_2B_4H_6$, like the *trans* form of $C_2B_3H_5$, arises from reactions of boron hydrides with acetylene. However, the *cis* form also is present, which presumably is the initial product inasmuch as the C-C proximity is preserved. The path of transformation of *cis*- $C_2B_4H_6$ to *trans*- $C_2B_4H_6$ may occur through the pentagonal pyramidal intermediate (Fig. 1b), but it is not yet possible to rule out the trigonal prism of D_{3h} symmetry as the intermediate. Here, however, the 5-6 isomer is predicted on theoretical grounds⁴ to be only somewhat more stable than the 4-5 isomer. As in the $C_2B_3H_5^{-2}$ example, we find here orbital degeneracy, and implied instability of $C_2B_4H_6^{-2}$ in D_{4h} symmetry. The other isomer is here accessible in energy.

(c) **The intramolecular rearrangement** proposed¹ for $B_{10}H_9OH^{-2}$ (apex to equatorial) as shown in Fig. 2c will convert $B_{10}H_9X_2^{-2}$ or $C_2B_8H_{10}$ to all possible isomers. Calculations of molecular orbitals by the LCAO method^{4,6,7} indicate that the various unknown $C_2B_8H_{10}$ isomers in order of predicted decreasing

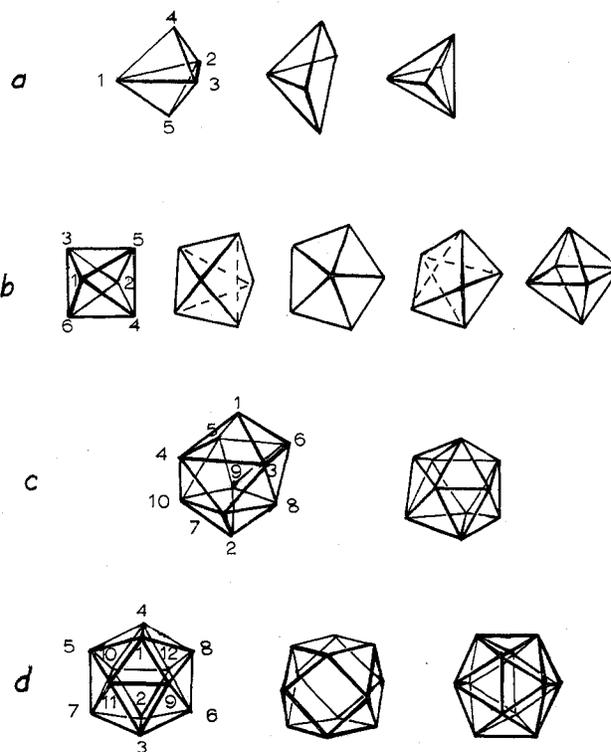


Fig. 1.—(a) Rearrangement of trigonal bipyramidal structure so that atoms 2 and 3 become non-adjacent. (b) Rearrangement of octahedral structure so that atoms 4 and 5 become non-adjacent. (c) Rearrangement of $B_{10}H_{10}^{-2}$ polyhedron so that atoms 4 and 8 become the new apices, and atom 7 inserts approximately between atoms 3 and 4. (d) Icosahedral rearrangement through the cuboctahedron so that two adjacent (*ortho*) positions become *meta* or remain *ortho*, but all *para* related substituents remain *para*.

stability are substituted at positions $1-2 > 1-8 > 1-3 > 3-5 > 3-10 > 3-4 > 3-7$ (Fig. 1c).

(d) **The cuboctahedral intermediate** suggested¹ as possible in rearrangements of $B_{12}H_{10}X_2^{-2}$ or $C_2B_{10}H_{12}$ will not convert opposed (*para*) substituents into adjacent (*ortho*) or intermediate (*meta*) substituents, as may be seen upon examination of models. The conclusion that this mechanism can only convert *ortho* into *meta* disubstituted $B_{12}H_{12}^{-2}$ is surprising, and could form a basis for a very severe test of this particular mechanism. Of course, the reverse transformation of *meta* to *ortho* also may occur, but it already has been argued from bonding principles³ and molecular orbital energies⁶ that *m*- $C_2B_{10}H_{12}$ is expected to be more stable than *o*- $C_2B_{10}H_{12}$. The stability of the *p*- $C_2B_{10}H_{12}$ is expected to be comparable with that of *m*- $C_2B_{10}H_{12}$.⁸ As a negative charge of -1 or, better, -2 is added to these three isomers of $C_2B_{10}H_{12}$, the *meta* and *para* are expected to become comparable in stability to the *ortho* ion.⁷ While a reversal in the *ortho*→*meta* transformation is not predicted for neutral $C_2B_{10}H_{12}$ isomers, the equilibrium situation may become accessible in the corresponding negative ions. Labeling of three sites, e.g., in the $C_2B_{10}H_{11}X$, gives other possibilities such as *ortho* to *ortho* and *meta* to *meta* transfor-

(8) In ref. 4, p. 4391, Table 4, the number $\Sigma E = -536.00$ should be corrected to $\Sigma E = -436.00$.

(1) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 729 (1962).

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(5) E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, **35**, 1329 (1961).

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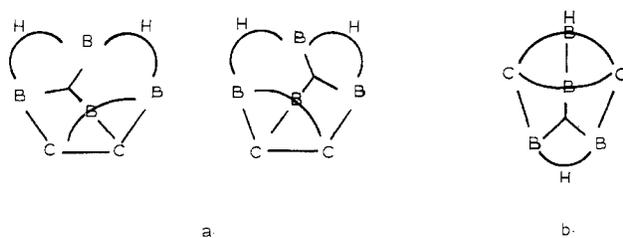


Fig. 2.—(a) Resonance structures for C₂B₄H₈ in which C atoms are adjacent. (b) Valence structure for C₂B₄H₈ in which C atoms are not adjacent. One H atom is to be added to each B and C atom.

mations, including the possibility of racemization of an optical isomer, provided that the driving force is present.

Another possibility of rearrangement is presented by C₂B₄H₈ (C_s). The valence structure proposed⁹ for C₂B₄H₈ does not satisfy the valency rules.¹⁰ However, a resonance hybrid type of three-center bond description can be written which does indeed have as satisfactory bond angles as those present in the known hydrides and derivatives (Fig. 2a). It also is possible to formulate an alternative bonding description based upon a different molecular geometry which also seems to be compatible with the nuclear magnetic resonance spectrum⁹; an isomerization is required inasmuch as the C atoms are not bonded (Fig. 2b). A structure determination by X-ray diffraction methods may settle this point.

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Kinetics of Iodination of 8-Quinolinol-5-sulfonic Acid and its Metal Chelates¹

Sir:

From a series of studies on the halogenation products obtained from certain aromatic amines, 8-quinolinol, and their metal coordination complexes,²⁻⁴ it was concluded that metal coordination has very little effect on the reactivity of these ligands. In contrast, our studies of the kinetics of iodination of 8-quinolinol-5-sulfonic acid and certain of its divalent transition metal chelates show that the coordinated metal ion has a profound effect on the rate of iodination of the ligand.

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The rate at which iodine (electrogenerated, using a direct current, at a known, constant rate from KI) reacted with 8-quinolinol-5-sulfonic acid or its metal chelate in an appropriately buffered solution was determined by recording the decrease in the diffusion current of the iodine-iodide system as a function of time.⁵

The iodination of 8-quinolinol-5-sulfonic acid in aqueous buffered solution at constant iodide ion concentration is first order in both 8-quinolinol-5-sulfonic acid and iodine (Table I). The apparent second order

TABLE I

IODINATION OF 8-QUINOLINOL-5-SULFONIC ACID AT 20°					
pH = 7.0 ^a ; [I ⁻] = 0.05 M		pH = 7.0 ^a ; [I ⁻] = 0.10 M		pH = 9.0 ^b ; [I ⁻] = 0.10 M	
[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	[Sulfonic acid] × 10 ⁴ , moles/l.	k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹
0.500	2.27	1.005	1.08	0.503	27.5
1.005	2.31	1.510	1.09	1.005	26.2
1.510	2.27			1.510	29.2
2.510	2.40				
5.000	2.27				

^a Runs at pH 7.0 were in a phosphate buffer with total phosphate = 0.10 M. ^b Runs at pH 9.0 were in a carbonate buffer with total carbonate = 0.10 M.

rate constant is inversely proportional to the iodide concentration and increases with increasing pH as well as with increasing concentrations of the buffer components. This behavior is similar to that observed previously for the iodination of phenol⁶⁻⁸ and suggests that the same mechanism may be operating in both cases, *i.e.*, the general base-catalyzed removal of the proton from the addition product of the phenolate anion of 8-quinolinol-5-sulfonic acid and I⁻.

When the iodination reaction was carried out with metal chelates of 8-quinolinol-5-sulfonic acid, formed in solution by the addition of a stoichiometric ratio (1:2) of metal ion to ligand, the same general rate expression found in the absence of metal ion was obeyed. Table II lists the observed apparent second order rate constants.

TABLE II

IODINATION OF METAL CHELATES OF 8-QUINOLINOL-5-SULFONIC ACID AT 20°		
1:2 Metal chelate ^a	pH = 7.0; [I ⁻] = 0.05 M k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹	pH = 9.0; [I ⁻] = 0.10 M k _{obs} × 10 ⁻³ , l. mole ⁻¹ min. ⁻¹
Mn ⁺⁺	1.86	7.96
Zn ⁺⁺	0.506	1.64
Fe ⁺⁺	0.482	2.05
Co ⁺⁺	0.375	~1.0 ^b
Ni ⁺⁺	~0.15 ^b	... ^c
Cu ⁺⁺	... ^c	1.3 ^b

^a The concentration of the metal chelate = 5.0 × 10⁻⁵ M. ^b Followed to <15% completion. ^c No reaction was observed under the conditions of the experiment.

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