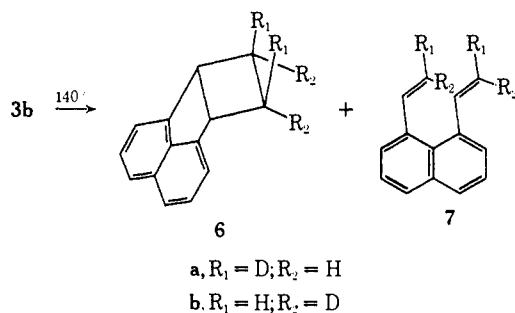


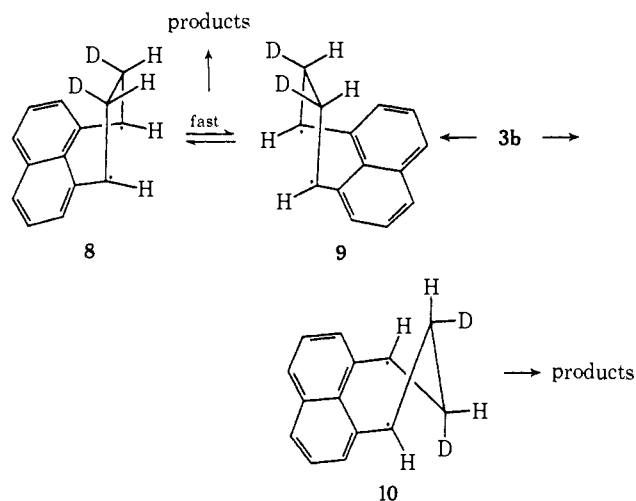
the two pathways, with or without the presence of **2**, to yield differing stereochemical results. To delve into this question, the deuterated molecule **3b** was prepared.¹⁹

When **3b** was decomposed in 1-chloronaphthalene at 140°, only deuterated **6** and **7** in a 6 to 1 ratio were



formed. Nmr analysis of the deuterated **6** showed the formation of 50% **6a** and 50% **6b**. Similar analysis of the deuterated 1,8-divinylnaphthalene revealed the formation of 50% **7a** and 50% **7b**.²⁰ The ratios, **6a/6b** and **7a/7b**, were shown to be constant by following the reaction as a function of time. Control experiments demonstrated that authentic **6a** did not equilibrate its label under the reaction conditions. Furthermore, Nelsen has shown^{6f} that **7a** undergoes *cis,trans* isomerization to the extent of only 10% at 350°, a temperature far higher than those used here. It seems clear that the product ratios and deuterium distributions reported above are indeed the initial ones.

The lack of inversion in **6** as well as the lack of preference for *cis*- or *trans*-**7** conclusively prove that **2** is an intermediate in these reactions and it reacts as if it were planar. Molecular models suggest, however, that planar **2** would be highly strained; on the other hand, a bent (**8**) and a twisted (**10**) form of **2** seem plausible intermediates. Both of these intermediates can give the observed stereochemistry by mechanisms shown below.²¹



(19) The deuterium was incorporated into the system by treating **5** with deuteriodiimide. Full details and assignments will be given in our full paper.

(20) This is actually not correct. One cannot say, in this case, the actual isomers of **7** which are present. One only knows that half the label is *cis* and half is *trans*.

(21) Twisted **2** and the nonplanar forms, **8** and **9**, may be related. Twisted **2** may be the species by which **8** and **9** interconvert.

In conclusion, this study has demonstrated the existence of 1,8-naphthoquinodimethane (**2**), a species which previously had not been characterized. Further work will attempt to determine which multiplicity of **2** and which conformation of **2** is responsible for the formation of the products **6** and **7**.

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Richard M. Pagni,* Charles R. Watson, Jr.

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

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Localized Orbitals in Large Boron Hydrides. $\text{B}_{16}\text{H}_{20}$ and Related Molecules

Sir:

The geometrical structures of the six large boranes ($\text{B}_{16}\text{H}_{20}$,¹ $\text{B}_{18}\text{H}_{22}$,² *i*- $\text{B}_{18}\text{H}_{22}$,³ $\text{B}_{20}\text{H}_{18}^{2-}$,⁴ photo- $\text{B}_{20}\text{H}_{18}^{2-}$,⁵ and $\text{B}_{20}\text{H}_{16}^{6-}$) established by X-ray diffraction methods are closely related to structures of smaller boranes. We have now established the corresponding relationships of the valence structures, exemplified here by a comparison of $\text{B}_{16}\text{H}_{20}$ with $\text{B}_{10}\text{H}_{14}$ and B_8H_{12} .⁷ Localized orbitals, objectively obtained, greatly simplify the earlier valence descriptions of these complex molecules.

In the method, widely applicable to complex molecules,⁸ we derive localized molecular orbitals (LMO's) by Boys' procedure^{8,9} from a high quality molecular orbital approximation (PRDDO¹⁰) to self-consistent field theory. The Boys procedure gives localized orbitals by maximizing the separation of the centroids of the molecular orbitals. Only dipole moment integrals over occupied molecular orbitals, $\langle \phi_i | \mathbf{r} | \phi_j \rangle$, are needed for the Boys method. (The Edmiston-Ruedenberg¹¹ (ER) method requires all two-electron integrals over occupied molecular orbitals.) The Boys procedure has been coupled here with the PRDDO technique yielding an efficient method for obtaining localized orbitals. The only significant difference, between these results and those obtained by the ER procedure, is found for 1,2- $\text{C}_2\text{B}_4\text{H}_6$ where the Boys procedure makes all three-center bonds central while ER yields two combinations each

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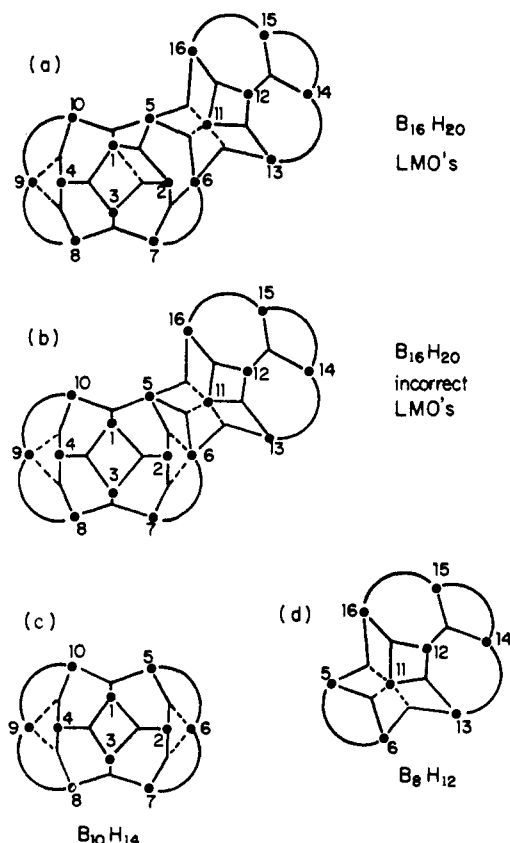


Figure 1. Localized molecular orbital structures and numbering schemes. The $B_{16}H_{20}$ numbering has been retained in the B_8H_{12} and $B_{10}H_{14}$ molecules: (a) $B_{16}H_{20}$, correct LMO structure; (b) $B_{16}H_{20}$, computationally unstable LMO structure; (c) $B_{10}H_{14}$ LMO structure; and (d) B_8H_{12} LMO structure. Solid lines correspond to normal three-center bonds, curved lines correspond to bridge hydrogens, and dashed lines correspond to fractional bonds at fractional centers. Except for B5 and B6, each boron in $B_{16}H_{20}$ has one terminal hydrogen. Each boron in $B_{10}H_{14}$ and B_8H_{12} has one terminal hydrogen.

consisting of a single bond and an open three-center BCB bond.¹²

Table I. PRDDO Energies and Boys Localization Criteria

Total energy	-406.1873 au
$-E/T$ (virial ratio)	0.998
Highest occupied MO	-0.3855 au
Lowest unoccupied MO(1) ^a	0.0294 au
Lowest unoccupied MO(2) ^a	0.0847 au
Initial D_B ^{b,c}	5778 au
Final D_B (Figure 1a) ^c	6615.3 au
Final D_B (Figure 1b) ^c	6614.7 au
Largest eigenvalue (2nd deriv) ^d	-1.49 au

^a Lowest unoccupied MO eigenvalues are given to show that they are near zero. Thus, low lying electronic states may be available. ^b Derived from a unitary matrix generated from random numbers. ^c Units of dipole moment squared. ^d Figure 1a.

Using coordinates for $B_{16}H_{20}$ from the X-ray study,¹ we obtain (Table I) energies and values of the sum of squares

$$D_B = \sum_{i=1}^N \langle \phi_i | \mathbf{r} | \phi_i \rangle^2$$

where N is the number of doubly occupied MO's, ϕ_i ,

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and \mathbf{r} is the vector from the origin. The PRDDO wave function includes all 100 electrons and a minimum basis set of 100 Slater atomic orbitals. Localized orbitals (Figure 1 and Table II), compared with those

Table II. LMO Populations (e)^a and Mulliken Charges (e) for $B_{16}H_{20}$ (Figure 1a)

A.							
Atom	Pop.	Atom	Pop.	Atom	Pop.	Atom	Pop.
10 ^b	0.73	16	0.70	13	0.83	11	0.53
9	0.32	12	0.74	11	0.29	6	0.71
4	0.72	11	0.34	6	0.85	5	0.76
3	0.74	9	0.52	13	0.72	16	0.84
2	0.72	8	0.65	12	0.72	11	0.37
1	0.26	4	0.73	11	0.37	5	0.77
7	0.47	10	0.76	4	0.71		
6	0.73	5	0.72	3	0.66		
2	0.72	1	0.50	1	0.52		
15	0.61	5	0.69	8	0.74		
14	0.65	2	0.71	7	0.67		
12	0.72	1	0.45	3	0.59		

B.							
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
1	0.05	5	0.03	9	0.10	13	-0.02
2	-0.01	6	-0.01	10	0.03	14	0.09
3	-0.03	7	0.12	11	0.09	15	0.11
4	-0.05	8	0.06	12	-0.06	16	0.01

^a Electrons. ^b Braces enclose contributions to a single LMO.

for $B_{10}H_{14}$ (1c) and B_8H_{12} (1d), show that the B_8H_{12} topology is completely retained in $B_{16}H_{20}$ and that for $B_{10}H_{14}$ nearly so. We did find, starting from many randomized MO sets, the valence structure (1b) for $B_{16}H_{20}$ which retains the $B_{10}H_{14}$ topology; however, the presence of a positive eigenvalue (0.75) in the second derivative test^{3,13} indicated that this valence structure is not at a maximum on the multidimensional localization surface. Thus, the preferred electron-pair description of $B_{16}H_{20}$ is 1a showing little change in the region of fusion as compared to the component molecules and no change in the outer $B_{10}H_{14}$ -like and B_8H_{12} -like regions of $B_{16}H_{20}$.

Comparison of the LMO structure for $B_{10}H_{14}$ with that found for $B_{16}H_{20}$ shows only one bond change. The 2,5,6 bond in $B_{10}H_{14}$ becomes a 2,5,1 bond in $B_{16}H_{20}$ shifting the site of fractional bonding from B6 in $B_{10}H_{14}$ to B1 in $B_{16}H_{20}$. The Mulliken charge (from the full SCF wave functions) at B6 drops from +0.10 in $B_{10}H_{14}$ to -0.01 in $B_{16}H_{20}$. However, B1 becomes slightly more positive in going from $B_{10}H_{14}$ (+0.03) to $B_{16}H_{20}$ (+0.05) while B2, B3, and B4 are negative in $B_{16}H_{20}$. We also note that an LMO structure for $B_{16}H_{20}$ (Figure 1b) with a 2,5,6 bond is not at a maximum on the surface. Thus the change in fractional site between related molecules can be correlated with a change in Mulliken charge allowing the following simple explanation. Fractional bonding can be viewed as donation of charge from electron-rich to electron-deficient regions, and fractional centers would be expected to occur in the more positive regions in a molecule. This correlation of fractional site with positive (Mulliken charge) centers is

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adhered to reasonably well in the close boranes and carboranes but does not apply as generally to the open boranes.^{7b}

Atom B₁₁ is an extraordinary fractional center, having five cage bonds and one external B-H_t bond. Also, B7 in B₁₆H₂₀ (charge 0.12) receives about 0.2 e from the 1,2,3 bond, supporting the ideas above. As noted for B₄H₁₀,^{13b} the usual two- and three-center bonds may become multicentered below a level of about 0.2 e donation.

We have recently completed PRDDO-Boys LMO studies on other large boron hydrides.¹⁴ Normal-B₁₈H₂₂ yields two B₁₀H₁₄ fragment structures which have the same LMO bonding as that found for the B₁₀H₁₄ fragment in B₁₆H₂₀. Also, B₂₀H₁₈²⁻ localizes to a regular three-center structure, and B₂₀H₁₆ localizes to a structure which preserves *D*_{2d} symmetry. *i*-B₁₈H₂₂ yields a slightly irregular structure and photo-B₂₀H₁₈²⁻ shows multiple maxima on the localization surface.

An LMO structure for B₁₆H₂₀ constructed from the LMO's of B₁₀H₁₄ and B₈H₁₂ is closely related to the correct LMO structure. This result, and similar results for other molecules, indicates substantial transferabilities of LMO's from smaller molecules to closely related regions of larger molecules. However, the LMO's do depend on the overall charge distribution. If the charge distributions in the smaller molecules are not similar to those in the appropriate region of the larger molecule, then complete transferability does not occur.

The results obtained here from PRDDO-Boys LMO's are consistent with bridging of icosahedral fragments in large boron hydrides, and they also clarify fractional bonding and simplify results on the topological theory.¹⁵

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David A. Dixon, Daniel A. Kleier
Thomas A. Halgren, William N. Lipscomb*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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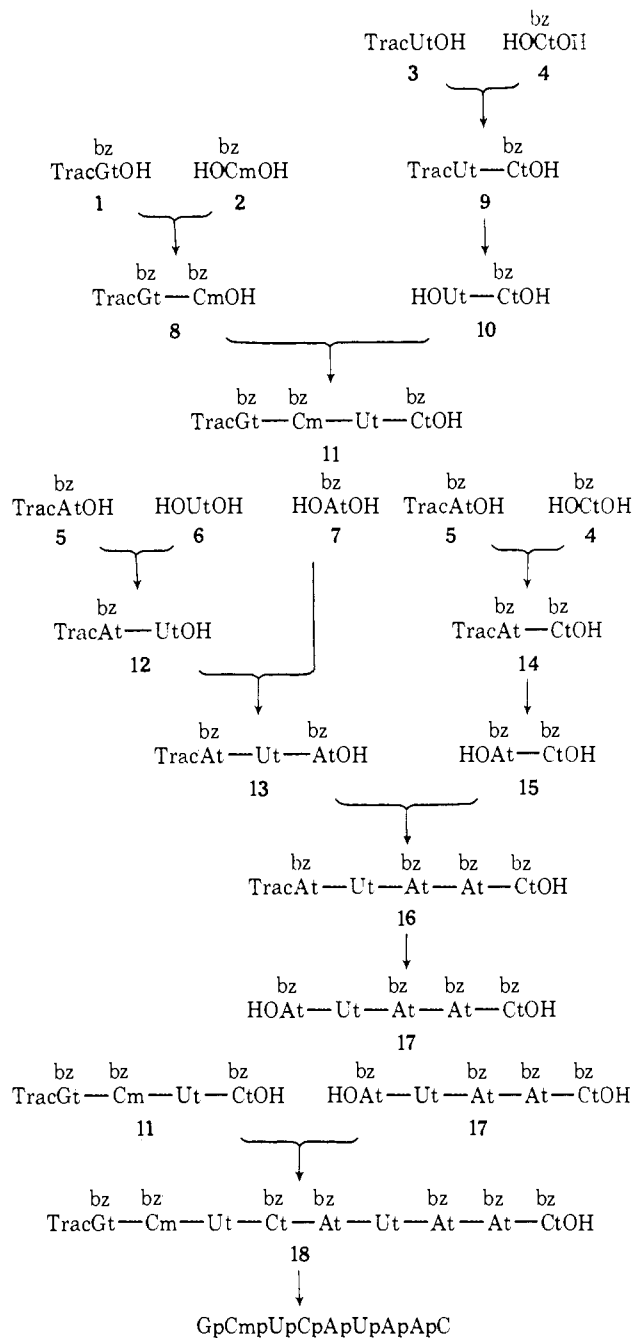
Synthesis of the Anticodon Loop of *Escherichia coli* Methionine Transfer Ribonucleic Acid¹

Sir:

Large scale synthesis of oligoribonucleotides corresponding to discrete sequences within native ribonucleic acids should encourage further studies in protein-nucleic acid recognition. One such chemical synthesis, the duplex stem region of yeast tRNA^{Ala}, has

(1) Communication constitutes Paper VII in a series entitled "Oligoribonucleotide Synthesis." Part VI: E. S. Werstik and T. Neilson, *Can. J. Chem.*, **51**, 1889 (1973).

Scheme I



been carried out² using a modification of the established phosphodiester method.³

We now report the synthesis of the nonaribonucleotide, GpCmpUpCpApUpApApC, which corresponds to the anticodon loop of tRNA^{Met} from *E. coli*,⁴ using the recently developed phosphotriester fragment coupling method.⁵ A summary is shown in Scheme I.⁶ Oligonucleotide synthesis using intermediates containing

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(6) Abbreviations are as suggested by the IUPAC-IUB commission, *Biochemistry*, **9**, 4022 (1970). Trac is 5'-*O*-triphenylmethoxyacetyl, t is 2'-*O*-tetrahydropyranyl, and m is 2'-*O*-methyl. Hyphen between two characters, e.g., At-Ut, indicates a 2,2,2-trichloroethyl phosphotriester internucleotide linkage.