combined with foreseeable improvements in probe and instrument design, should greatly improve spectral quality and permit careful examination of structural details of DNA alone and in combination with specific chemical agents.

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(9) The DNA was dissolved in 0.195 M NaCl, 5 mM Na_2EDTA, 10 mM Tris, 1 mM cacodylic acid, and 0.02% NaN_3. This DNA was fractionated on a Bio-Gel A0.5 m column (5 × 100 cm) eluted with the above buffer made 34% in sucrose (flow rate, 112 mL/h).
(10) DNA fractions from the column were assayed for size (determined by electrophoresis according to Peacock A. C.; Dingman, C. W. *Biochemistry* **1967,** *6,* 1818), pooled, and dialyzed against 1.0 M NaCl. The DNA was precipitated with 1.5 vol. of isopropyl alcohol. After lyophilization to remove volatile impurities, the sample was dissolved in phosphate buffer or NaCl (Table I).
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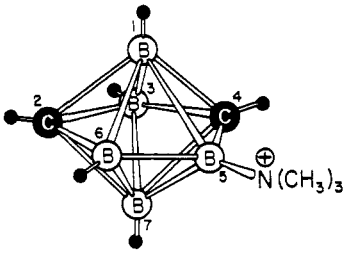
Synthesis of a Nitrogen Derivative of *closo*-2,4-$C_2B_5H_7$

Sir:

Most of the known boron-substituted derivatives of the nonicosahedral *closo*-carboranes, $C_2B_nH_{n+2}$ (n = 3-9), contain either halogen or alkyl attachments, and there are no known compounds containing boron-bonded group 5 substituents.[1,2] Furthermore, it is known that the parent *closo*-2,4-$C_2B_5H_7$ does not react with trimethylamine below the nucleophile decomposition temperature; however, secondary and primary amines cleave this pentagonal bipyramidal cage compound to noncage fragments.[3]

We report here a nitrogen derivative of *closo*-2,4-dicarbaheptaborane, [5-$(CH_3)_3$N-2,4-$C_2B_5H_6$]$^+$ (I), which is



I

prepared from 5-Cl-2,4-$C_2B_5H_6$ and trimethylamine followed by the removal of the halogen in what might be termed a "net two-step displacement" reaction. The first step is the formation of a 1:1 adduct (II) of the two reagents to form $(CH_3)_3$N·$ClC_2B_5H_6$. The same adduct is formed both in the absence of solvent and also upon employing solvents such as methylene chloride or chloroform. Further, an excess of either reagent, the amine or the chlorocarborane, results in the formation of a 1:1 adduct only, with the excess reagent removed by vacuum distillation. The adduct (II), dissolved in methylene chloride or chloroform, exhibits proton decoupled ^{11}B NMR resonances at δ −19.4 (upfield), +2.3 (downfield), +6.3, +17.4 ppm from $(C_2H_5)_2O{\cdot}BF_3$ in an area ratio of 2:1:1:1; the undecoupled ^{11}B NMR spectrum shows the low-field peak at δ + 17.4 to be a singlet resonance and the other three resonances to be 1:1 doublets with $J(^{11}BH)$ = 179, ~130, and ~160 Hz from high to low field, respectively. Boron-11 decoupled proton resonances were observed at τ (relative to internal H_2CCl_2, τ 4.67) 2.37 (HC), 4.32 (HC), 5.43 (HB), 6.23 (HB), 6.60 (Me_3N), and 9.64 (HB) in an area ratio of 1:1:0.8:0.8:9:1.6, respectively. (Note that the ^{10}B isotope, ~20% of naturally occurring boron, remains coupled to the terminal boron-attached hydrogens and does not substantially contribute of the measured areas of the boron-11 decoupled proton singlets.)

The addition of BCl_3 to adduct II removes chloride ion to form the quaternary ammonium salt [5-$(CH_3)_3$N-*closo*-2,4-$C_2B_5H_6$]$^+$[BCl_4]$^-$ (I): ^{11}B NMR δ −19.3 ($J(^{11}BH)$ = 190 Hz) for B(1,7), +1.7 ($J(^{11}BH)$ = 156 Hz) for B(6), +6.3 ($J(^{11}BH)$ = 183 Hz) for B(3), +10.3[4] for BCl_4^-, +16.8 ppm for B(5); ^{11}B decoupled ^{1}H NMR τ 3.73 (m) for HC(2 or 4), 4.14 (m) for HC(4 or 2), 5.12 (skewed t, J[H(3), H(2)] ≃ J[H(3), H(4)] = 5 to 7 Hz) for HB(3), 5.79 (1:1 d, J[H(6), H(2)] ≃ 9 Hz) for H(6), 6.59 for $(CH_3)_3$N, 9.32 ppm for HB(1,7). The marked similarity of the ^{11}B NMR of I to both 5-Cl- and 5-CH_3-2,4-$C_2B_5H_6$[5-7] as well as the coupling patterns, particularly in the ^{11}B decoupled ^{1}H NMR,[8] leaves little doubt that the assigned substituted *closo*-carborane structure is correct. In addition, the trimethylphosphine analogue of compound I, prepared in a fashion similar to that for I, shows a ^{31}P-^{11}B(5) coupling of 158 Hz, verified by decoupling experiments. The structure of the initial adduct (II) is more speculative. By analogy to the 1:1 adduct of trimethylamine and 1,6-$C_2B_4H_6$,[3,9,10] adduct II might be expected to be that of a *nido*-C_2B_5 moiety,[11] but the close similarity of ^{11}B NMR resonance positions of the compound to those of 5-X-2,4-$C_2B_5H_6$ (X = Cl, CH_3)[5-7] suggests that II may have retained a substantial closo bipyramidal character. The broadness of the resonances additionally suggests some degree of cage fluxional behavior in which a closo framework equilibrates with the expected nido structure and/or with a [$(CH_3)_3$N-$C_2B_5H_6$]$^+$$Cl^-$ ion pair.

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Preliminary studies on trimethylamine reactions with the halogenated *closo*-carboranes 5,6-Cl_2-2,4-$C_2B_5H_5$ and 2-Cl-1,6-$C_2B_4H_5$ definitely implicate pyramidal nido adducts, although the subsequent removal of halide ion appears more complicated than in the case of the 5-chloro-2,4-dicarbaheptaborane adduct.

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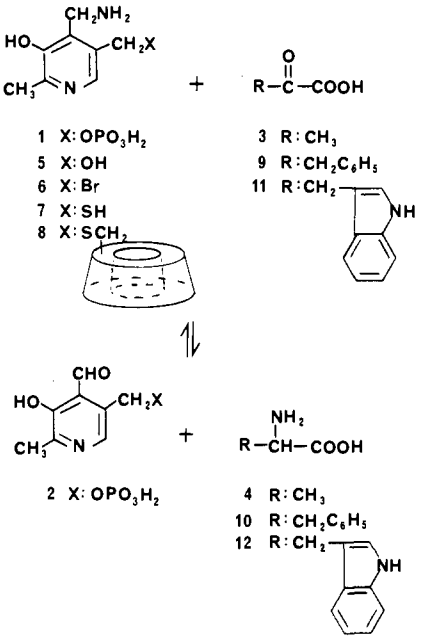
Selective Transamination and Optical Induction by a β-Cyclodextrin–Pyridoxamine Artificial Enzyme

Sir:

Pyridoxamine phosphate (**1**) and pyridoxal phosphate (**2**) are the characteristic coenzymes of amino acid metabolism.[1] Along with appropriate enzymes they perform a variety of carbon-carbon bond formations and cleavages, rearrangements, etc., on the paths to and from amino acids. However, the prototypical reaction involving these coenzymes is transamination. Pyridoxamine phosphate reacts with an α-keto acid such as pyruvic acid (**3**) to form a Schiff base which tautomerizes and cleaves to pyridoxal phosphate (**2**) and an amino acid, in this case alanine (**4**). In the complete cycle the sequence is then reversed, using a different amino acid such as phenylalanine (**10**) to convert the pyridoxal coenzyme back into **1**, while the amino acid **10** is converted into keto acid **9.**



Model studies[1,2] have shown that all of the known enzymatic reactions in which pyridoxal or pyridoxamine phosphate play a role can be duplicated to some extent with the coenzyme alone, without an enzyme. However, the reactions without an enzyme are much slower and are quite unselective among the possible reactions which the coenzymes can catalyze. Since β-cyclodextrin (cycloheptaamylose)[3] can be used in enzyme models which under the best circumstances show rate accelerations of enzymatic magnitude,[4] and since reactions of substrates bound into the cyclodextrin cavity are frequently very selective with respect to substrate and pathway,[5] it was attractive to link the pyridoxal-pyridoxamine coenzymes to β-cyclodextrin. We report here the first example of such a linked molecule (**8**). As expected, the combination in this molecule of an enzyme-like binding site with a coenzyme has led to good substrate specificity in transaminations and to some chiral induction.

Pyridoxamine (**5**) dihydrochloride was converted into the bromomethyl derivative (**6**) dihydrobromide[6,7] with 48% HBr. This with potassium thioacetate and then acetic anhydride afforded the *O,S,N*-triacetyl derivative[7] of **7**, mp 168–169 °C, in 85% yield (Anal. C, H, N, S) which with 48% HBr at 100 °C for 5 h gave a 70% yield of **7** dihydrobromide.[7,8] The air-sensitive thiol was heated at 60 °C for 16 h in H_2O-NH_4HCO_3 with β-cyclodextrin 6-tosylate;[9] isolation on Sephadex CM-25 with NH_4HCO_3 afforded **8**, which was analyzed[10] as a hexahydrate.[7]

To examine the selectivity of this compound in a typical pyridoxamine reaction, **8** was compared with simple pyridoxamine (**5**) and with **5** plus 1 equiv of added β-cyclodextrin in the reductive amination of three α-keto acids, **3**, **9**, and **11.** Reactions of the keto acids were run either singly or competitively, with, e.g., 1 equiv each of pyruvic acid (**3**), phenylpyruvic acid (**9**), and pyridoxamine (**5**) at concentrations of 0.05–5 mM in 4.0 M phosphate buffer,[11] pH 8. After a given time at room temperature, an excess of dinitrofluorobenzene was added in ethanol-water and the mixture was heated[12] at 60 °C for 90 min. Acidification, extraction with ether, and concentration were followed by LC analysis,[13] calibrated with authentic samples of dinitrophenyl derivatives of **4**, **10**, and **12.**

With pyridoxamine (**5**) the three keto acids had similar reactivity, reaction leading to equal yields of each amino acid in 1:1 competitive studies. When β-cyclodextrin was also present the result was similar, although the aromatic substrate **9** was now ~20% less reactive than was pyruvic acid (**3**), presumably because of some binding of **9** by β-cyclodextrin. However, with the artificial enzyme **8** the results were strikingly different. Indolepyruvic acid (**11**) was converted into tryptophan (**12**) by **8** at a rate[14] ~200 times than that for reaction of **11** with **5**, but **3** reacted at essentially the same rate[15] with **8** or with **5.** As expected from this, competitive reaction of **8** with **11** and **3** led almost exclusively to the formation of tryptophan (**12**) under appropriate conditions. At early times (~10 min), the product from 1:1 competition is at least 97% tryptophan, although the ratio then decreases as the system equilibrates. With phenylpyruvic acid (**9**) vs. pyruvic acid (**3**) the product is at least 98% phenylalanine (**10**) before equilibration decreases the ratio.

The preferential reaction of **8** with substrates **9** and **11** is expected from models, which show that the aromatic rings of **9** or **11** can bind into the cyclodextrin cavity during transam-

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