nation of $PhCH_3$ vs. $PhCD_3$ is 3.6, and the chlorination of ring-substituted toluenes is characterized by a Hammett ρ^+ value of -1.7. The H-abstracting agent in this system is believed to be the ClO· radical. For comparison, a Hammett ρ value of -1.6 has been reported for the cumene hydroperoxide supported P-450 catalyzed benzylic hydroxylation of substituted toluenes.[30] The isotope analyses of the benzyl chlorides resulting from the phase-transfer chlorinations of **1** and **2** are given in Table III. Processing of these data as described for the hydroxylation data reveals that $r_1 = 11.87 \pm 0.12$ and $r_2 = 2.96 \pm 0.03$; thus $r_1/r_2 = 4.01 \pm 0.07$, which is in excellent agreement with the predicted value.

In light of this result is is interesting to compare the chlorination data to the hydroxylation data directly. One immediately notices that the hydroxylation data have a much greater variance than the chlorination data. Such variance in data derived from microsomal systems is not atypical,[3,5-7,12,16,25] but as mentioned above it softens the contrast between theory and experiment. It is also interesting that both systems gave nearly identical results with toluene **2**, which means that most of the difference in the r_1/r_2 values derived from these two data sets derives from differences in the data for substrate **1**. In absolute terms this difference is only about 5 mol %, but since this is only slightly more than the relative standard deviation of the hydroxylation data, statistical analyses were performed to test the hypothesis that differences between the observed r_1/r_2 values (Table II) and the predicted values are due to random experimental error. The results of these analyses (p values) are reported in Table II; they indicate that it is rather unlikely that random errors can account for the difference between theory and experiment.

Returning now to the chlorination data with the information that $r_3 = 3.6$,[12] we can solve eq 7–9 for explicit values of P and S rather than only their ratio, whereupon we find that $P = 5.01$ and $S = 0.85$ per deuterium. The value of 5.0 for P appears quite reasonable for a primary kinetic deuterium isotope effect on a

hydrogen-abstraction reaction. The finding that the secondary effect is *inverse* is somewhat surprising. Ordinarily one would expect a *normal* secondary effect as the hybridization at the benzylic carbon changes from sp^3 toward sp^2. While the exact value of S is subject to some experimental uncertainty, it would require a combination of unrealistically large errors in r_1, r_2, and r_3 for S to approach unity or greater. Furthermore, although S may be inverse, its value is not unrealistically small. Thus it would appear that there is substantial C–H bond breaking in the transition state for the rate-limiting step in the chlorination sequence and that the bonding of the secondary hydrogens is becoming tighter rather than looser. This could possibly be explained by approach of the H-abstracting species in such a way as to impede the out-of-plane bending motions of the secondary hydrogens. Other explanations may also be possible, however.

In conclusion, it would appear from the chlorination results that eq 1–9 represent a reasonable model for the analysis of *concurrent* primary and secondary kinetic deuterium isotope effects at a methyl group reaction center. Their failure to accommodate data for the microsomal hydroxylation of toluene is surprising, and at present we have no logical explanation for this. Further studies with other reagents that lead to the benzylic functionalization of toluene are planned.

(30) Blake, R. C., II; Coon, M. J. *J. Biol. Chem.* **1981**, *256*, 12127–12133.

Synthesis and Crystal Structure of an Enantiomerically Pure, Internally Coordinated Alkylchloroborane. The Boron-Centered Anomeric Effect

Christopher S. Shiner,* Charles M. Garner, and R. Curtis Haltiwanger

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309. Received March 22, 1985

Abstract: The synthesis and crystal structure of (S)-(O–B)-chloro[(1S,2R,3S,5S)-2-[2(R)-methoxyethyl]-6,6-dimethyl-3-norpinyl]borane, an enantiomerically pure, internally coordinated alkylchloroborane monomer, are described. This is the first crystallographic structure determination for a chiral organoborane, and the first complete X-ray analysis of a monoborane–ether complex. The crystals are monoclinic of space group $P2_1$, with $Z = 2$ in a unit cell of dimensions $a = 7.468$ (3) Å, $b = 10.887$ (3) Å, $c = 7.898$ (3) Å, and $\beta = 95.29$ (3)°. The structure was determined by a heavy atom method from 1676 unique reflections and refined to a final R value of 0.046. Key features of the structure, including the configuration of the stereogenic boron atom, the unusually long B–Cl bond ($d = 1.890$ Å), and the geometry of the trivalent oxygen, are manifestations of a novel boron-centered anomeric effect. An improved preparation of $BH_2Cl·SMe_2$ has also been devised.

Chiral organoboranes are versatile and effective reagents for asymmetric synthesis of organic structures.[1,2] We are investigating a new approach to asymmetric hydroboration of alkenes. In this process, a chiral borane A adds selectively to one face of a prochiral alkene B, affording an intermediate organoborane C which contains one or two new tetrahedral stereocenters. Further transformations of C furnish alcohols and other structurally diverse

products D (X = OH or other functional group) in non-racemic form.

(1) Asymmetric hydroboration: (a) Brown, H. C.; Singaram, B.; Cole, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 460–464 and references cited therein. (b) Brown, H. C.; Jadhav, P. K. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 1. (c) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547–3587.
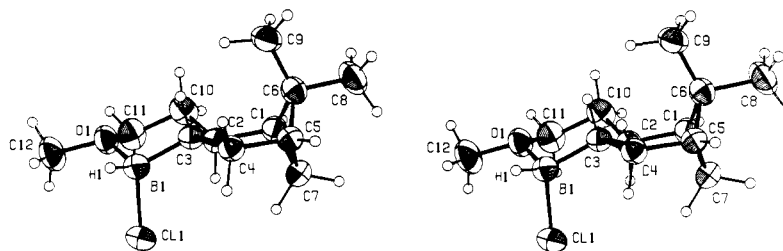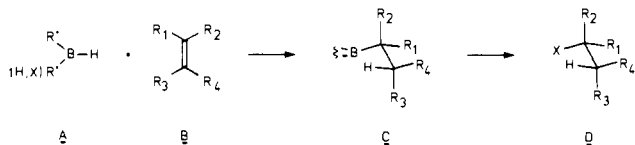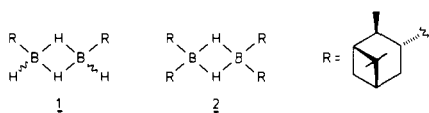
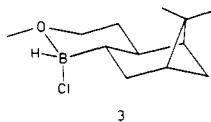**Figure 1.** ORTEP stereoview and numbering scheme for **3**.

Mono- and diisopinocampheylboranes, the most useful asymmetric hydroboration reagents yet reported,[1] are simple alkylboranes which exist preferentially as the dimers **1** and **2**, respectively. Both monomeric and dimeric alkylboranes are

plausible reactive species in hydroboration. Furthermore, dimers **1** and **2** and the related monomers presumably possess significant rotameric mobility. These considerations have complicated efforts to rationalize the sense and efficiency of the asymmetric induction expressed in hydroboration reactions of these reagents.[3]

We have sought to design and synthesize *monomeric* chiral boranes, for which dimerization is suppressed by internal coordination of boron to an ether or sulfide moiety.[4] Several attributes of these structures, including enhanced molecular rigidity and the stereogenic character of the boron atom, could be advantageous in asymmetric hydroboration. We describe here the synthesis and structure of a prototypical monomeric reagent **3**,[5,6] a crystalline compound which is easily prepared in quantity and in very high chemical and enantiomeric purity. The crystal structure of **3** has

3

been determined by X-ray diffraction. Key features of the structure are rationalized by invoking a novel boron-centered anomeric effect.

Synthesis and Physical Properties of Borane 3. (−)-Nopol (**4**), an inexpensive homoallylic alcohol, was converted to the methyl ether derivative **5** under phase-transfer conditions[7] (Me$_2$SO$_4$, *n*-Bu$_4$NHSO$_4$, CH$_2$Cl$_2$/aqueous NaOH, room temperature) in 85–90% yield. Hydroboration of **5** with BH$_2$Cl·SMe$_2$ afforded borane **3**. Optimization of this reaction entailed careful study of the preparation of BH$_2$Cl·SMe$_2$. We have found that the redistribution reaction of BCl$_3$·SMe$_2$ with vacuum-transferred BH$_3$·SMe$_2$ is greatly accelerated by small quantities of LiBH$_4$, reproducibly affording a colorless equilibrium mixture of BH$_2$Cl·SMe$_2$ (ca. 72%), BHCl$_2$·SMe$_2$, and BH$_3$·SMe$_2$ (ca. 14% each) within 1 h at ambient temperature.[8,9] In the absence of LiBH$_4$, reaction times of one or more days were required under otherwise identical conditions. The redistribution reaction is suppressed by excess dimethyl sulfide, and reaction of LiBH$_4$ with BCl$_3$·SMe$_2$ presumably creates an advantageous insufficiency of the sulfide by generating additional borane.

Reaction of BH$_2$Cl·SMe$_2$ prepared in this fashion with **5** (hexanes, 35 → 75 °C) furnished (−)-**3** as large white plates (mp 84–86.5 °C), in 65–70% yield, after two recrystallizations from hexanes. Spectroscopic analysis indicates that warming to 75 °C effects favorable redistribution of the initially formed product mixture. Satisfactory ^{11}B, ^{1}H, and ^{13}C NMR spectra, infrared and mass spectra, and elemental (C, H, and Cl) analysis were obtained for **3**. The ^{1}H resonance of the *O*-methyl group in nopol methyl ether (**5**) shifts 0.47 ppm downfield upon conversion to **3**, reflecting the electron-withdrawing effect of B–O bonding.[10]

4. R = H
5. R = Me
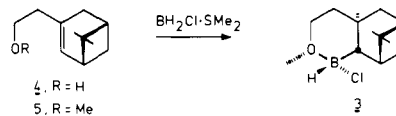
The single ^{11}B resonance of **3**, at 14.5 ppm, is also consistent with an internally coordinated solution structure. ^{13}C NMR analysis indicates that the material prepared in this fashion is 98–99% chemically pure. The remainder comprises largely a single impurity which appears to be an oxidation product.

Although the enantiomeric purity (ee) of commercial nopol, prepared by ene reaction of β-pinene with formaldehyde,[11] is only 92–94%,[12] further resolution of borane **3** occurs during recrys-

(2) Other asymmetric reactions of chiral boranes: (a) Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564–2565. (b) Brown, H. B.; Pai, G. G. *J. Org. Chem.* **1985**, *50*, 1384–1394. (c) Midland, M. M.; McLoughlin, J. I. *J. Org. Chem.* **1984**, *49*, 1316–1317. (d) Midland, M. M. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 2. (e) Matteson, D. S.; Sadhu, K. M.; Ray, R.; Jesthi, P. K.; Peterson, M. L.; Majumdar, D.; Tsai, D. J. S.; Hurst, G. D.; Erdik, E. *J. Organomet. Chem.* **1985**, *281*, 15–23 and references cited therein. (f) Hoffmann, R. W.; Landmann, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 427–428 and references cited therein.

(3) (a) For a summary of early work, see ref 1b, pp 21–2. (b) Recent kinetics studies indicate that monomeric boranes are the reactive species in hydroboration reactions of several other dialkylborane dimers: Chandrasekharan, J.; Brown, H. C. *J. Org. Chem.* **1985**, *50*, 518–520 and references cited therein. (c) A recent theoretical analysis of the asymmetric hydroboration reactions of mono- and diisopinocampheylborane monomers accounts for the major stereochemical features of these transformations: Houk, K. N.; Rondan, N. G.; Wu, Y.-D.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* **1984**, *40*, 2257–2274.

(4) (a) For a general discussion of borane–Lewis base complexes, see: Odom, J. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 1, pp 298–301. (b) A few internally coordinated borane monomers are known. See, for example: Adams, R. M.; Poholsky, F. D. *Inorg. Chem.* **1963**, *2*, 640. Braun, R. A.; Brown, D. C.; Adams, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 2823–2824.

(5) IUPAC name: (*S*)-(*O-B*)-Chloro[(1*S*,2*R*,3*S*,5*S*)-2-[2(*R*)-methoxyethyl]-6,6-dimethyl-3-norpinyl]borane.

(6) During the course of our study, a related monomeric reagent for asymmetric hydroboration, prepared from a dithiane related to nopol, was described: Aspisi, C.; Bonato, M.; Jacquier, R. European Patent Application EP 61 408, 1982; *Chem. Abstr.* **1983**, *98*, 89646*j*.

(7) For discussion of ether synthesis under phase-transfer conditions, see: Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977; Chapter 5 and references cited therein.

(8) (a) The composition of this mixture was unchanged after standing at ambient temperature for several months. This product distribution was also reported in a recent publication,[8b] superceding earlier reports[8c] that BH$_2$Cl·SMe$_2$ can be obtained in >90% purity by redistribution. In the present work, the yield of **3** presumably could be improved if the borane reagent were available in pure form. (b) Brown, H. C.; Sikorski, J. A. *Organometallics* **1982**, *1*, 28–37. (c) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938–2940. Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1977**, *42*, 2533–2534.

(9) BH$_2$Cl·SMe$_2$ reportedly is formed essentially quantitatively by reaction of BH$_3$·SMe$_2$ with CCl$_4$: Paget, W. E.; Smith, K. *J. Chem. Soc., Chem. Commun.* **1980**, 1169–1170. We found that this procedure afforded the usual equilibrium mixture of products and was generally inferior to the method described herein.

(10) Coyle, T. D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 4138–4142.
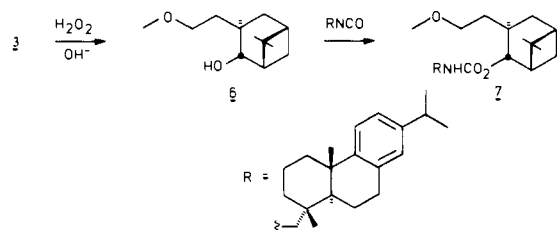(11) Bain, J. P. *J. Am. Chem. Soc.* **1946**, *68*, 638–641.
(12) Midland, M. M.; Kazubski, A. *J. Org. Chem.* **1982**, *47*, 2814–2816.

Table I. Bond Distances and Angles for **3**

Bond Distances, Å[a]

CL1-B1	1.890 (6)	O1-B1	1.596 (6)
O1-C11	1.467 (6)	O1-C12	1.455 (5)
B1-C3	1.569 (6)	C1-C2	1.549 (6)
C1-C6	1.543 (6)	C1-C7	1.553 (6)
C2-C3	1.549 (6)	C2-C10	1.506 (6)
C3-C4	1.533 (6)	C4-C5	1.533 (6)
C5-C6	1.568 (6)	C5-C7	1.518 (6)
C6-C8	1.550 (6)	C6-C9	1.507 (7)
C10-C11	1.529 (7)	H1-B1	1.08 (5)

Bond Angles, deg

C11-O1-B1	119.2 (3)	C12-O1-B1	116.1 (4)
C12-O1-C11	111.8 (4)	O1-B1-CL1	106.4 (3)
C3-B1-CL1	114.4 (3)	C3-B1-O1	104.1 (3)
C6-C1-C2	115.6 (3)	C7-C1-C2	104.4 (3)
C7-C1-C6	87.6 (3)	C3-C2-C1	111.0 (3)
C10-C2-C1	118.2 (3)	C10-C2-C3	108.0 (3)
C2-C3-B1	110.2 (4)	C4-C3-B1	118.0 (3)
C4-C3-C2	112.9 (3)	C5-C4-C3	112.9 (3)
C6-C5-C4	112.2 (4)	C7-C5-C4	108.0 (3)
C7-C5-C6	88.0 (3)	C5-C6-C1	84.8 (3)
C8-C6-C1	109.2 (3)	C8-C6-C5	109.2 (4)
C9-C6-C1	122.5 (4)	C9-C6-C5	121.6 (4)
C9-C6-C8	107.6 (4)	C5-C7-C1	86.2 (3)
C11-C10-C2	109.8 (4)	C10-C11-O1	110.4 (4)
CL1-B1-H1	102 (3)	O1-B1-H1	108 (3)
C3-B1-H1	121 (3)		

Torsion Angles, deg

C11-O1-B1-CL1	-71.3 (4)	C6-C1-C7-C5	27.6 (3)
C12-O1-B1-CL1	67.1 (4)	C1-C2-C3-B1	-161.1 (4)
C11-O1-B1-C3	49.9 (5)	C1-C2-C3-C4	-26.8 (5)
C12-O1-B1-C3	-171.7 (4)	C10-C2-C3-B1	67.8 (4)
B1-O1-C11-C10	-50.2 (6)	C10-C2-C3-C4	-157.9 (4)
C12-O1-C11-C10	169.8 (4)	C1-C2-C10-C11	168.2 (4)
CL1-B1-C3-C2	60.0 (5)	C3-C2-C10-C11	-64.8 (5)
O1-B1-C3-C4	172.6 (3)	B1-C3-C4-C5	153.5 (4)
CL1-B1-C3-C4	-71.6 (5)	C2-C3-C4-C5	23.1 (5)
O1-B1-C3-C2	-55.7 (5)	C3-C4-C5-C6	37.1 (5)
C6-C1-C2-C3	-30.1 (5)	C3-C4-C5-C7	-58.1 (5)
C6-C1-C2-C10	95.5 (5)	C4-C5-C6-C1	-81.2 (4)
C7-C1-C2-C3	64.2 (4)	C4-C5-C6-C8	170.2 (4)
C7-C1-C2-C10	-170.2 (4)	C4-C5-C6-C9	44.1 (5)
C2-C1-C6-C5	78.1 (4)	C7-C5-C6-C1	27.4 (3)
C2-C1-C6-C8	-173.3 (4)	C7-C5-C6-C8	-81.2 (4)
C2-C1-C6-C9	-46.4 (5)	C7-C5-C6-C9	152.7 (4)
C7-C1-C6-C5	-26.7 (3)	C4-C5-C7-C1	85.5 (4)
C7-C1-C6-C8	81.8 (4)	C6-C5-C7-C1	-27.1 (3)
C7-C1-C6-C9	-151.2 (4)	C2-C10-C11-O1	55.2 (5)
C2-C1-C7-C5	-88.2 (3)		
H1-B1-O1-C11	-42 (3)	H1-B1-O1-C12	180 (3)
H1-B1-C3-C2	-178 (3)	H1-B1-C3-C4	51 (3)
H1-B1-C3-H4	-59 (3)		

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in all tables.

tallization.[13] The ee of recrystallized **3** was determined by oxidation (H_2O_2/OH⁻) to methoxy alcohol **6**, followed by reaction

of **6** with the isocyanate derived from (+)-dehydroabietylamine.[14] HPLC analysis of the resulting carbamate **7** revealed that the ee of recrystallized **3** is $\geq 99.5\%$.[15]

The absolute configuration of (−)-**3**, engendered by the starting material (−)-nopol (**4**) of known absolute configuration,[16] was confirmed by X-ray analysis as described in the Experimental Section.

Pure **3** is not highly oxygen- or moisture-sensitive, but prolonged exposure to air is deleterious and handling under inert atmosphere is recommended. The borane is slightly soluble in hexanes, moderately soluble in diethyl ether, and very soluble in methylene chloride, chloroform, tetrahydrofuran, and benzene. The material appears to be stable indefinitely both in crystalline form and in solution.

Crystal Structure of 3. The Boron-Centered Anomeric Effect. Single-crystal X-ray diffraction analysis of **3** was performed as described in the Experimental Section. This is the first crystal structure determination for a chiral organoborane and the first complete X-ray analysis of a monoborane–ether complex.[17] An ORTEP stereoview of the structure and the numbering scheme are shown in Figure 1. Table I gives the bond lengths and bond angles.

The most singular features of the structure are associated with the heterocyclic ring and are well accounted for by invoking a boron-centered anomeric effect. The anomeric effect is the propensity of certain triatomic arrays, $X-Y-Z$, to adopt conformations in which a filled nonbonding orbital on Z is antiperiplanar to the $X-Y$ bond. When X is more electronegative than Y, such conformations are significantly stabilized by overlap of the filled nonbonding orbital and the σ^*_{X-Y} antibonding orbital.[18] The boron-centered anomeric effect (i.e., Y = boron) has not been observed previously.

When the electronegative atom X is a substituent on a chair six-membered ring containing atoms Y and Z, anomeric stabilization is possible only when X occupies a sterically unfavorable axial site. In the chair conformation of the heterocyclic ring found in crystalline **3**, the chlorine atom is indeed axial and the borane hydrogen equatorial. The pseudoequatorial disposition of the O-methyl group permits overlap between the axial nonbonding electron pair on oxygen and the σ^*_{B-Cl} antibonding orbital. All four of the normally nonbonding electrons of the ether oxygen participate in bonding to boron in **3**.[19] The thermodynamically preferred configurations of the stereogenic boron and oxygen atoms can be established by equilibration involving B–O bond dissociation.

The geometries at oxygen and boron are also consistent with a boron-centered anomeric effect. The geometry of the trivalent oxygen atom is intermediate between tetrahedral and planar; the angle between the O–B bond vector and the C(11)–O–C(12) plane is 34.1°.[20,21] This feature is consistent with partial B–O π-bonding and is typical of anomeric donor oxygen atoms.[22] In contrast, planarization of the tetravalent central atom of an anomeric array is disfavored sterically and not generally discernible. In **3**, the geometry at boron is approximately tetrahedral.

(13) For discussion of the recrystallization of partially resolved enantiomer mixtures, see: Jacques, J.; Collet, A.; Wilen, S. H. "Enantiomers, Racemates and Resolutions"; Wiley: New York, 1981; pp 181–182. See also Chapter 4.

(14) Corey, E. J.; Hashimoto, S. *Tetrahedron Lett.* **1981**, *22*, 299–302.

(15) A sample of racemic **6** was prepared by metalation of racemic α-pinene (n-BuLi/TMEDA, hexanes, 25 °C), addition of formaldehyde, O-methylation, and hydroboration–oxidation. Treatment with the isocyanate derived from dehydroabietylamine afforded a 1:1 mixture of diastereomeric carbamates. This mixture was employed in determining a lower limit for the enantiomeric purity in **3** by HPLC analysis. The metalation of α- and β-pinene will be the subject of a subsequent report.

(16) For a review of the stereochemistry and absolute configurations of pinene derivatives, see: Banthorpe, D. V.; Whittaker, D. *Chem. Rev.* **1966**, *66*, 643–656.

(17) (a) Structures of several boranometallacarborane·THF complexes have been determined: Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1928–1936. (b) Preliminary diffraction data were reported for a monoborane S₇NBH₂·OEt₂: Mendelsohn, M. H.; Jolly, W. L. *Ibid.* **1972**, *11*, 1944–1945.

(18) (a) An excellent monograph has recently been published: Kirby, A. J. "The Anomeric Effect and Related Stereoelectronic Effects at Oxygen"; Springer-Verlag: New York, 1983. (b) See also: Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon Press: Oxford, 1983.

(19) A few well-characterized compounds contain four-coordinate oxygen atoms; cf.: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 487. See also ref 21.

(20) The limiting values for tetrahedral and planar geometries are 54.8 and 0°, respectively.

7170 *J. Am. Chem. Soc., Vol. 107, No. 24, 1985*

Shiner et al.

Anomeric structures are further characterized by lengthening of the X–Y bonds and shortening of the Y–Z bonds.[23] The B–Cl bond in 3 is longer ($d = 1.890$ Å) than any other B–Cl bond of which we are aware; 50 other B–Cl bond lengths determined by X-ray diffraction are in the range 1.72–1.877 Å.[24] Shortening of the B–O bond cannot be confirmed due to the lack of suitable reference values.

While we find no evidence for a boron-centered anomeric effect in other reported structures,[25] we envision that the effect may influence the relative stabilities of haloborane–Lewis base complexes and the conformations of haloborane–ether and –sulfide complexes.

The pinane hydrocarbon nucleus in 3 is essentially identical with that reported for crystals of 3-[(N-methylamino)methyl]-pinane hydrobromide (8).[26] Whereas the hydrogen atoms were

8
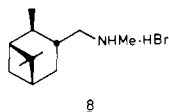
not located in the crystal structure of 8, the present work confirms that the relatively large C(2)–C(1)–C(6) and C(4)–C(5)–C(6) bond angles are influenced by a very close (1.71 Å) intramolecular contact between the axial C(3) hydrogen and a C(9) methyl hydrogen.[27]

Summary. The monomeric, internally coordinated alkylchloroborane 3 is easily prepared in very high chemical and enantiomeric purity from readily available materials. Key features of the crystal structure of 3 are attributable to a novel boron-centered anomeric effect. Asymmetric alkene hydroboration reactions of 3 will be described in due course.

Experimental Section

Syringes and needles were oven-dried and stored in a desiccator. Other glassware was flame-dried under vacuum and flushed with argon immediately prior to use, except as noted. Solvents and liquid reactants were transferred by syringe through septa. Air- and moisture-sensitive solids were transferred under an argon atmosphere in a glovebag. All reaction mixtures were magnetically stirred unless otherwise indicated.

Melting points were determined by using a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were measured by using a Perkin-Elmer Model 727B spectrophotometer; frequencies are reported in inverse centimeters. ^{1}H NMR spectra were obtained by using a Varian EM-390 or Bruker WM-250 spectrometer operating at 90 or 250 MHz, respectively. ^{1}H chemical shifts are reported in parts per million (ppm) downfield from internal Me₄Si (δ) and J values are in hertz. ^{11}B and ^{13}C spectra were measured on a Bruker WM-250 spectrometer operating at 80.24 and 62.9 MHz, respectively. ^{11}B spectra were referenced to external BF₃·Et₂O (0 ppm) with chemical shifts at low field assigned as positive. ^{13}C spectra were referenced to internal CDCl₃ (77.0 ppm).

Mass spectra were measured by using a Varian MAT CH5 instrument. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA.

HPLC analyses were performed by using an IBM 9533 Chromatograph with a 254-nm UV detector. Thin-layer chromatography plates (silica, 0.25-mm layer) were purchased from E. Merck. Silica (230–400 mesh) from E. Merck was employed in flash chromatography.

Nopol was purchased from Aldrich Chemical Co. and stored over K₂CO₃. BH₃·SMe₂ was purchased from Aldrich and vacuum-transferred prior to use (vide infra). BCl₃·SMe₂ and LiBH₄ were purchased from Aldrich and used as received; purity was checked by ^{11}B NMR. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under argon immediately prior to use. Reagent-grade hexane was distilled from lithium aluminum hydride and stored under argon. (+)-Dehydroabietylamine was purchased from Aldrich and purified as described.[14]

Nopol Methyl Ether (5).[28] In a 2-L, three-necked flask equipped with a reflux condenser and mechanical stirrer, 234 g (5.85 mol) of sodium hydroxide was dissolved in 234 mL of water, and the solution was cooled to room temperature. A solution of 194.6 g of (−)-nopol (200 mL, 1.17 mol) in 230 mL of methylene chloride and 8.0 g (23.6 mmol) of Bu₄NHSO₄ were added, and the mixture was stirred vigorously for 15 min. The flask was then placed in a water bath at ca. 20 °C, and 294.5 g (2.34 mol, 221 mL) of dimethyl sulfate was added to the vigorously stirred reaction mixture, through an additional funnel, over ca. 8 h. After stirring 0.5 h further, 60 mL of concentrated ammonium hydroxide solution was added slowly, and the mixture was stirred for one additional hour. The mixture was then partitioned between 200 mL of hexanes and 300 mL of water, and the aqueous phase was extracted with 200 mL of hexanes. The combined organic solutions were washed once with brine, dried over potassium carbonate, filtered, and concentrated. The pale yellow liquid thus obtained was distilled from lithium aluminum hydride (4.5 g, 0.119 mol), affording 181.2 g (86% yield) of 5 as a colorless liquid (bp 83–85 °C/4.5 mmHg). The product was homogeneous by TLC (R_f 0.22 using 3.5% ethyl acetate/hexanes for development): ^{1}H NMR (CDCl₃) 0.83 (s, 3 H), 1.16 (d, 1 H, $J = 9$), 1.27 (s, 3 H), 1.9–2.5 (m, 9 H), 3.32 (s, 3 H), and 5.28 (br m, 1 H); ^{13}C NMR (CDCl₃) 20.9, 26.2, 31.2, 31.4, 36.9, 37.8, 40.7, 45.8, 58.0, 70.9, 117.5, and 145.1; IR (film) 1668 (w), 1121 (s); mass spectrum (70 eV), m/e 180 (M+), 148, 105 (base), 45; $[\alpha]^{26}_D$ −32.60° (neat); d^{25} 0.901. Anal. (C₁₂H₂₀O) C, H.

BH₂Cl·SMe₂. Commercial BH₃·SMe₂ was purified and freed of most excess dimethyl sulfide by vacuum transfer. The commercial material was placed in a trap-to-trap distillation apparatus and the excess dimethyl sulfide removed by reducing the pressure to ca. 10 mmHg (the residual pressure is argon). The distillation and collection bulbs were maintained at ambient temperature. When ebullition nearly ceased, the collection bulb was cooled to −78 °C and the pressure reduced to 0.05 mmHg. The clear, colorless distillate was ca. 10.5 M BH₃·SMe₂.

For the preparation of BH₂Cl·SMe₂, 27.52 g of BCl₃·SMe₂ (0.1535 mol) and 0.45 g of LiBH₄ (20.7 mmol) were weighed into a 100-mL flask in a glovebag. Vacuum-transferred BH₃·SMe₂ (26.5 mL, ca. 0.278 mol) was added by cannula, and the mixture was swirled until the BCl₃·SMe₂ dissolved. The resulting opaque brown suspension gradually warmed to ca. 40 °C, affording a colorless solution containing a small amount of white solid. After 1 h, ^{11}B NMR analysis showed the presence of 72% BH₂Cl·SMe₂ (t, −7.2 ppm), 14% BHCl₂·SMe₂ (d, 1.7), and 14% borane–methyl sulfide (q, −20.2).[8]

(S)-(O-B)-Chloro[(1S,2R,3S,5S)-2-[2(R)-methoxyethyl]-6,6-dimethyl-3-norpinyl]borane (3). BH₂Cl·SMe₂ (33 mL, ca. 72% pure) and 90 mL of dry hexanes were transferred by cannula to an argon-filled 500-mL flask fitted with a distillation head and receiver. The rapidly stirred, biphasic mixture was warmed to 35 °C in a water bath, and 60 mL of 5 (0.300 mol) was added dropwise over 10–15 min. The bath then was warmed to 70–80 °C and a mixture of Me₂S and hexanes was distilled. After 1–1.5 h, 90–100 mL of distillate were collected, and the distillation slowed markedly. The flask was cooled to room temperature, the distillation assembly quickly replaced by a vacuum adapter, and the swirled product mixture concentrated further at 0.05 mmHg for 5 min. For recrystallization, the resulting moist white solid was dissolved in 85 mL of dry hexanes at 60–65 °C (bath temperature). The hot solution was transferred by cannula to a coarse-porosity Kramer filter tube, which was connected to a 250-mL flask for collection of the filtrate. The filter tube contained ca. 3 mm of dry Celite if the solution was cloudy. Crystallization was induced while the solution was hot, by briefly cooling a small area of the flask with a piece of dry ice. The flask was then placed in a warm water bath, which was allowed to cool slowly. If small crystals formed, the suspension was reheated, leaving a few seed crystals, and the resulting solution allowed to cool slowly. After the flask reached

(21) Trivalent oxygen is usually pyramidal in oxonium ions, but in complexes containing ethers ligated to metals, essentially planar oxygen is not uncommon. See, for example: (a) Li⁺·THF, in Li₄[Mo₂(CH₃)₈]·4THF: Cotton, F. A.; Troup, J. M.; Webb, T. R.; Williamson, D. H.; Wilkinson, G. *J. Am. Chem. Soc.* **1974**, *96*, 3824–3828. (b) Ti^{III}·THF, in TiCl₃·3THF: Handlovic, M.; Miklos, D.; Zikmund, M. *Acta Crystallogr., Sect. B* **1981**, *37*, 811–814.

(22) Cf., ref 18a, pp 70–71.

(23) For discussion, see ref 18a, pp 52–61.

(24) The longest B–Cl bond reported previously occurs in BH₂Cl·PPh₂·BH₂·PPh₂Cl: Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1978**, 40–44.

(25) Oxygen geometries intermediate between tetrahedral and trigonal were observed in a gas-phase electron diffraction study of BF₃·Me₂O (Iijima, K.; Yamada, T.; Shibata, S. *J. Mol. Struct.* **1981**, *77*, 271–276) and in X-ray diffraction studies of BF₃·2H₂O (Mootz, D.; Steffen, M. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1110–1112) and of BF₃·H₂O and BF₃·CH₃OH (Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, *483*, 171–180). Boron-centered anomeric effects are not evident in other features of these structures, however.

(26) Reck, G.; Kutschabsky, L. *Acta Crystallogr., Sect. B* **1970**, *B26*, 578–582.

(27) In the final model, the positions of the hydrogens bound to carbon were refined by using idealized sp³ geometries [d(C–H) = 1.08 Å]; see Experimental Section. When the positions of the hydrogens were refined without constraint, a severe van der Waals interaction was retained. The distance between the C(3) hydrogen and the C(9) methyl hydrogen increased only to 2.02 Å, significantly less than the van der Waals distance (2.4 Å).

(28) This preparation has also been carried out by using 3 times the amounts of reagents and solvents shown herein, affording 5 in 85–90% yield.

room temperature, it was cooled to −20 °C in a freezer for 6 h and then supernatant was removed by cannula. After washing with 20 mL of cold hexanes, drying at 0.05 mmHg (room temperature, 15 min) afforded 53.6 g (78% yield) of large, sticky crystals. After a second recrystallization from 85 mL of hexanes, the crystals were collected at room temperature (i.e., cooling was omitted) and washed with two 20-mL portions of hexanes, afforded after drying 47.1 g of (−)-3 (69% yield) as large, dry white plates: mp 84−86.5 °C: ^{11}B NMR (CDCl$_3$) 14.4 (s) (line width at half-height: 358 Hz proton decoupled, 452 Hz coupled); ^{1}H NMR (CDCl$_3$) 0.83 (d, 1 H, $J = 9$), 1.17 (s, 3 H), 1.24 (s, 3 H), 1.5−2.5 (m, 10 H), 3.79 (s, 3 H), 3.98 (m, 1 H), and 4.23 (m, 1 H); ^{13}C NMR (CDCl$_3$) 22.7, 28.4, 29.3, 29.8, 35.1, 38.1, 38.9, 40.7, 42.6, 47.2, 66.5, and 79.3; IR (CDCl$_3$) 2465 (s, B−H); mass spectrum (70 eV), m/e 228 (M+), 193, 105, 79 (base); $[\alpha]^{26}$D −30.06° (c 14.2, CCl$_4$). Anal. (C$_{12}$-H$_{22}$BCl) C calcd, 63.06, found, 62.90, H calcd, 9.70, found, 9.72, Cl calcd, 15.51, found, 15.43. An impurity, apparently an oxidation product, was detected and quantitated (ca. 2.0%) by integrating ^{13}C NMR signals at 83.2 (−CH$_2$OCH$_3$) and 62.7 (−CH$_2$OCH$_3$) ppm.[29]

Methoxy Alcohol 6. A solution of 3.93 g (17.2 mmol) of **3** in 10 mL of THF was cooled to 0 °C under argon, and 11.5 mL (34.5 mmol) of 3 M aqueous NaOH was added slowly. The solution was warmed to 20 °C, and 2.0 mL (19.6 mmol) of 30% hydrogen peroxide solution was added slowly, using an all-plastic syringe and a Teflon needle. After stirring 1 h, the layers were separated and the aqueous phase was extracted with 30 mL of diethyl ether. The combined organic solutions were washed successively with saturated aqueous sodium thiosulfate solution and brine, dried over MgSO$_4$, and filtered. After removal of solvent, the product was purified by flash chromatography on 150 g of silica, using 27% ethyl acetate/hexanes as eluant, affording 3.19 g of methoxy alcohol **3** as a clear, colorless oil (94% yield): ^{1}H NMR (CD-Cl$_3$) 0.90 (s, 3 H), 1.09 (d, 1 H, $J = 9$), 1.20 (s, 3 H), 1.43−2.08 (m, 6 H), 2.2−2.7 (m, 2 H), 3.07 (s, 1 H), 3.33 (s, 3 H), 3.41−3.66 (m, 2 H), and 3.98−4.32 (m, 1 H); ^{13}C NMR (CDCl$_3$) 23.1, 27.0, 33.2, 35.6, 37.4, 37.5, 41.1, 46.5, 50.2, 57.7, 69.1, and 71.7; IR (neat) 3445 (s) and 1125 (s); mass spectrum (70 eV), m/e 198 (M+), 129, 97 (base), 96, 81; $[\alpha]$D^{27} 26.02° (neat); d^{25} 0.9824. Anal. (C$_{12}$H$_{22}$O$_2$) C, H.

Carbamate 7. The isocyanate derived from (+)-dehydroabietylamine was prepared as described by Corey.[14] Rapid flash chromatography using 5% ethyl acetate/hexanes as eluant afforded pure isocyanate as a viscous, colorless oil. In a 10-mL flask under argon, 41.6 mg of methoxy alcohol **6** (0.21 mmol), 193.8 mg of (+)-dehydroabietyl isocyanate (0.622 mmol), and 36.6 mg of 4-(dimethylamino)pyridine (0.30 mmol) were dissolved in 1 mL of benzene. The solution was heated at 50 °C for 6 h. The solution then was diluted with diethyl ether, washed successively with water and brine, dried over MgSO$_4$, and filtered. After removal of solvent, the product was purified by flash chromatography on 20 g of silica, using 12% ethyl acetate/hexanes as eluant. Combination of all fractions which could have contained either diastereomer afforded 99.0 mg of **7** (93% yield) as a white foam. HPLC analysis, performed with a 25 cm × 4 mm cyanopropyl column and hexanes as eluant, showed that less than 0.25% of the minor diastereomer was present.[15] Spectral and analytical data were obtained for a sample of the major diastereomer which was purified by flash chromatography: ^{1}H NMR (CDCl$_3$) 0.93 (s, 6 H), 1.06 (d, 1 H, $J = 9.2$), 1.21 (s, 6 H), 1.24 (d, 6 H, $J = 4$), 1.58 (s, 2 H), 1.30−2.10 (m, 12 H), 2.20−2.42 (m, 2 H), 2.53−2.72 (m, 1 H), 3.13 (s, 3 H), 2.7−3.4 (m, 7 H), 4.60−4.73 (m, 1 H), 4.92−5.05 (m, 1 H), 6.89 (s, 1 H), 6.99 (d, 1 H, $J = 8.5$), and 7.17 (d, 1 H, $J = 8.5$); ^{13}C NMR (CDCl$_3$) 18.6, 18.9, 23.7, 23.9, 25.2, 27.3, 30.2, 33.0, 33.4, 35.4, 36.0, 36.5, 37.4, 38.1, 38.4, 41.3, 45.1, 45.4, 45.7, 51.7, 58.3, 71.0, 73.3, 123.8, 124.1, 126.8, 134.7, 145.6, 147.2, and 156.8; IR (CCl$_4$) 1716 (s), 1511 (s), and 1231 (s); mass spectrum (70 eV), m/e 509 (M+), 327, 326, 180, 173 (base); $[\alpha]^{25}$D 30.1° (c 0.54, cyclohexane). Anal. (C$_{33}$H$_{51}$NO$_3$) C, H.

X-ray Structural Analysis of 3. Under a dry nitrogen atmosphere in a glovebox, a small crystal of **3** was cut from a larger crystal, which had been grown from diethyl ether solution. The small crystal was mounted and sealed in a glass capillary.

Details of the crystal data, experimental conditions, and a summary of the solution and refinement are given in Table II.   Because **3** is somewhat air-sensitive, initial low-angle data ($3° \leq 2\theta \leq 40°$) were collected at a scan rate of 4.0 deg/min (data set I). These data were used for the solution and initial refinement of the structure. Concurrent with these calculations, additional data were collected at higher 2θ angles and the low-angle measurements were repeated at slower scan speeds (data set II). The latter data were collected over the complete sphere. The

Table II. Crystal Data and Details of the Structure Determination for **3**

Crystal Data	
formula	C$_{12}$H$_{22}$OBCl
M_r, amu	228.57
mp, °C	84−86.5
space group[a]	$P2_1$
cryst system	monoclinic
a, Å[b]	7.468 (3)
b, Å	10.887 (3)
c, Å	7.898 (3)
α, deg	90.00
β, deg	95.29 (3)
γ, deg	90.00
volume, Å^3	639.4 (4)
Z	2
d(calcd), g/cm^3	1.19
F(000)	248
Mu, cm^{-1}	2.7

Data Collection and Reduction	
diffractometer	Syntex P$\bar{1}$
radiation, Å	Mo Kα (0.71069)
takeoff ang for graphite monochromator, deg	4.0
temp, K	294−296
cryst dimensions, mm	0.30 × 0.23 × 0.25
scan technique	$\theta - 2\theta$
2θ, min − max, deg	3.0−45.0
hkl values scanned	±h; ±k; ±l
scan speed, deg/min	2.0−24.0
scan range, deg below Ka_1 and above Ka_2	0.7, 0.7
background	stationary crystal−stationary counter background time = scan time
check reflections	(−1,3,−1), (−2,1,1), (1,2,−2), (−2,5,1)
frequency	every 100 measurements
variation	random, net 9% decay
no. of reflections measured	3208
no. of unique reflections	1676
agreement factor during averaging[c]	0.091
no. of observed reflections	1102
σ criterion	$F > 6\sigma(F)$
absorption correction	none

Structure Determination and Refinement	
method of phase determination	Patterson, DIRDIF[d]
programs	SHELX,[e] PLATO,[f] and others[g]
scattering factors	neutral atoms[h]
R_1 and R_2[i]	0.037, 0.045
weight	0.535/(σ^2(F) + 0.001*F*F)
no. of parameters	149
ratio of observations to parameters	7.4/1
max shift/error	0.04
residual electron density, e/Å^3	0.22

[a] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 15 reflections with 2θ in the range 12−22°. [c] The agreement factor during averaging, R_{av}, is given by $R_{av} = \{\sum_{i=1}^{M} \sum_{j=1}^{N} |\langle F_i^2 \rangle - F_{ij}^2|\}/\sum_{i=1}^{M} N^* \langle F_i^2 \rangle$ where N is the number of times that a given reflection is observed through its equivalent forms, M is the number of unique reflections observed more than once, and $\langle F_i^2 \rangle$ is the average value of F^2 for the unique reflection i. [d] Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A.; Noordik, J. H.; Buerskens, G.; Parthasarthi, V.; BruinsSlot, H. J.; Haltiwanger, R. C. "DIRDIF, Technical Report". Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983/1. [e] Sheldrick, G. M. "SHELX76, A Program for Crystal Structure Determination"; University of Cambridge: England. [f] Spek, A. L. In "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982; p 528. [g] The data reduction program was written in this laboratory. Other programs were contained in or derived from the Northwestern Crystallographic Computing Library of Dr. J. A. Ibers. [h] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4. [i] The quantity minimized in the least-squares procedures is $\sum \{w(|F_o| - |F_c|)^2$. $R_1 = \sum |(|F_o| - |F_c|)|/\sum |F_o|$. $R_2 = \sum \{w(|F_o| - |F_c|)^2\}/\sum w(F_o)^2$.

(29) The combustion analysis data agree with values calculated for a mixture comprising 98% **3** and 2% of an oxidation product C$_{12}$H$_{22}$BClO$_3$: C, 62.90; H, 9.68; Cl, 15.47. A monooxidized impurity C$_{12}$H$_{22}$BClO$_2$ would also be accommodated by the elemental analysis.

Table III. Atomic Parameters for **3**

atom	x/a	y/b	z/c	$U(eq)^a$
CL1	0.2092 (1)	$^1/_4$	0.1071 (1)	0.0617 (4)
O1	0.3397 (3)	0.4905 (3)	0.0964 (4)	0.055 (1)
B1	0.2841 (7)	0.3921 (5)	0.2319 (7)	0.048 (2)
C1	0.7719 (5)	0.2775 (4)	0.3703 (5)	0.046 (2)
C2	0.6181 (5)	0.3366 (4)	0.2527 (5)	0.044 (1)
C3	0.4595 (5)	0.3745 (4)	0.3549 (5)	0.042 (1)
C4	0.4474 (5)	0.2967 (4)	0.5151 (5)	0.044 (1)
C5	0.6271 (4)	0.2373 (5)	0.5789 (5)	0.045 (1)
C6	0.7909 (5)	0.3238 (5)	0.5558 (5)	0.047 (2)
C7	0.6878 (5)	0.1583 (4)	0.4366 (6)	0.053 (2)
C8	0.9629 (6)	0.2679 (6)	0.6504 (6)	0.071 (2)
C9	0.7870 (6)	0.4583 (5)	0.6004 (7)	0.060 (2)
C10	0.6629 (6)	0.4442 (5)	0.1443 (6)	0.057 (2)
C11	0.5047 (7)	0.4712 (5)	0.0126 (7)	0.062 (2)
C12	0.1944 (7)	0.5376 (6)	−0.0212 (8)	0.078 (2)
H1	0.160 (6)	0.422 (5)	0.280 (6)	0.067 (4)

^{a} The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

check reflections showed, in addition to the random statistical variations expected for such measurements, a net 9% decline over the course of the data collection. The data were corrected for this decline by using a linear decay curve. Standard corrections for Lorentz and polarization factors were also applied.

The position of the chlorine atom was determined from a Patterson map. This was input to the program DIRDIF,[30] which gave positions for the other atoms. Tentative assignments of the atom types were based upon the method of synthesis, the NMR data, and the oxidative conversion of **3** to **6**. The assignments were confirmed by examination of isotropic thermal parameters at various stages of refinement and by the final difference electron density map. Least-squares refinement using data set I, with all atoms isotropic, converged with $R_1 = 0.087$ and $R_2 = 0.115$. Further refinement was carried out by using data set II after averaging equivalent reflections; however, Friedel pairs were not averaged. At convergence ($R_1 = 0.104$, $R_2 = 0.137$) with all atoms isotropic, the positions of all hydrogen atoms were clearly visible in the calculated difference electron density map. The hydrogen atoms were then included in the model in idealized sp³ geometries [d(C–H) = 1.08 Å] with methyl groups treated as rigid entities. They were refined by using two common isotropic temperature factors, one for the methyl hydrogens and one for the borane hydrogen and other non-methyl hydrogens. This refinement converged with $R_1 = 0.037$ and $R_2 = 0.046$. Because these geometric constraints might be inappropriate for the borane hydrogen, this atom

was freed of all constraints in the final model.[31] The results of least-squares calculations on the final model are given in the tables. A final difference electron density map was featureless.

The absolute configuration of **3** (vide supra) was confirmed by using the method of Hamilton.[32] The real and imaginary anomalous dispersion terms were included for the non-hydrogen atoms,[33] and R_2 values were calculated for both enantiomers. The ratio of the resulting R_2 values (0.0476, 0.0459) is 1.0370, significantly greater than the $R_{1,1000,0.005}$ value of 1.0039. Thus, at the 99.5% confidence level, the absolute configuration shown for **3** is correct.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

(30) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A.; Noordik, J. H.; Buerskens, G.; Parthasarthi, V.; BruinsSlot, H. J.; Haltiwanger, R. C. "DIRDIF, Technical Report"; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983/1.

(31) This treatment of the hydrogen atoms minimizes the number of variables in the refinement and is expected to afford the most accurate interatomic distances involving hydrogen nuclei. We also undertook least-squares refinement of a model with no constraints on any hydrogen atoms. This refinement resulted in no statistically significant shifts (i.e., changes greater than 3σ) in the positional parameters for the non-hydrogen atoms. The C(2)–C(3) bond distance decreased by 0.020 Å and the C(8)–C(6)–C(1) angle increased by 1.2°.

(32) Hamilton, W. C. *Acta Crystallogr.* 1965, *18*, 502–510.

(33) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Communications to the Editor

Photoelectron Spectrum of [1.1.1]Propellane: Evidence for a Nonbonding MO?

Ev. Honegger, Hanspeter Huber, and Edgar Heilbronner*

Physikalische-Chemisches Institut, Universität Basel
4056 Basel, Switzerland

William P. Dailey and Kenneth B. Wiberg*

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received April 4, 1985

The sequence and overall contours of the bands in the He(Iα) PE spectrum of [1.1.1]propellane (**1**) (=tricyclo[1.1.1.0¹,³]pentane)[1,2] (Figure 1) correspond exactly to the expectation based
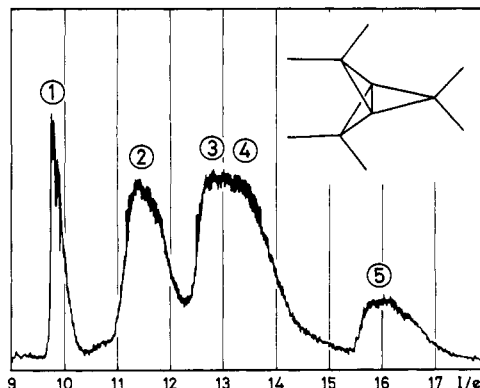

Figure 1. He(Iα) PE spectrum of [1.1.1]propellane (**1**). Sample temperature −10 to −15 °C; temperature 20 °C.

on available molecular orbital calculations,[3] assuming the validity of Koopmans' theorem. For example, the results of ab initio

(1) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* 1982, *104*, 5239. Wiberg, K. B. *Acc. Chem. Res.* 1984, *17*, 379.