Conformational Analysis of Triarylboranes[1]

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Abstract: An X-ray structure determination shows that trimesitylborane assumes a propeller conformation in the crystal lattice. The low-temperature ¹H-nmr spectra of diverse triarylboranes which have substituents other than hydrogen in all six ortho positions are consistent with this geometry in solution. At higher temperatures, the spectra reflect rapid stereoisomerizations, which are interpreted in terms of two-ring flip mechanisms. These processes have activation energies of *ca.* 14–16 kcal/mol, and separation of stereoisomers at ambient temperatures is therefore precluded.

The conformations and conformational isomerizations of triarylboranes have been the subject of occasional studies during the last several decades.[3–5] However, in contrast to the more thoroughly investigated isoelectronic carbonium ions,[6] there has been a dearth of information on the ground-state geometry and conformational dynamics of triarylboranes. The present work was designed to fill this gap.

Ground-State Geometry of Triarylboranes

A number of years ago, Brown and Sujishi[3a] suggested, on the basis of an examination of molecular models, that tris(1-naphthyl)borane exists in a propeller-like conformation in the ground state, with the three aryl groups twisted out of the plane defined by the three carbon atoms attached to boron (the *reference plane*). The sense of twist of each of the aromatic groups was proposed to be the same. Figure 1 shows the generalized structure of a (substituted) triarylborane in the propeller conformation; the same ground-state geometry is adopted by triarylcarbonium ions.[6,7]

In 1962, Lapkin and Yuzhakova[3c] suggested that the mesityl groups of trimesitylborane are twisted out of the reference plane. Weismann and coworkers[4] assumed a similar geometry for a variety of triarylboranes. Using simple force field and molecular orbital schemes, Weismann and Schug[4b] calculated that trimesitylborane should have a propeller conformation in which each phenyl ring is twisted out of the reference plane by 45°, as compared to a value of 37° derived from experimental ¹H-nmr chemical shift data.[4b]

In order to secure incontrovertible experimental evidence concerning the conformation of triarylboranes in the solid state, an X-ray structural analysis was undertaken for trimesitylborane. Large tabular crystals suitable for X-ray analysis were obtained by slow evaporation of a 1,2-dimethoxyethane solution. The structure analysis was successfully carried out in the centrosymmetric space group *C2/c* (see Experimental Section for details). The analysis demonstrates that the trimesitylborane molecule lies on a crystallographic twofold axis, and therefore the boron and the three carbon atoms bonded to it are coplanar. The angle of rotation out of this plane is 51.1° for the aromatic ring which lies on the crystallographic twofold axis, and 49.6° for the rings which are not on this axis. The corresponding B–C distances are 1.580 (4) and 1.573 (4) Å, respectively (Figure 2). Thus, the trimesitylborane molecule has idealized D_3 symmetry even though its exact symmetry in the crystal is only C_2. It should be noted that because the crystal symmetry includes mirror planes, each crystal is racemic. Figure 3 shows a stereoview of one trimesitylborane molecule in the crystal.

The twist angle of the mesityl groups in trimesitylborane calculated by Weismann and Schug (45°)[4b] is seen to be in reasonable agreement with those found in the X-ray determination.

All the evidence to be discussed below is consistent with the hypothesis that in solution the triarylboranes under study also maintain propeller conformations in the ground state; although the twist angle in solution will necessarily be somewhat different from that in the crystal, it is difficult to estimate either the direction or the magnitude of the deviation. Therefore, in the absence of compelling evidence requiring the postulation of an overall conformation in solution which is substantially different from that found in the solid state, this study assumes propeller ground-state conforma-
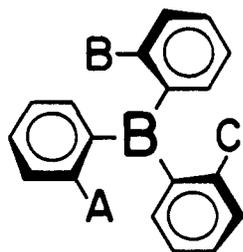
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Figure 1. A triarylborane in the propeller conformation.

tions for all the compounds examined, at least on the nmr time scale.

Dynamics of Conformational Interconversion

In the few accounts of this subject which have appeared in the literature, attention has been devoted mostly to trinaphthylborane systems.[3a,4] It is thus appropriate to begin our discussion with results obtained for compounds of this type.

Tris-1-(2-methylnaphthyl)borane. The synthesis of tris-1-(2-methylnaphthyl)borane (1) was reported by Chu and Weismann in 1956,[4a] who suggested on the basis of melting point behavior that this compound exhibits rotational isomerism. Weismann and Schug subsequently (1964) reported that 1 has a temperature-dependent ^{1}H-nmr spectrum.[4b] As part of our more general study, we reinvestigated the spectral behavior of 1.[8]

Assuming that in solution the ground state of 1 is a propeller (helical) conformation, the possibilities for stereoisomerism and isomerization may be analyzed exhaustively and systematically.[9] Four isomeric propeller conformations are possible for a molecule of this type. These isomers make up two diastereomeric sets of enantiomers (Figure 4). One set of enantiomers (A and $\overline{A}$, hereafter $A\overline{A}$) is of C_3 symmetry and consequently each enantiomer has three equivalent (homotopic) methyl groups. The other two (B and $\overline{B}$, hereafter $B\overline{B}$) have C_1 symmetry and each enantiomer has three nonequivalent (diastereotopic) methyl groups. Therefore, in an achiral solvent and in the absence of accidental isochrony, the ^{1}H-nmr spectrum of a mixture of both diastereomers will exhibit four resonance signals in the methyl region.

Possible interconversions of the stereoisomers of 1 may be discussed in terms of the flip mechanisms postulated by Kurland, et al.[6b,9] In each of these four mechanisms, zero, one, two, or all three of the aryl ring systems "flip," i.e., rotate about their respective B–C bonds through planes perpendicular to the reference plane, while the remaining rings rotate in the opposite direction through the reference plane. All data in the literature to date concerning conformational interconversions of triarylcarbonium ions and related systems are consistent with one or more of these mechanisms,[9] and it is therefore reasonable to postulate similar mech-
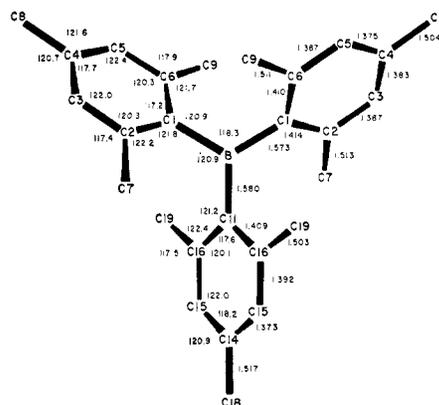

Figure 2. A drawing of a trimesitylborane molecule which depicts bond lengths to the right of the crystallographic twofold axis and bond angles to the left of this axis. The standard deviations of the bond lengths are $\leqslant 0.004$ Å in all cases.

anisms for possible interconversions in the triarylboranes.[10]

The effect of the operation of each of these four mechanisms upon the isomers of 1 may be depicted graphically (Figure 4). In these graphs, the labeled vertices represent isomers and the edges represent interconversions. Thus, the three-ring flips or zero-ring flips only interconvert enantiomers. The graph for the one- or two-ring flips is more complicated. Since all three aryl groups in A and $\overline{A}$ are homotopic, there is only one distinct one- or two-ring flip possible for each of these isomers. These processes interconvert A and $\overline{B}$, or $\overline{A}$ and B. However, because B and $\overline{B}$ each have three nonequivalent (diastereotopic) methyl groups, each of these isomers has two additional pathways available for isomerization by the one- or two-ring flip mechanisms. Each of these additional pathways interconverts B and $\overline{B}$, but for the two-ring flip these pathways are enantiomeric, whereas they are diastereomeric for the one-ring flip. These conclusions may be clarified by an examination of isomer $\overline{B}$ in Figure 4. If, during interconversion by the two-ring flip, the labeled aryl group (asterisk) and either one of the two additional groups flip, $\overline{B}$ is converted to B (two enantiomeric pathways). However, if the labeled group does not flip, $\overline{B}$ is converted to A. Similarly, for the one-ring flip mechanism, flipping of the labeled group leads to A, whereas flipping of either one of the other two groups results in conversion to B (two diastereomeric pathways). Thus, if one considers all possible interconversions by the four flip mechanisms, there are a total of 12 distinct pathways for isomerization.

The effect of rapid interconversion by means of any of the 12 pathways upon the nmr spectrum of 1 in an achiral medium can be determined by an examination of the idealized transition state for the process (which may be represented by some point along the edge of the graph connecting the two isomers in question).

It is readily apparent that neither the three-ring flip

(8) Attempts to study the isomeric tris-2-(1-methylnaphthyl)borane, whose spectral properties had also been reported by Weismann and Schug,[4b] were frustrated by our inability to repeat the reported[4b] preparation: all attempts resulted in the isolation of 1,1'-dimethyl-2,2'-binaphthyl as the principal product (see Experimental Section). We are thus unable to confirm the reported[4b] nmr spectrum of this compound.

(9) D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 1535 (1973).

(10) The flip rearrangements all involve the change in helicity (sense of twist) of the molecular propeller. There is also in principle an additional set of rearrangements (in the permutational sense) which involve no such change. Since the experiments described below do not detect changes of helicity directly, they do not allow us to distinguish between these two sets. However, since studies[6h] on triarylcarbonium ions have shown that permutations are accompanied by helicity changes in these systems, we have considered only the flip rearrangements for the closely analogous triarylboranes.
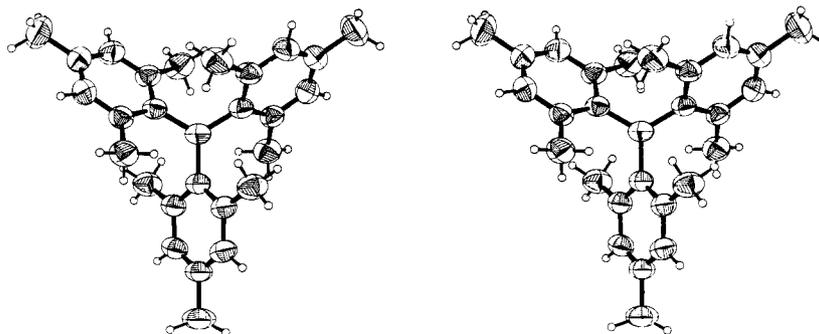
Figure 3. A stereoview of a trimesitylborane molecule. The crystallographic twofold axis passes through the vertical B–C bond. The thermal ellipsoids of the non-hydrogen atoms are scaled to 50% probability. The hydrogens are shown as spheres of arbitrary size.
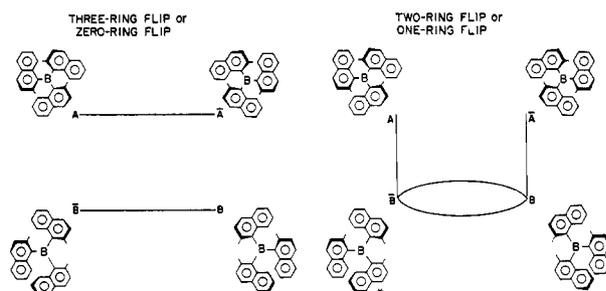

Figure 4. Graphs depicting stereoisomerization of 1 by the flip mechanisms.

Figure 5. The effect of the enantiomeric two-ring flips on the interchange of environments for a given methyl group in B$\bar{\text{B}}$ (asterisk). Diastereotopic methyl group environments have been labeled with lower case letters, and diastereotopic aryl ring environments have been labeled with numerals. Barred letters or numerals denote enantiomeric relationships. The numerals along the arrows identify the rings which flip during the specified interconversion. Note that since the [1,3]- and [2,3]-flips are enantiomeric, the reverse of the [1,3]-flip, for example, is the [$\bar{2}$,$\bar{3}$]-flip.

nor the zero-ring flip connecting A and Ā has any effect upon the nmr spectrum, and therefore these processes are not detectable by this method. Similarly, the zero-ring flip connecting B̄ and B cannot be observed. Rapid interconversion by the three-ring flip linking B̄ and B, however, renders two of the aryl groups enantiotopic on the time average, and will therefore result in the collapse of the three equal-intensity resonances of the methyl groups to two lines in a ratio of 2:1. The three methyl groups of A or Ā are homotopic, and the one- or two-ring flips interconverting A and B̄, or Ā and B, will therefore cause the coalescence of the four methyl resonances of the two diastereomers to a singlet. Either of the two one-ring flips interconverting B and B̄ will result in the collapse of the three methyl resonances of these enantiomers to two lines in a ratio of 2:1. The enantiomeric two-ring flips interconverting B and B̄ will necessarily occur at identical rates and therefore the results of rapid interconversions by these pathways have been considered together. This mechanism will cause the coalescence of the three methyl signals of B and B̄ to a singlet, since, as illustrated by Figure 5, an arbitrarily labeled methyl group (asterisk) occupies all three magnetically distinguishable positions during the course of interconversions by the two-ring flips in question.

The complete analysis presented above provides a sound basis for the design of experiments to investigate isomerism and isomerization of 1 and for the interpretation of experimental data. The results of a ^{1}H-nmr investigation of 1 are as follows.

At −70° the 100-MHz ^{1}H-nmr spectrum of 1 in CS$_2$ solution consists, in the methyl region, of four signals in the ratio of intensities of ca. 1:1:1:2.7 (Figure 6). On the basis of the analysis given above, the

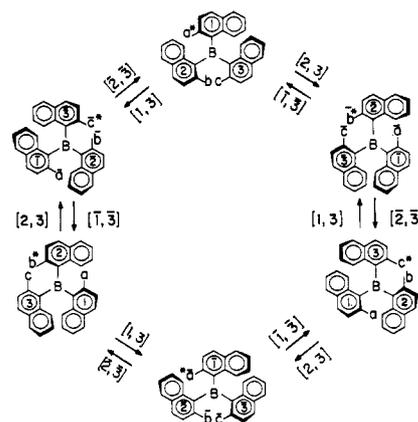first three resonances must correspond to the three diastereotopic methyl groups of B and B̄, while the more intense peak is assigned to the three homotopic methyl groups of A and Ā. Thus, the spectrum of 1 in the low-temperature limit is consistent with the postulated propeller geometry for the ground-state conformation, and with a ratio of BB̄ to AĀ of 3.0:2.7.

As illustrated by the spectrum at −25° (Figure 6), all four resonances begin to converge as the sample is warmed above −70°. Since there is no concurrent broadening of resonances, the observed changes in the spectrum are due to temperature-dependent chemical shifts rather than to exchange phenomena. At ca. −20°, the two central signals are so close together that they are no longer resolvable under the conditions of measurement. The chemical shifts of all of these signals were found to be linear functions of temperature in the region −70 to −25°, within experimental error (see Experimental Section).

When the sample was warmed to ca. 0°, noticeable line broadening occurred and further warming resulted in coalescence of all four peaks to a singlet (Figure 6), which became sharp at ca. 85°. The analysis given above indicates that the only mechanisms which can explain such behavior are those which interconvert A and
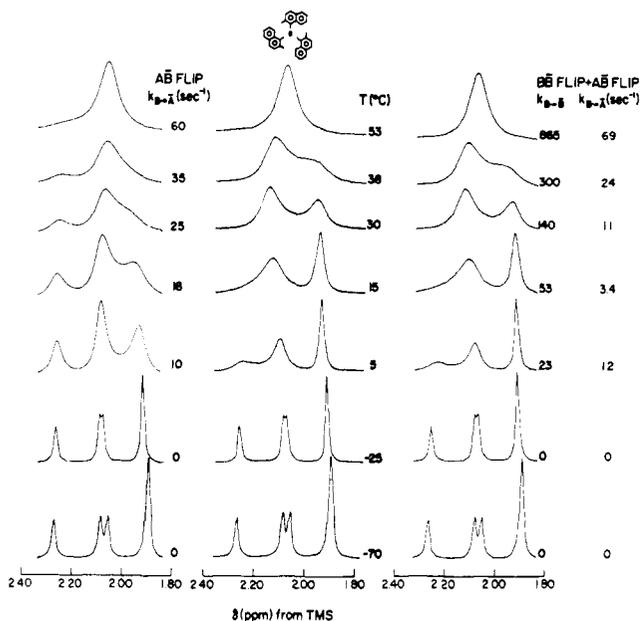
Figure 6. A triptych depicting the 100-MHz ^{1}H-nmr spectrum (methyl region) of 1 at various temperatures. The central section displays the experimental spectra. The left-hand panel shows the calculated spectra based upon the A$\overline{\text{B}}$-flip alone ($k_{\text{B}\rightarrow\overline{\text{A}}}$ or $k_{\overline{\text{B}}\rightarrow\text{A}}$). The right-hand panel shows calculated spectra for the combinations of the B$\overline{\text{B}}$ ($k_{\text{B}\rightarrow\overline{\text{B}}}$ or $k_{\overline{\text{B}}\rightarrow\text{B}}$) and A$\overline{\text{B}}$-flips which match the experimental spectra (see text).

$\overline{\text{B}}$ (and $\overline{\text{A}}$ and B), i.e., the appropriate one- or two-ring flips (Figure 4), or a combination of these with other pathways. It seems likely that the one-ring flips (and, to an even greater extent, the zero-ring flips) of 1 would involve an exceedingly high degree of steric hindrance in the transition states, relative to the two-ring flips, because of the presence of bulky groups in the ortho positions of the aryl rings. These processes may thus be safely ruled out for 1 as well as for the other compounds discussed in this paper, all of which also have bulky groups in the ortho positions.[11] Therefore, the observed coalescence in 1 is taken to be the result of the two-ring flip which interconverts diastereomers (the "A$\overline{\text{B}}$-flip"), occurring either alone, or in combination with other pathways.

The simplest explanation for coalescence is the sole operation of the A$\overline{\text{B}}$-flip. However, when the nmr line shape to be expected for this process in the region of coalescence was calculated[12] and compared with the experimental spectra, no correspondence was observed (Figure 6). It follows that more than one mechanism must be involved. The enantiomeric two-ring flips which interconvert (enantiomerize) B and $\overline{\text{B}}$ (the "B$\overline{\text{B}}$-flips") might be expected to have activation parameters not too far different from those of the A$\overline{\text{B}}$-flips; in fact, employing rate ratios (k_1/k_2) of 0.05–0.08 for A$\overline{\text{B}}$-flips (k_1 for $\overline{\text{B}} \rightarrow$ A) to B$\overline{\text{B}}$-flips (k_2), calculated line shapes were obtained which gave satisfactory matches to the experimental spectra at five temperatures (Figure 6).

(11) This statement does not preclude the possible observation of the one-ring flip in other systems.

(12) The computer program employed was adapted from one developed by M. Saunders (see M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. C. Malmström, and T. Vänngård, Ed., Pergamon Press, New York, N. Y., 1967, p 85). We are grateful to Professor Saunders for providing us with a copy of his program.
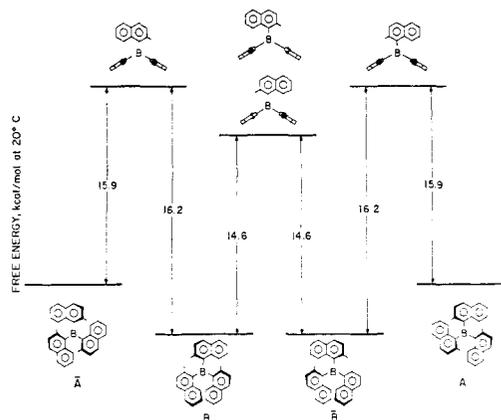

Figure 7. A schematic representation of the energetics of stereo-isomerization of 1. The black circles projecting toward (solid circle) or away from (broken circle) the observer represent methyl groups.

It should be noted that in the absence of accidental isochrony or fortuitously equivalent free energies of activation, the enantiomeric two-ring flips are the only flip mechanisms which will account for the observed coalescence of the methyl group resonances of B and $\overline{\text{B}}$. This fact provides strong support for our postulate that the one-ring flip pathways are high-energy pathways in these systems.

The spectral data permitted the calculation of the energy relationships among the stereoisomers of 1 and the magnitudes of the barriers separating these isomers. The relative intensities of the nmr signals at $-70°$ show that B$\overline{\text{B}}$ is slightly more stable than A$\overline{\text{A}}$ at this temperature. As the sample is warmed, the population of B$\overline{\text{B}}$ increases relative to that of A$\overline{\text{A}}$. Qualitatively, this indicates a positive entropy for the equilibrium A$\overline{\text{A}}$ $\leftrightarrows$ B$\overline{\text{B}}$, and a crossover temperature, below which A$\overline{\text{A}}$ is the more stable diastereomer. A plot of $\Delta G°_T$ (derived from T and the equilibrium constant as determined from relative peak areas) vs. T for seven temperatures over the range -70 to $+5°$ yields, for the equilibrium A$\overline{\text{A}}$ $\rightleftarrows$ B$\overline{\text{B}}$, $\Delta H° = 0.61 \pm 0.05$ kcal/mol and $\Delta S° = 3.1 \pm 0.2$ eu.[13] The temperature at which $\Delta G°$ equals zero (crossover temperature) is therefore ca. $-76°$. The major part of the entropy difference is accounted for by the difference in symmetry (C_3 vs. C_1) of the two diastereomers ($R \ln 3 = 2.18$ eu, for the equilibrium as shown).

The rate data determined by the line-shape analysis were used to calculate free energies of activation for the various exchange processes at $20°$. The results are shown schematically in Figure 7. For the equilibrium B$\overline{\text{B}}$ $\rightleftarrows$ A$\overline{\text{A}}$, $\Delta G°_{20}$ is 0.3 kcal/mol. For the conversion of B$\overline{\text{B}}$ to A$\overline{\text{A}}$, the calculations yielded $\Delta G^{\ddagger}_{20} = 16.2$ kcal/mol, and for the reverse reaction (A$\overline{\text{A}}$ $\rightarrow$ B$\overline{\text{B}}$), $\Delta G^{\ddagger}_{20} = 15.9$ kcal/mol. The barrier to enantiomerization of B and $\overline{\text{B}}$ (B $\rightarrow$ $\overline{\text{B}}$) is $\Delta G^{\ddagger}_{20} = 14.6$ kcal/mol. Thus, at $20°$ the enantiomerization of B and $\overline{\text{B}}$ is energetically more favorable by 1.6 kcal/mol than that of A and $\overline{\text{A}}$.

Since all the possible two-ring flips have been implicated in the observed interconversions of 1, the only

(13) Error limits are standard deviations, and as such do not reflect systematic errors.

other process to be considered is the three-ring flip which enantiomerizes B and B̄. As previously noted, this process interconverts only two of the three methyl groups of BB̄. In principle, enantiomerization by this pathway could be occurring rapidly on the nmr time scale above ca. −20°, where two of the three methyl groups become accidentally isochronous due to temperature-dependent chemical shifts, if the two accidentally isochronous methyl groups are the ones which are exchanging. The Gutowsky–Holm equation[14] was employed to calculate an upper limit to the rate at −20°, and the Eyring equation was used to estimate a lower limit for the three-ring flip of $\Delta G^{\ddagger}_{-20} =$ 14.3 kcal/mol. The activation energy for this process is therefore at least as great as that for the two-ring flips, within experimental error.

In summary, the lowest-energy pathways for the observed isomerizations of 1 are the two-ring flip processes, all of which have roughly similar activation energies. None of the other mechanisms can account for all of the experimental results, and in addition the one-ring and zero-ring flips are ruled out on steric grounds.

The results of our study of 1 are seriously at variance with the interpretation of an earlier variable-temperature nmr study of this compound by Weismann and Schug.[4b] The previous workers described the 40-MHz ¹H-nmr spectrum of the methyl region of 1 at −50° as "a doublet, with approximately a 2:1 intensity ratio,"[4b] with peaks at δ^{TMS} 1.96 and 2.07 ppm, respectively. The spectrum at +113° was reported as a singlet at δ^{TMS} 2.06 ppm. At 0°, three methyl group signals were observed, and these were interpreted as reflecting a combination of the low-temperature doublet and the high-temperature singlet. On the basis of their interpretation of these spectra, the authors tentatively assigned the "low-temperature 2:1 doublet as the most stable isomer," and asserted that "the occurrence of the central peak at higher temperatures must correspond to another rotational isomer."[4b] In fact, at −50° the 100-MHz ¹H-nmr spectrum of 1 actually consists of four signals at $\delta^{TMS}_{CS_2}$ 2.27, 2.09, 2.07, and 1.90 ppm, with a ratio of intensities of ca. 1:1:1:2.5, respectively. These resonances reflect a mixture of stereoisomers (AĀ and BB̄) rather than a single diastereomer. When the sample is warmed to 0°, three signals are indeed observed, but these broad resonances are indicative of exchange processes denoting stereoisomerization, rather than of a mixture of isomers whose interconversion is slow on the nmr time scale. At 85°, a single sharp resonance is observed (in bromobenzene solution), in accord with the observation of the previous workers.[4b] However, this signal is clearly not attributable to a single rotational isomer, but is due to a mixture of conformers which are rapidly interconverting on the nmr time scale.

This misinterpretation of their nmr results by the previous workers led them to conclude that among several triarylboranes investigated, 1 was "the only one having a thermally accessible rotational isomer."[4b] The discussion presented above provides unambiguous evidence that, to the contrary, 1 consists of a mixture of stereoisomers even at the low-temperature limit

(−50°) of the reported study,[4b] and that the barriers to stereoisomerization are far lower than those required by the earlier interpretation.[4b]

Stereochemical Correspondence of Triarylboranes and Tris Chelates. It is interesting to note that the conformational analysis of 1 reported above bears some striking points of formal resemblance to a recent study of an entirely different class of compounds, the transition metal tris chelates.[15] As was previously pointed out,[9] compounds belonging to these two systems have features which show stereochemical correspondence.[16]

For example, the nmr spectrum of the methyl region of tris(α-isopropenyltropolonato)cobalt(III) (2) at −24° consists of four resonances. One of these corresponds to the three equivalent methyl groups of the enantiomeric cis isomers, while the others are assigned to the three nonequivalent (diastereotopic) methyl groups of the enantiomeric trans isomers. As the temperature is raised, two of the trans methyl signals coalesce. This coalescence was attributed to enantiomerization by a trigonal twist mechanism (a non-bond-breaking mechanism with a C_s intermediate structure). When the temperature is increased still further, all the methyl signals coalesce; this process corresponds to cis ⇌ trans isomerization by an unspecified mechanism.[15]

The similarities to 1 are immediately apparent. The nmr spectra described for the cis and trans isomers of 2 correlate with those of AĀ and BB̄, respectively. The lower temperature coalescence in the chelate system parallels that expected for a three-ring flip interconversion of B and B̄, whereas the higher temperature process bears some similarity to the results expected for interconversions of A and Ā.

Although triarylboranes and tris chelates are chemical systems which differ enormously in their constitution, properties, and reactions, the similarities noted above are not coincidental. It is not an accident but a necessary consequence of stereochemical correspondence that an analysis of the effect of the trigonal twist on 2 leads to the same result as an analysis of the effect of the three-ring flip on 1.

Tris-1-(4-methylnaphthyl)borane. The nmr spectrum of this compound shows a singlet in the methyl region which remains sharp even upon cooling to −95°. Although this result could well be due to accidental isochrony and thus cannot yield concrete information about the barriers to interconversion of isomers in this system, it is at least consistent with the reasonable assumption that such barriers will be appreciably lower than those for compounds in which steric hindrance to rotation is expected to be greater (i.e., 1 and other compounds reported below). It follows that barriers to interconversion of stereoisomers of tris-1-(4-methylnaphthyl)-borane are expected to be a great deal less than ca. 15 kcal/mol. This conclusion is bolstered by observations on dimesityl-o-tolylborane (see below).

In the light of this conclusion, it is appropriate to comment on two previous reports concerning tris(1-naphthyl)borane. Brown and Sujishi[3a] prepared this compound and noted several discrepancies between its

(14) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(15) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 6411 (1972).

(16) This statement is strictly correct only with reference to the appropriate time scale of observation; in the present example, one assumes that rotation about the appropriate C–C single bonds is rapid on the nmr time scale.

properties and those reported earlier for tris(1-naphthyl)borane by Krause and Nobbe.[17] It was tentatively suggested[3a] that these discrepancies could be rationalized by assuming that each of the two groups of investigators had isolated a different rotational isomer of tris(1-naphthyl)borane.

However, if we assume a *maximum* activation energy for stereoisomerization of E_a = 15 kcal/mol for tris(1-naphthyl)borane and a preexponential Arrhenius factor (A) of 10^{13}, it follows that even at $-65°$ the half-life of a diastereomer in solution is at most on the order of only 5–10 min. Thus, it is out of the question that the discrepancies mentioned above are the result of the presence, in solution and at ambient temperatures, of a single diastereomer of tris(1-naphthyl)borane, as previously suggested.[3a] On the other hand, the relatively low barriers to interconversion for rotational isomers described here are not inconsistent with the higher barriers proposed for the addition compounds of tris(1-naphthyl)borane and amines;[3a] such adducts would have a roughly tetrahedral geometry about boron, which would lead to increased steric repulsion among the groups.

A Caveat on the Use of Molecular Models. In connection with their above mentioned study, Brown and Sujishi suggested, on the basis of an examination of Fisher–Hirschfelder models, that stereoisomerization of tris(1-naphthyl)borane would be "difficult."[3a] Similarly, during their discussion of 1, Weismann and Schug reported that "Inspection of a scale model for TMeNB$_\alpha$ [1] shows that isomerization under the conditions laid down for the present model is impossible."[4b] From the discussion presented above, it is evident that although space-filling (*e.g.*, Fisher–Hirschfelder or CPK) molecular models can be useful aids in the visualization of ground-state structures and in the comparison of relative energetics of different conformations, they are often grossly misleading as guides for the estimation of absolute transition-state energies.[18] As we have been at pains to point out, the use of these models to estimate activation energies by the workers cited above led to serious overestimations of the barriers involved.

Trimesitylborane and Tris(2,6-dimethyl-4-isopropylphenyl)borane. As detailed above, trimesitylborane exhibits a propeller conformation in the crystal lattice. It has been reported[4b] that the nmr spectrum of this compound shows only one signal for the *o*- and one signal for the *p*-methyl groups; this result is consistent with the propeller geometry (D_3), as well as with the time-averaged (D_{3h}) structures.

Similarly, we have found that tris(2,6-dimethyl-4-isopropylphenyl)borane in CS_2 or toluene-d_8 shows only one signal for the *o*-methyl groups in the 60-MHz ^{1}H-nmr spectrum, even at $-100°$. However, although the two methyl groups in the isopropyl portion of each ligand of tris(2,6-dimethyl-4-isopropylphenyl)-borane must be diastereotopic in the ground-state conformation (since the propeller is chiral), only a single doublet is seen for these groups over the temperature range $+40$ to $-100°$. If one makes the reasonable assumption that the barrier to interconversion of

(17) E. Krause and P. Nobbe, *Chem. Ber.*, **63**, 934 (1930).
(18) A similar observation was made by Kessler, *et al.*, in a report concerning sterically congested triarylmethanes: H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

enantiomers of this compound is similar in magnitude to those found for 1 and other hindered boranes (see below), then the observed equivalence of isopropyl methyl signals at $-100°$ must be due to accidental isochrony.

This conclusion is further substantiated by the observation that dimesityl-*o*-tolylborane need be cooled to only *ca.* $-60°$ in order to detect evidence of restricted rotation. A complete line-shape analysis was not performed because of the small chemical shift differences and accidental isochronies involved, but an approximate method yielded a barrier to interconversion on the order of 11 kcal/mol.

Dimesityl-9-anthrylborane (3) is capable of existing in two enantiomeric propeller conformations. Since there is a C_2 axis coincident with the anthryl–boron bond, the molecule in the ground state has two diastereomeric sets of homotopic *o*-methyl groups, and similarly two diastereomeric sets of aromatic hydrogens on the mesityl rings. Therefore, the nmr spectrum of 3 in the propeller conformation should include two *o*-methyl resonances and two resonances for the mesityl ring hydrogens. The possible interconversion mechanisms are the three-ring flip and two diastereomeric two-ring flips (excluding, as before, the zero- and one-ring flips on steric grounds). Since rapid interconversion of enantiomers by any of these mechanisms would result in the time-averaging of the two *o*-methyl signals in the nmr spectrum, and likewise of the two mesityl ring hydrogen signals, the observation of such coalescences, while allowing for a measurement of the rate of interconversion, would not provide the means for deciding among the possible mechanisms.

The 60-MHz ^{1}H-nmr spectrum of a $CDCl_3$ solution of 3 at $-16°$ shows two resonances of equal intensity for the *o*-methyl groups at $\delta_{CDCl_3}^{TMS}$ 1.60 and 2.18 ppm, a peak for the *p*-methyl groups at 2.25 ppm, and two equal-intensity resonances for the ring hydrogens on the mesityl groups at 6.63 and 6.88 ppm. Thus, the spectrum is in accord with the above analysis. Upon warming, the signals for the ring hydrogens broaden as the rate of enantiomerization increases, and finally coalesce at $3°$, and those of the *o*-methyl groups coalesce at $15°$. The Gutowsky–Holm equation[14] was used to calculate rate constants for these two site exchanges, and the Eyring equation to derive free energies of activation of 13.8 and 13.9 kcal/mol, respectively, for enantiomerization by the two-ring flip.

Dimesityl-1-(2-methylnaphthyl)borane (4). This compound is also capable of existing in two enantiomeric propeller conformations, but, in contrast to 3, there is no C_2 axis coincident with the naphthyl–boron bond. This reduction in symmetry removes the degeneracies associated with the C_2 axis in 3, and thus leads to the potential for discriminating among the possible flip mechanisms. A topological analysis[9] yields the graph shown in Figure 8. This graph illustrates the interconversion of the two enantiomers (vertices) by means of the three-ring flip and the three two-ring flips (edges); as before, the zero- and one-ring flips have been excluded on steric grounds. Since the [1,2]- and [1,3]-flips are enantiomeric and must occur at equal rates in an achiral medium, these pathways have been considered together in terms of their effects.

In the propeller conformation, the four *o*-methyl

Figure 9. The effect of enantiomeric [1,2]- and [1,3]-flips on the interchange of environments (letters) of a given methyl group (asterisk) in **4**. The aryl ring environments are labeled with numerals, and the numerals along the arrows identify the rings which flip during the specified interconversion. In the text, the flip pathways (undirected) are identified only by the unbarred designations.
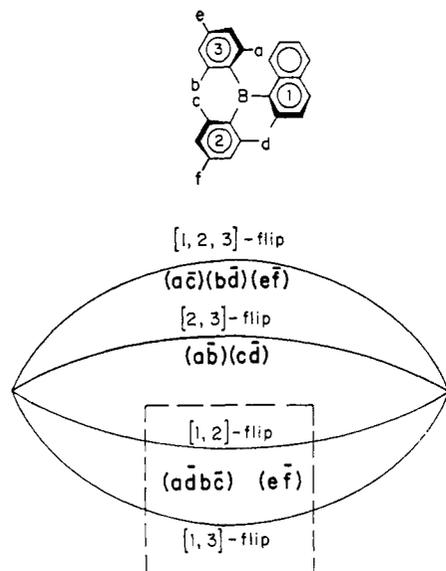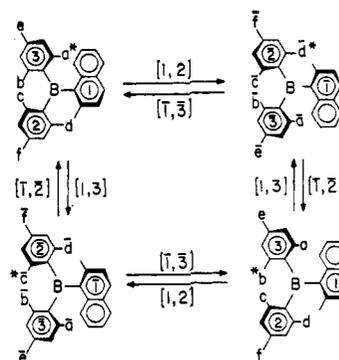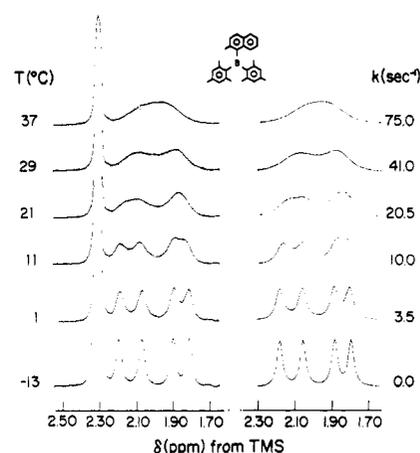
Figure 8. Graph depicting enantiomerization of **4** by two- and three-ring flips. The methyl group environments have been labeled with lower case letters, and barred letters designate enantiomeric relationships. The site exchange (a$\bar{d}$b$\bar{c}$) signifies that the methyl group is carried from environment a into $\bar{d}$, etc.

Figure 10. The 60-MHz ¹H-nmr spectrum (methyl region) of **4** at various temperatures (left), and the corresponding calculated spectra (o-mesityl methyl portion) based upon the two-ring flip mechanism (right).

groups of each enantiomer of **4** are diastereotopic, as are the two p-methyl groups. In addition, each enantiomer has one naphthyl methyl group. Each edge of the graph is labeled with the environments of the methyl groups which are exchanged by the indicated flip process. Only one of the two enantiomeric sets of interconversions is shown for each pathway. These site exchanges are readily derived from an examination of the transition states for the three-ring flip and the [2,3]-flip. The combination of the [1,2]- and [1,3]-flips results in the interchange of all four mesityl o-methyl groups, as is illustrated by Figure 9. This figure demonstrates that an arbitrarily labeled methyl group (asterisk) occupies all four diastereomeric environments during the course of the interconversions. Thus, as summarized in Figure 8, rapid interconversion by the three-ring flip or the [2,3]-flip on the nmr time scale will cause coalescence of the four o-mesityl methyl resonances to two signals, while rapid interconversion by the remaining two-ring flips will result in coalescence of all four signals to a singlet.

With the results of this analysis in hand, the experimental nmr spectra of **4** can be discussed. At −13°, the 60-MHz ¹H-nmr spectrum of the methyl region consists of four resonances, each corresponding to one methyl group, and a fifth signal corresponding in intensity to three methyl groups (Figure 10). As the sample is warmed, the four one-methyl signals broaden and finally coalesce to a singlet (which becomes sharp at ca. 100°) while the three-methyl signal remains essentially unchanged. Coalescence of four equal-intensity methyl signals to a singlet can be explained only if these four resonances derive from the four diastereotopic mesityl o-methyl groups; the three-methyl signal is accordingly derived from accidentally isochronous p-methyl and naphthyl methyl protons. In addition, according to the preceding analysis (Figure 8), the interconversions giving rise to coalescence must include at least one of the two-ring flip processes. The

simplest explanation consistent with the temperature dependence of the nmr spectra is interconversion of enantiomers by the [1,2]- and [1,3]-flips. Nmr line shapes based upon this mechanism were calculated[12] for the region of coalescence. Although there are 4! distinct ways of assigning the chemical shifts of the four sites, many of these assignments give equivalent exchange matrices. As a result of these degeneracies, there are only three unique exchange patterns (each corresponding to eight assignments of chemical shifts), and only one of these produces a satisfactory fit to the experimental spectra (Figure 10). The calculated rate constants at five temperatures were employed to derive $\Delta G^{\neq}_{20} = 15.4$ kcal/mol for the interconversion of enantiomers.

Combinations of mechanisms (e.g., the three-ring flip plus the [2,3]-flip) would also be consistent with the observed spectra, if both processes had nearly the same activation energies. However, since the data can be satisfactorily rationalized by invoking a single mechanism (i.e., the enantiomeric [1,2]- and [1,3]-flips) there is no need to postulate this more complicated explanation (Ockham's (or Occam's) razor).[19,20]

(19) The [2]- and [3]-flips of **4** are diastereomeric, and therefore would have different activation energies. Thus, as was the case for **1**,

Triarylboranes and Triarylcarbonium Ions

As revealed in the present study, the ground-state geometry and the conformational dynamics of triarylboranes are quite similar to those of the triarylcarbonium ions. The X-ray structure analysis of trimesitylborane shows that this compound exists in a propeller conformation in the solid state, and the nmr investigation of various triarylboranes indicates that the ground-state conformation of all these compounds in solution on the nmr time scale is also consistent with the propeller form. These results parallel similar findings for triarylcarbonium ions.[7]

A detailed study of the temperature-dependent [1]H-nmr spectra of two sterically crowded triarylboranes (1 and 4) indicates that the lowest energy pathways for isomerizations in these compounds are the two-ring flips. Similar studies have suggested that the two-ring flip mechanism is also the lowest energy mechanism for the isomerization of triarylcarbonium ions.[6h,9]

The variable-temperature [1]H-nmr studies of substituted (in both ortho positions) triarylboranes have revealed that these substances are mixtures of stereoisomers on the nmr time scale at low temperatures, and that interconversion of these stereoisomers occurs with activation energies of *ca.* 14–16 kcal/mol. These energies are only slightly larger than the activation energies of *ca.* 10–14 kcal/mol found for triarylcarbonium ions which have only hydrogen atoms in the ortho positions.[6c,h] It follows that for systems with comparable substituent patterns in the ortho positions, *i.e.*, systems whose ortho ligands offer comparable steric encumbrance, triarylcarbonium ions (Ar_3C^+) have substantially higher barriers than the corresponding boranes (Ar_3B). No doubt this is at least in part due to the greater length of the C–B bond (*ca.* 1.58 Å[21]) compared to that of the C–C$^+$ bond (*ca.* 1.45 Å[22]), a factor which leads to a significantly less crowded structure in the arylboranes. Differences in conjugative effects are also bound to play some role in determining the relative barriers to rotation in arylboranes as compared to triarylcarbonium ions. It has been reported that in triphenylborane the conjugative interaction between the phenyl rings and boron is negligible (3 ± 2 kcal/mol),[23] whereas for arylcarbonium ions calculations indicate a much higher resonance energy.[24] This comparison

suggests that in contrast to the carbonium ions, where conjugative effects seem to play a major role, the barriers to rotation in arylboranes are mainly steric in origin.[25]

Recent *ab initio* LCAO–MO–SCF calculations[26] support this conclusion. The minimal STO-3G basis,[27] applied to standard geometrical models[28] of phenylborane ($C_6H_5BH_2$) and the benzyl cation ($C_6H_5CH_2^+$), gives barriers to rigid rotation of 6.3 and 36.6 kcal/mol, respectively. In part the difference reflects the smaller interaction between boron and the ring due to the greater C–B bond distance, but more important is the difference in conjugative ability, as given by Mulliken population analysis. In the planar benzyl cation, π-type overlap population between the formally empty p orbital on C$^+$ and the coplanar p orbital on the adjacent ring carbon is 0.185; upon 90° rotation the value is reduced to 0.060. Corresponding quantities for phenylborane are 0.072 and 0.022. Thus loss of conjugation upon rotation is greater for the cation, and for these systems having minimal steric crowding, this is sensitively reflected in the rotational barrier.

Differences in solvation may also play some role in determining relative barrier heights in these two systems, but the magnitude of any such effect is unknown.

Experimental Section[29]

Trimesitylborane, obtained as a commercial product (Willow Brook Laboratories), was purified by recrystallization from ethyl acetate. **Tris-1-(2-methylnaphthyl)borane** (1),[4a] mp 205–206.5° (lit.[4a] mp 198°), was synthesized according to the procedure reported in the literature.

Tris-1-(4-methylnaphthyl)borane. An anhydrous ethyl ether solution of 1-bromo-4-methylnaphthalene (11.0 g, 50 mmol) was added dropwise with stirring to a 500-ml flask containing magnesium turnings (1.2 g, 50 mmol) and 100 ml of anhydrous ether. The reaction mixture was refluxed during the addition period, and toward the end of the addition the Grignard reagent began to crystallize. Dry benzene (100 ml) was added to dissolve the precipitate, and addition of the ether–halide mixture was completed. A total of 5 hr was required to complete the reaction. The flask was then cooled in an ice bath, and a solution of boron trifluoride etherate (2.0 ml, 17 mmol) in 50 ml of benzene was added. When addition was complete, the mixture was heated at reflux for 30 min and then poured onto ice containing 5% aqueous HCl. The separated organic layer was dried (Na_2SO_4) and the solvent was distilled at reduced pressure. Addition of a 50:50 mixture of ethanol-n-pentane to the resulting yellow oil caused a solid to precipitate. This material was recrystallized from ethyl acetate to yield 4.0 g of pale yellow crystals of the desired product (56%), mp 230–232°. The [1]H-nmr spectrum showed absorptions at $\delta_{CDCl_3}^{TMS}$ 2.72 (3 H, s, CH_3), 7.40 (4 H, m, aromatic H), and 7.91 (2 H, m, aromatic H).

the enantiomeric two-ring flips are the only pathways consistent with the spectra, and the assumption that the one-ring flips are of higher energy is again shown to be justified.

(20) It might be argued that coordination of solvent with the triarylboranes might play some role in the observed stereoisomerization phenomena. However, previous workers[3b,5a] have found that sterically congested boranes such as those studied here do not form complexes with solvent or with stronger bases such as ammonia and sodium alkoxides. Although solvent effects will necessarily have some influence on the energetics of the processes studied here, the studies cited above suggest that these effects will be minor.

(21) For trimesitylborane. This value is comparable to the C–B bond lengths of 1.57 and 1.59 Å found for (Mes)$_2$BN=C(C$_6$H$_5$)$_2$: G. J. Bullen and K. Wade, *Chem. Commun.,* 1122 (1971).

(22) For trityl cation.[7j]

(23) (a) Zh. S. Galuashvili, I. P. Romm, E. N. Gur'yanova, I. M. Viktorova, N. I. Sheverdina, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR,* **207**, 99 (1972). (b) As mentioned above, the free energy of activation for the two-ring flip of 3 is 13.9 kcal/mol. The free energy of activation for the corresponding interconversion in dimesityl-9-(10-methoxyanthryl)borane is $\Delta G^\ddagger_{14} = 14.1$ kcal/mol. This negligible substituent effect is consistent with the reported magnitude of conjugation between boron and phenyl groups.[23a]

(24) (a) F. Strohbusch, *Tetrahedron,* **28**, 1915 (1972); (b) V. Gold, *J. Chem. Soc.,* 3944 (1956); (c) M. Shanshal, *J. Chem. Soc., Perkin Trans. 2,* 335 (1972).

(25) This conclusion is in accord with a report that in cyclopropyldimethylborane and cyclopropyldifluoroborane the cyclopropyl group appears to undergo rapid rotation on the nmr time scale even at −100°: A. H. Cowley and T. A. Furtsch, *J. Amer. Chem. Soc.,* **91**, 39 (1969).

(26) J. A. Pople, P. v. R. Schleyer, and J. D. Dill, unpublished studies. We thank J. D. Dill for providing us with these results, and for helpful discussions.

(27) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.,* **92**, 2191 (1970).

(28) J. A. Pople and M. Gordon, *ibid.,* **89**, 4253 (1967). To the table of standard bond lengths have been added B–C = 1.58 and B–H = 1.16 Å.

(29) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Unless specified otherwise, nmr spectra were recorded on a Varian A-60A spectrometer at ambient temperature (*ca.* 37°) and refer to *ca.* 20% solutions in CDCl$_3$ containing tetramethylsilane (TMS) as internal reference. Mass spectra were obtained on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. All reactions which involved the use of organometallic compounds as reagents were carried out under a dry high-purity nitrogen atmosphere. Melting points were measured in a Thomas-Hoover apparatus in sealed tubes and are corrected.

Mass spectral analysis was consistent with the assigned structure; exact mass, 434.220600 (calcd, 434.220573).

Anal. Calcd for $C_{33}H_{27}B$: C, 91.25; H, 6.27; B, 2.49. Found: C, 91.24; H, 6.53; B, 2.33.

Tris-2-(1-methylnaphthyl)borane. Attempts to prepare this compound by reaction of either the organomagnesium or organolithium compound with boron trifluoride etherate gave as principal product 1,1'-dimethyl-2,2'-binaphthyl, mp 232–233° (lit.[30] mp 227°). The ¹H-nmr spectrum showed absorptions at $\delta_{CS_2}^{TMS}$ 2.49 (3 H, s, CH₃) and 7.60 (6 H, m, aromatic H). The mass spectrum showed the parent ion at m/e 282.

Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.16; H, 6.76.

Tris-(2,6-dimethyl-4-isopropylphenyl)borane. A sample of 1-bromo-2,6-dimethyl-4-isopropylbenzene (20 g, 88.1 mmol), prepared according to Schubert, *et al.*,[31] dissolved in 30 ml of anhydrous ether was added dropwise with stirring to a 250-ml flask containing magnesium turnings (2.57 g, 106 mmol) and 40 ml of ether. The reaction mixture was refluxed for 4 hr. A solution of 1.4 ml (12 mmol) of boron trifluoride etherate in 20 ml of ether was added dropwise to the refluxing solution. Toluene (40 ml) was added and the ether was removed by distillation. The toluene solution was heated at reflux for 8 hr and then poured onto crushed ice (300 ml) containing 20 ml of concentrated aqueous HCl. The organic layer was diluted with benzene, separated, and dried over MgSO₄, and the solvent was distilled at reduced pressure. Addition of 75 ml of ethanol to the resulting yellow oil caused the product to precipitate as white crystals, which were recrystallized from ethanol to yield 2.38 g (44%) of the desired product, mp 198–199°. The ¹H-nmr spectrum featured absorptions at $\delta_{CDCl_3}^{TMS}$ 1.23 (18 H, d, ³J_{HH} = 6.80 Hz, CH(CH_3)₂), 1.92 (18 H, s, CH₃), 2.77 (3 H, heptet, ³J_{HH} = 6.80 Hz, CH(CH₃)₂), and 6.70 (6 H, s, aromatic H). Mass spectral analysis was consistent with the assigned structure, and showed the parent ion at m/e 452.

Anal. Calcd for $C_{33}H_{45}B$: C, 87.59; H, 10.02; B, 2.39. Found: C, 87.53; H, 10.15; B, 2.39.

Dimesityl-o-tolylborane. A solution of o-bromotoluene (1.7 g, 10 mmol) in 50:50 benzene–ether was converted to the organolithium compound by treatment with n-butyllithium (10 mmol, 4.3 ml of a 2.35 M solution in hexane, Alfa Inorganics). Fluorodimesitylborane[3b] (2.68 g, 10 mmol) dissolved in 20 ml of dry benzene was added dropwise to the solution of organometallic compound at room temperature with stirring. The mixture was worked up as described above and the crude product was recrystallized from ethyl acetate to yield 1.5 g (43%) of white crystals, mp 136–137°. The ¹H-nmr spectrum featured resonances at $\delta_{CDCl_3}^{TMS}$ 1.96 (12 H, s, CH₃), 2.06 (3 H, s, CH₃), 2.27 (6 H, s, CH₃), 6.75 (4 H, s, aromatic H), and 7.15 (4 H, m, aromatic H). Mass spectral analysis showed the parent ion at m/e 340; exact mass, 340.236894 (calcd, 340.236222).

At −89° the ¹H-nmr spectrum of this compound featured methyl resonances at $\delta_{CS_2}^{TMS}$ 1.77, 1.88, 1.93, 2.00, and 2.23 ppm in a ratio of 1:1:1:2:2. Coalescence of the resonances at 1.88 and 1.93 ppm occurred at ca. −63°, and this observation was used to estimate[14] the rate at −63° from which the activation energy reported in the text (ca. 11 kcal/mol) was calculated.

Anal. Calcd for $C_{25}H_{29}B$: C, 88.23; H, 8.59; B, 3.18. Found: C, 88.14; H, 8.73; B, 2.89.

Dimesityl-9-anthrylborane (3). In a three-necked flask equipped with a dropping funnel, magnetic stirrer, condenser, and nitrogen inlet was placed 9-bromoanthracene (2.20 g, 8.6 mmol) dissolved in 100 ml of anhydrous ether. A solution of n-butyllithium in hexane (8.6 mmol, 2.35 M) was added with stirring, and after 5 min, fluorodimesitylborane[3b] (2.35 g, 8.8 mmol) dissolved in 30 ml of ether was added dropwise. After the addition was complete, the reaction mixture was refluxed for 5 min and then poured onto crushed ice. The resulting mixture was worked up as described above, and the crude product was recrystallized from ethyl acetate to yield 2.9 g (78%) of greenish yellow fluorescent needles, mp 239–240°. The ¹H-nmr spectrum featured absorptions at $\delta_{CDCl_3}^{TMS}$ 1.88 (12 H, br s, CH₃), 2.24 (6 H, s, CH₃), 6.72 (4 H, s, aromatic H), 7.22 (4 H, m, aromatic H), 7.96 (4 H, m, aromatic H), and 8.45 (1 H, s, aromatic H). Mass spectral analysis was consistent with the assigned structure, with the parent ion at m/e 426.

Anal. Calcd for $C_{32}H_{31}B$: C, 90.14; H, 7.33; B, 2.54. Found: C, 90.07; H, 7.57; B, 2.76.

Dimesityl-9-(10-methoxyanthryl)borane. A solution of 9-bromo-10-methoxyanthracene[32] (2.10 g, 7.3 mmol) in 50:50 benzene–ether was treated with n-butyllithium (7.3 mmol, 2.2 M solution in hexane). Fluorodimesitylborane[3b] (2.0 g, 7.3 mmol) dissolved in 10 ml of dry benzene was added dropwise to the solution of the organolithium compound at room temperature with stirring. The mixture was worked up as described above, and the crude product was recrystallized from ethyl acetate to yield 3.1 g (91%) of greenish-yellow needles, mp 203–204°. The ¹H-nmr spectrum featured absorptions at $\delta_{CDCl_3}^{TMS}$ 1.88 (12 H, br s, CH₃), 2.26 (6 H, s, CH₃), 4.18 (3 H, s, OCH₃), 6.75 (4 H, s, aromatic H), 7.25 (4 H, m, aromatic H), and 8.07 (4 H, m, aromatic H). Mass spectral analysis showed the parent ion at m/e 456; exact mass, 456.262381 (calcd, 456.262435).

At −1° the ¹H-nmr spectrum of this compound featured methyl resonances at $\delta_{CDCl_3}^{TMS}$ 1.62, 2.17, and 2.26 ppm in a ratio 1:1:1. Coalescence of the resonances at 1.62 and 2.17 ppm occurred at 18°, and this observation was used to estimate the rate[14] at 18° from which the activation energy reported in the text (14.1 kcal/mol) was calculated for the two-ring flip mechanism.

Anal. Calcd for $C_{33}H_{33}BO$: C, 86.84; H, 7.29; B, 2.37. Found: C, 86.96; H, 7.48; B, 2.59.

Dimesityl-1-(2-methylnaphthyl)borane (4). A solution of 1-bromo-2-methylnaphthalene (1.0 g, 4.6 mmol) in 50:50 benzene–ether was treated with n-butyllithium (4.7 mmol, 2.35 M solution in hexane). Fluorodimesitylborane[3b] (1.3 g, 4.8 mmol) dissolved in 10 ml of dry benzene was added dropwise to the solution of the organolithium compound at room temperature with stirring. The mixture was worked up as described above, and the crude product was recrystallized from ethyl acetate to yield 1.1 g (59%) of white crystals, mp 179–180°. The ¹H-nmr spectrum featured resonances at $\delta_{CDCl_3}^{TMS}$ 1.95 (12 H, br s, CH₃), 2.23 (9 H, s, CH₃), 6.74 (4 H, s, aromatic H), 7.23 (3 H, m, aromatic H), and 7.73 (3 H, m, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 390.251799 (calcd, 390.251871).

Anal. Calcd for $C_{29}H_{31}B$: C, 89.23; H, 8.00; B, 2.77. Found: C, 89.40; H, 8.07; B, 2.67.

Dnmr Measurements. ¹H-nmr spectra were recorded on Varian A-60A or Varian HA-100 spectrometers equipped with variable-temperature accessories. Temperature measurements were based on the chemical-shift separation of the protons of a methanol sample, and utilized the temperature-shift correlation of Van Geet.[33] Temperatures are believed to be accurate to ±2°, although within a given series of measurements smaller differences (ca. ±0.5°) are considered significant. Saturation of the nmr signals was avoided. The HA-100 spectra were calibrated using the difference frequency between the lock signal and pen position (DIFF 1 of the signal monitor) as measured on the V-4315 signal counter. Dnmr samples were ca. 25% v/v solutions with ca. 5% v/v TMS. TMS was used as the lock signal for the 100-MHz (frequency sweep mode) spectra. Samples were sealed under vacuum in precision thin-wall nmr tubes. The line-shape analyses[12] were performed on an IBM 360/91 computer equipped with a Calcomp plotting accessory.

The 100-MHz ¹H-nmr spectrum of tris-1-(2-methylnaphthyl)-borane (1) at −70° consists of four lines in the methyl region: $\delta_{CS_2}^{TMS}$ 1.89 (peak 1), 2.06 (2), 2.09 (3), and 2.27 (4) ppm, in the ratio of intensities of 2.7:1:1:1, respectively. The chemical shifts of resonances 1, 2, and 4 are temperature dependent, and shifts in the region of coalescence were estimated by linear extrapolation from the region where direct measurement was possible (−70 to −25°). The temperature dependence was expressed in terms of the difference in chemical shift, in Hz, of signal i and signal 3 ($\Delta\nu_i$) as a function of temperature (T, °C). The equations are as follows: $\Delta\nu_1 = -0.038T + 16.57$, $\Delta\nu_2 = -0.034T + 0.34$, and $\Delta\nu_4 = 0.011T - 17.48$. An exchange matrix for use in the Saunders computer program[12] was constructed for a combination of the AB and BB̄ flip mechanisms, and the ratio of rate constants of these two processes was varied as necessary to obtain a satisfactory fit to the experimental spectra (Figure 6). The calculated rates at five temperatures (Figure 6) were used to calculate $\Delta H^{\neq}$ and $\Delta S^{\neq}$ from a least-squares treatment of ln (k/T) vs. (1/T)[34] for each process, and the resulting parameters were employed to derive $\Delta G^{\neq}_{20}$ for each process, as reported in the text.

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(33) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); **40**, 2227 (1968).
(34) The transmission coefficient was assumed to be unity.[35]
(35) See G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

Table I. Final Atomic Parameters for $B(C_9H_{11})_3{}^a$

Atom	x	y	z	B
B	0	−0.0695 (2)	0.2500	b
C(1)	0.0198 (1)	−0.1387 (1)	0.33132 (11)	b
C(2)	−0.0453 (2)	−0.1158 (1)	0.38753 (12)	b
C(3)	−0.0329 (2)	−0.1847 (2)	0.45521 (13)	b
C(4)	0.0449 (2)	−0.2750 (2)	0.47180 (13)	b
C(5)	0.1103 (2)	−0.2956 (2)	0.41825 (14)	b
C(6)	0.0991 (2)	−0.2307 (2)	0.34882 (13)	b
C(7)	−0.1333 (2)	−0.0196 (2)	0.37548 (17)	b
C(8)	0.0561 (5)	−0.3482 (3)	0.54567 (20)	b
C(9)	0.1756 (3)	−0.2608 (2)	0.29422 (19)	b
C(11)	0	0.0659 (2)	0.25000	b
C(14)	0	0.3083 (2)	0.25000	b
C(15)	0.0897 (2)	0.2478 (2)	0.29981 (13)	b
C(16)	0.0912 (2)	0.1285 (2)	0.30144 (12)	b
C(18)	0	0.4383 (3)	0.25000	b
C(19)	0.1944 (2)	0.0713 (2)	0.35760 (18)	b
H(3)	−0.084 (2)	−0.173 (2)	0.492 (1)	6.5 (6)
H(5)	0.168 (2)	−0.357 (2)	0.430 (1)	6.2 (5)
H(7)A	−0.186 (3)	−0.018 (3)	0.318 (2)	8.7 (8)
H(7)B	−0.179 (3)	−0.023 (2)	0.414 (2)	8.1 (7)
H(7)C	−0.101 (3)	0.052 (3)	0.379 (2)	9.3 (9)
H(8)A	0.054 (3)	−0.306 (3)	0.595 (2)	10.6 (10)
H(8)B	−0.024 (4)	−0.371 (4)	0.552 (3)	12.7 (13)
H(8)C	0.110 (3)	−0.392 (3)	0.553 (2)	9.5 (10)
H(9)A	0.211 (2)	−0.190 (2)	0.276 (2)	6.9 (6)
H(9)B	0.239 (3)	−0.307 (2)	0.323 (2)	8.0 (7)
H(9)C	0.127 (3)	−0.302 (3)	0.243 (2)	10.1 (10)
H(15)	0.155 (2)	0.288 (2)	0.337 (2)	6.5 (6)
H(18)A	0.034 (6)	0.463 (5)	0.199 (4)	6.6 (12)
H(18)B	0.046 (5)	0.473 (4)	0.302 (3)	5.1 (10)
H(18)C	−0.086 (6)	0.459 (5)	0.248 (5)	8.4 (16)
H(19)A	0.174 (3)	0.025 (3)	0.402 (2)	10.3 (9)
H(19)B	0.226 (3)	0.008 (3)	0.333 (2)	11.0 (10)
H(19)C	0.249 (3)	0.119 (3)	0.388 (2)	9.5 (8)

^{a} Standard deviations are in parentheses. ^{b} Anisotropic thermal parameters are given in Table II.

were small (ca. −2 to −6 eu), but since the values obtained for $\Delta H^{\pm}$ and $\Delta S^{\pm}$ from nmr line shape methods are sometimes greatly in error,[35] they are not reported here.

Crystallography. The crystal data for trimesitylborane are $a = 11.928$ (4), $b = 11.669$ (3), $c = 17.142$ (5) Å, $\beta = 105.40$ (2)°, $D_m = 1.06$, $D_x = 1.063$ g cm^{-3} for $Z = 4$, μ(Cu Kα) = 4.4 cm^{-1}. The extinctions observed, $h + k$ odd for all data and l odd for $h0l$ data, indicated either space group Cc or $C2/c$. The structure analysis was successfully carried out in the centrosymmetric space group $C2/c$. The intensity data were measured on a Hilger–Watts four-circle diffractometer by a θ–2θ scan method. Nickel-filtered Cu Kα radiation and pulse height analysis were used. The size of the crystal was ca. 0.15 × 0.40 × 0.45 mm. A total of 2415 unique reflections was measured ($\theta < 76°$), of which 1802 had intensities significantly greater than background.

The structure was solved by analysis of the $E^2 - 1$ Patterson function. Since there are only four molecules in the unit cell, and since the molecules are chiral, the B atom and one mesityl of each molecule must lie on a twofold axis in the crystal, if space group $C2/c$ is assumed. Thus, to solve the structure in $C2/c$, it is only necessary to deduce the orientation of the molecule in the crystal and its location along the twofold axis. The orientation was easily obtained by matching the intramolecular vectors calculated for the idealized molecule to those in the neighborhood of the origin of the Patterson. The y coordinate of the center of the phenyl ring which lies on the twofold axis was obtained from the strong Patterson peak at $^1/_2$, y, $^1/_2$. At this point the structure was known except for a twofold ambiguity in the placement of the trimesitylborane molecule on the twofold axis. That is, if the center of the phenyl ring which lies on the rotation axis is at 0, y, $^1/_4$ and the distance from the center of this ring to the B atom is Δ, then the B atom is located at either 0, $y + \Delta$, $^1/_4$ or 0, $y - \Delta$, $^1/_4$. The correct placement of the molecule on the rotation axis was established by calculating structure factors for both of these orientations. The R factors were 0.40 and 0.52 for all atoms except the hydrogens.

The structure was refined by full-matrix least squares. Hydrogen atoms were located from a difference Fourier calculated after preliminary refinement of the heavier atoms. In the final cycles of least squares the heavier atoms had anisotropic thermal parameters and the hydrogens had isotropic temperature factors. A difference

Table II. Final Anisotropic Thermal Parameters for $B(C_9H_{11})_3{}^a$

Atom	$B_{11} \times 10^4$	$B_{22} \times 10^4$	$B_{33} \times 10^5$	$B_{12} \times 10^4$	$B_{13} \times 10^5$	$B_{23} \times 10^5$
B	72 (2)	64 (2)	512 (12)	0	235 (13)	0
C(1)	85 (1)	65 (1)	470 (7)	5 (1)	227 (8)	−9 (7)
C(2)	94 (2)	76 (1)	463 (7)	6 (1)	239 (9)	−46 (8)
C(3)	124 (2)	99 (2)	452 (8)	8 (1)	301 (10)	−27 (9)
C(4)	144 (2)	96 (2)	451 (8)	14 (2)	225 (11)	81 (10)
C(5)	132 (2)	86 (2)	548 (9)	30 (2)	249 (12)	87 (10)
C(6)	105 (2)	74 (1)	533 (9)	17 (1)	285 (10)	35 (9)
C(7)	112 (2)	98 (2)	635 (12)	26 (2)	380 (13)	−5 (12)
C(8)	252 (6)	152 (3)	565 (13)	57 (4)	501 (22)	315 (17)
C(9)	129 (2)	110 (2)	732 (13)	50 (2)	482 (15)	154 (14)
C(11)	87 (2)	65 (2)	476 (10)	0	246 (12)	0
C(14)	130 (3)	63 (2)	586 (13)	0	474 (17)	0
C(15)	109 (2)	75 (1)	559 (9)	−12 (1)	345 (11)	−97 (9)
C(16)	98 (2)	74 (1)	493 (8)	−4 (1)	271 (9)	−37 (8)
C(18)	185 (5)	66 (2)	848 (25)	0	465 (32)	0
C(19)	105 (2)	96 (2)	657 (12)	−5 (2)	68 (12)	−47 (12)

^{a} Standard deviations are in parentheses. The anisotropic temperature factor has the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

At −13° the 60-MHz ^{1}H-nmr spectrum of dimesityl-1-(2-methylnaphthyl)borane (**4**) includes resonances for the four o-methyl groups of the mesityl ligands at $\delta_{CDCl_3}^{TMS}$ 1.79, 1.92, 2.05, and 2.18. The line-shape analysis of this spectrum was carried out as described above for **1**, with the exception, noted in the text, that frequency assignments for the four diastereomeric o-methyl environments are ambiguous since eight distinct assignments will all give identical calculated spectra which match the experimental spectra. Thus, actual chemical shifts remain unknown. One arbitrary set of static parameters which produced a satisfactory fit to the experimental spectra was: $a = 1.92$, $b = 2.05$, $c = 2.18$, and $d = 1.79$ ppm (see Figure 8 for significance of letters).

The values of $\Delta S^{\pm}$ calculated for all interconversions of **1** and **4**

Fourier based on the final parameters has no features greater than 0.1 e in magnitude. The final R is 0.052 for the 1802 observed data.[36]

The results of a rudimentary molecular mechanics calculation are in excellent agreement with the experimental angles of rotation discussed above. The energy due to the nonbonded interactions was calculated as a function of the angle of rotation about the C–B bond. For these calculations, ideal D_3 geometry was assumed and (exp-6) potential functions[37] were used. The energy minimum

(36) See paragraph at end of paper regarding supplementary material.

(37) D. E. Williams, *J. Chem. Phys.*, **47**, 4680 (1967).

occurs when the rings are rotated 50.7° out of the reference plane. This result is in reasonable accord with that (45°) of a previous calculation.[4b]

Supplementary Material Available. A listing of the final atomic parameters and of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7019.

Conformational Dynamics of Alkoxydiarylboranes[1]

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Abstract: The low-temperature ^{1}H-nmr spectra of several alkoxydiarylboranes are shown to be consistent with three alternatives: the molecules adopt propeller conformations, and stereoisomerization is slow on the nmr time scale; the molecules adopt propeller conformations with rapid stereoisomerization by means of one-flip pathways; the molecules adopt perpendicular conformations with slow stereoisomerization. Stereoisomerization phenomena observed at elevated temperatures are discussed in terms of flip mechanisms, and pathways which involve the flipping of aryl groups only are found to have lower activation energies than those which also involve flipping of the alkoxy group. An analysis of the isomerization processes reveals restricted rotation about the B–O bond, and arguments are presented which suggest that conjugative effects between boron and oxygen play a significant role in the stereochemistry of alkoxyarylboranes.

In conjunction with a stereochemical study of triarylboranes,[3] we have examined the temperature-dependent nmr spectral behavior of alkoxydiarylboranes. Reports concerning restricted rotation about boron-nitrogen[4a–c] and boron–oxygen[4d] bonds suggest that π-bonding between boron and oxygen,[5] as well as other conjugative and steric interactions, might be expected to play a significant role in the stereochemistry of alkoxydiarylboranes. The present paper reports the results of our investigation and provides a basis for understanding the major stereochemical features of these systems.

Ground-State Geometry of Alkoxydiarylboranes

Since this study deals with stereoisomerism due to restricted rotation about the B–C and B–O bonds in alkoxydiarylboranes, the conformation of these compounds may be defined, for our purposes, in terms of the orientations of three planes (the *ligand planes*), i.e., the planes of the two aryl rings and the B–O–C plane, with respect to the plane defined by the two carbon atoms and the oxygen atom bonded to boron (the *reference plane*). For a given ligand plane, there are two unique orientations: the ligand plane may be perpendicular to the reference plane (case I), or the ligand plane may coincide with the reference plane (case II).[6] In addition to these two special cases, there are an infinite number of intermediate orientations.

At present, there are no X-ray structural data available in the literature for alkoxydiarylboranes. Solid state and solution studies of hindered triarylboranes demonstrate that these compounds have a propeller-like conformation in the ground state, in which the sense of twist of all three groups is the same.[3] Similarly, an X-ray analysis of $(Mes)_2BN=C(C_6H_5)_2$ shows that the mesityl rings are rotated out of the C–B–C plane.[7] By analogy, it might be tentatively postulated that in the ground state, alkoxydiarylborane molecules also adopt a propeller conformation (Figure 1).[8]

9-Anthrylmesitylmethoxyborane (1)

If it is assumed that **1** has a propeller conformation in the ground state, four stereoisomers (two diastereomeric *dl*-pairs) are possible, labeled A, $\bar{A}$, B, and $\bar{B}$ in Figure 2. The methoxy methyl group resides near the anthryl group in A and $\bar{A}$, and near the mesityl group in B and $\bar{B}$. It is apparent that each stereoisomer has two diastereotopic *o*-methyl groups, as well as one *p*-methyl group and one methoxy group. Thus, in the absence of accidental isochrony, the ^{1}H-nmr spectrum

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(6) A more general and rigorous definition of case II geometry is that for a given ligand, the normal to the ligand plane which passes through the atomic center bonded to boron lies in a plane which is perpendicular to the reference plane and which contains boron and the atom bonded thereto.

(7) G. J. Bullen and K. Wade, *Chem. Commun.*, 1122 (1971).

(8) Any alkoxydiarylborane in the propeller conformation is necessarily asymmetric. The probability that the angles of twist of the three ligand planes, relative to the reference plane, are not all different, even on the time average (e.g., on the nmr time scale, in solution), is therefore vanishingly small.