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Crystal and Molecular Structure of $(CH_3)_2B_5H_7$

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The apex-basal dimethylpentaborane, 1,2-$(CH_3)_2B_5H_7$, is shown by X-ray diffraction methods to rearrange to the *cis* basal-basal product, 2,3-$(CH_3)_2B_5H_7$, in which the methyl groups are on adjacent basal B atoms of the square-pyramidal B_5 unit. Absence of the 2,4 isomer is attributed to H(methyl)···H(bridge) repulsions in a proposed trigonal bipyramidal intermediate. The space group is Pmcn, and there are four molecules in the unit cell having parameters $a = 12.55$, $b = 6.39$, and $c = 9.10$ A. The value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.11 for the 343 observed reflections.

Base-catalyzed rearrangements of pentaborane(9) derivatives proceed at lower temperatures than do uncatalyzed thermal rearrangements. At room temperature 2,6-dimethylpyridine catalyzes the complete conversion[1] of 1-$CH_3B_5H_8$ to 2-$CH_3B_5H_8$. The conversion of $B_{10}H_{16}$, which is a B_5H_8 dimer, to a $B_{10}H_{14}$ derivative also occurs[2] in the presence of 2,6-dimethylpyridine. Plausible internal rearrangement mechanisms[1-4] facilitated by H tautomerism were proposed; but the possibility of a mechanism in which the base cleaved[5] a BH_3 unit which later recombined was not eliminated at these low temperatures until the isolation[6] of the $(CH_3)_3NH^+ \cdot B_5H_7C_2H_5^-$ intermediate and the study[7] of the 1-DB_5H_8 rearrangement in which a B_5H_9 complex with Lewis base was suggested. Later studies have included rearrangements of monohalogenated derivatives of B_5H_9 catalyzed by $AlCl_3$[8] and hexamethylenetetramine.[9]

Thermal rearrangements of 1-RB_5H_8 to 2-RB_5H_8, where R is CH_3 or C_2H_5, occur[10] at 200°. About 80% rearrangement of 1-DB_5H_8 to 2-DB_5H_8 is found[7] in 20 hr at 145°, but there is little evidence that this intramolecular rearrangement takes place at a lower temperature than intermolecular H atom exchange,[11] which complicates the question of the nature of the intermediate steps. Nevertheless, the preference of a substituent which is more electron donating than H for the basal position is consistent with the predictions of molecular orbital studies[4,12] which indicate that the apex B atom is more negative than the basal B atoms.

The base-catalyzed and thermal rearrangements of 1,2-$(CH_3)_2B_5H_7$ might then be expected to yield a mixture of 2,3-$(CH_3)_2B_5H_7$ (*cis*) and 2,4-$(CH_3)_2B_5H_7$ (*trans*) isomers. Surprisingly, however, in the 2,6-dimethylpyridine-catalyzed reaction only a single product was obtained. We show here by single crystal X-ray diffraction methods that it is the *cis* product,[13] 2,3-$(CH_3)_2B_5H_7$. Examination of bond distances and unpublished molecular orbital results indicates no significant thermodynamic difference between these two possible products, and we therefore have searched for a mechanistic interpretation, which may have wider application in the study of rearrangement paths in other polyhedral or near-polyhedral molecular species.

Structure Determination

The liquid sample of $(CH_3)_2B_5H_7$ was distilled[14] and then fractionated into Pyrex capillaries 0.5 mm in diameter. After sealing, these capillaries were mounted on a Weissenberg or precession goniometer and were cooled[15] to −50° by means of a cold stream of N_2 which was obtained by evaporation of liquid N_2. After careful growth of a single crystal, a sample was maintained on a Weissenberg goniometer for some 2 months, during the recording of photographic X-ray (Cu Kα) diffraction data of levels hkL for $0 \leqslant L \leqslant 8$. A second crystal mounted on a precession goniometer and photographed with the use of Cu Kα radiation yielded levels $h0l$ and $0kl$, before the "Great Blackout" (New York Times, Nov 10–15, 1965) terminated the experiment. Although the films covered 74% of the Cu Kα sphere of reflection, only 343 diffraction maxima were observed while 301 reflections were classified as below the observational limit.

Reciprocal lattice symmetry of D_{2h} and systematic absences of $hk0$ for $h + k$ odd and of $h0l$ for l odd suggest that the orthorhombic space group is either $C_{2v}{}^9$-$P2_1cn$ or $D_{2h}{}^{16}$-Pmcn. Later work proved that the space group Pmcn, in which the molecule lies on a mirror plane, is the correct choice. Unit cell dimensions of $a = 12.55 \pm 0.04$, $b = 6.39 \pm 0.01$, and $c = 9.10 \pm 0.04$ A were obtained from photographs which had been calibrated with a diffraction pattern of powdered Al. Assumption of four molecules in the unit cell yields a calculated density of 0.830 g cm^{-3}, which is in reasonable agreement with that expected from a related compound, B_5H_9, for which the density is[16] 0.761 g cm^{-3}.

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Intensities were estimated visually with the aid of an intensity scale prepared from the crystal on the Weissenberg goniometer. The usual Lorentz and polarization corrections were applied, and a preliminary single scale factor was established from exposure times for the various levels. Corrections for oblique incidence of X-rays into the films were not made for the higher levels, but the associated error is absorbed into the empirical scaling and thermal parameters for the different levels. A three-dimensional Patterson function, having sharpened coefficients and an origin peak reduced to a single B–B interaction, was computed and then searched for mutually consistent peaks in the regions $^1/_2, 2y, 2z$; $2x, {}^1/_2, {}^1/_2 + 2z$; $2x + {}^1/_2, 2y + {}^1/_2, {}^1/_2$; $^1/_2, {}^1/_2, 2z + {}^1/_2$; $2x + {}^1/_2, 0, 0$; $0, 2y + {}^1/_2, {}^1/_2$; and the centrosymmetric interaction, $2x, 2y, 2z$. Our initial assumption of the space group, Pmcn, proved to be satisfactory: we found eight mutually consistent peaks, which were then carefully examined, taking into account all equivalent positions and symmetry ambiguities, for possible square-pyramidal B_5 arrangements. After a few false starts, an arrangement with apex B on the crystallographic mirror plane was found and was then shown to be consistent with those peaks sufficiently near the origin that they must necessarily be intramolecular vectors. Further examination then led to all B and C positions. The value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.44$ for this unrefined structure decreased to 0.27 after three cycles in which isotropic thermal parameters and distances were refined. Anisotropic thermal parameters then led to $R = 0.22$, including all reflections, observed and also absent, at one-half of each limit of observation. For observed reflections only the value of R was 0.18 at this stage.

Hydrogen atoms were located from difference electron density maps from which B and C were subtracted. The first map contained five largest peaks, from 673 down to 471 in arbitrary units, at the five H positions of the B_5H_7 half-molecular unit, of which three were on the crystallographic mirror plane and two were not. Of the remaining seven peaks in the asymmetric unit of this map, three were residuals at B or C, three at 400, 386, and 268 were at about tetrahedral angles around the C atom, and one at 274 was half-way between two bonded B atoms (less than 1 A from each) and thus deemed to be false. When the eight H atoms of the asymmetric unit were included as fixed atom contributions we obtained a value of $R = 0.133$ which led finally to a value of $R = 0.109$ for the 343 observed reflections after refinements of all position parameters for three cycles, of anisotropic thermal parameters of B and C for three cycles, of isotropic thermal parameters for H atoms for three cycles, and of scale factors for individual levels of the Weissenberg data for three cycles. Although the isotropic thermal parameters for H were converted to anisotropic equivalents, they were not further refined. Observed structure factors and refined scale factors are listed in Table I. It has, of course, been uniformly[17] realized for some time that one cannot simultaneously refine scale factors about a single axis and those thermal parameters which interact with these scale factors.

TABLE I

LIST OF OBSERVED F VALUES[a]

```
F(0,0,0)  (SCALED) = 1872.4
L=0 (K)(H)(0) (1,15),344/17,,197/10,,37/5,,121/6,,45/2,,
156/8,,95/5,,(1) (0,15),244/12,,392/20,,227/11,,170/8,,
46/2,,*,,*,,55/3,(2) (0,15)*,,122/6,,166/8,,34/4,,36/4,,
44/2,,*,,*,,(3) (0,14),*,,142/7,,56/3,,82/4,,76/4,,*,,*,,
(4) (0,13)55/3,,156/8,,*,,192/10,,75/4,,*,,*,,(5) (0,12),
131/7,,*,,*,,*,,50/3,,31/4,,(6) (0, 5)*,,*,,*,,
(7) (0, 4),*,,*,
L=1 (K)(H)(0) (0,15),,,,,,,,,,,,,,,,(1) (0,15)240/12,267/
13,149/7,166/8,89/4,*,35/4,57/3,*,97/5,*,*,66/3,66/3,39/
2,*,(2) (0,14)208/10,*,156/8,152/8,79/4,30/4,166/8,*,38/
5,54/3,56/3,*,46/2,*,*,(3) (0,14)108/5,40/2,124/6,171/9,*,
101/5,80/4,131/7,41/2,*,*,*,*,*,33/4,(4) (0,13)84/4,111/
6,40/2,51/3,*,*,*,*,48/2,*,41/2,38/5,36/5,38/5,
(5) (0,10)*,*,*,42/2,*,43/2,*,*,*,*,*,(6) (0, 5)63/3,*,*,*,
*,*,(7) (0, 7)37/5,39/2,*,*,*,*,*,*
L=2 (K)(H)(0) (0,15)U,U,206/10,134/7,174/9,133/7,92/5,140/
7,44/2,128/6,70/3,47/2,*,101/5,36/5,35/4,(1) (0,14)52/3,
233/12,177/9,123/6,30/4,*,184/9,*,66/3,84/4,*,*,*,62/3,
35/4,(2) (0,14)69/3,*,59/3,47/2,31/4,*,152/8,50/2,116/6,*,
*,*,*,*,*,(3) (0,13)66/3,*,*,40/2,37/5,103/5,*,109/5,*,
47/2,*,*,*,*,(4) (0,13)74/4,81/4,38/5,69/3,43/2,99/5,43/
2,116/6,44/2,*,42/2,*,36/4,30/4,(5) (0,12)108/5,*,*,75/
4,44/2,*,*,*,52/3,42/2,*,*,36/5,(6) (0, 4)64/3,44/2,*,*,*,
(7) (0, 3)*,*,*,*
L=3 (K)(H)(0) (0,15),,,,,,,,,,,,,,,,(1) (0,14)190/10,63/
3,41/2,47/2,174/9,61/3,116/6,62/3,134/7,*,80/4,*,45/2,*,
27/3,(2) (0,13)48/2,60/3,62/3,61/3,51/3,140/7,74/4,116/
6,*,*,35/4,35/4,*,29/4,(3) (0,13)37/5,76/4,80/4,47/2,34/
4,30/4,129/6,*,54/3,52/3,*,*,*,32/4,(4) (0,12)42/2,*,38/
5,49/2,*,43/2,54/3,43/2,38/5,59/3,*,*,*,(5) (0,10)63/3,
25/3,66/3,*,*,*,48/2,*,*,*,*,(6) (0, 9)37/5,48/2,*,34/4,*,
32/4,*,31/4,*,41/2,(7) (0, 3)35/4,*,*,*
L=4 (K)(H)(0) (0,14)U,53/3,*,138/7,31/4,*,118/6,73/4,84/
4,44/2,*,*,*,*,*,(1) (0,14)146/7,17/8,25/3,27/3,62/3,*,*,*,
63/3,*,45/2,*,50/2,*,28/3,(2) (0,13)46/2,111/6,*,56/3,50/
3,77/4,74/4,126/6,68/3,59/3,*,*,*,46/2,(3) (0,13)39/2,*,
70/4,37/5,*,42/2,95/5,50/3,53/3,43/2,*,*,*,*,(4) (0,11)
53/3,39/2,*,44/2,*,*,*,*,*,41/2,*,*,(5) (0, 9)*,*,*,*,*,
43/2,44/2,40/2,*,*,(6) (0, 7)39/2,41/2,*,*,*,*,*,*,
(7) (0, 3)30/4,*,*,*
L=5 (K)(H)(0) (0,15),,,,,,,,,,,,,,,,(1) (0,13)77/4,71/4,
31/4,20/10,*,71/4,68/3,85/4,*,55/3,*,*,50/3,39/2,
(2) (0,13)27/3,*,33/4,110/5,*,*,52/3,*,33/4,65/3,*,*,*,*,
(3) (0,12)40/2,27/3,30/4,*,35/4,39/5,48/2,35/4,*,*,*,28/
4,*,(4) (0,10)*,37/5,*,*,*,37/5,*,48/2,*,*,*,(5) (0, 9)*,
52/3,*,*,*,42/2,39/5,48/2,*,26/3,(6) (0, 8)45/2,33/4,30/
4,*,*,*,33/4,*,28/3,(7) (0, 2)*,*,*
L=6 (K)(H)(0) (0,13)U,43/2,19/9,41/2,*,*,36/4,25/3,*,43/
2,*,*,37/5,22/10,(1) (0,12)14/7,23/11,40/2,26/3,*,22/11,
70/4,37/5,29/4,43/2,*,*,*,(2) (0,12)89/4,63/3,69/3,*,*,
51/3,70/3,58/3,58/3,38/5,*,*,43/2,(3) (0,11)66/3,64/3,29/
4,49/2,25/3,*,26/3,28/3,42/2,*,*,20/10,(4) (0,10)*,*,*,
38/5,*,*,28/3,25/3,*,*,*,(5) (0, 5)29/4,26/3,*,*,*,*,
(6) (0, 4)22/11,*,*,21/10,*
L=7 (K)(H)(0) (0,15),,,,,,,,,,,,,,,,(1) (0,12)42/2,33/4,
56/3,*,30/4,*,38/5,*,*,28/4,27/3,*,19/9,(2) (0,10)26/3,
51/3,*,*,26/3,*,29/4,*,*,*,*,(3) (0,10)42/2,27/3,*,34/4,*,
*,*,39/2,*,*,*,(4) (0, 6)29/4,*,*,*,*,*,*,(5) (0, 4)32/
4,*,*,*,*
L=8 (K)(H)(0) (0,11)U,13/6,*,16/8,32/4,21/10,25/3,27/3,
31/4,*,*,*,(1) (0,10)13/6,*,*,18/9,*,30/4,*,33/4,*,*,*,
(2) (0, 9)39/2,27/3,29/4,*,*,21/10,21/10,22/11,*,*,
(3) (0, 6)21/10,41/2,*,*,*,*,*,(4) (0, 7)*,24/12,21/10,*,*,
*,22/11,*,(5) (0, 3)*,*,*,*


                SCALE  FACTORS

                 L=0   0.8205
                 L=1   0.8830
                 L=2   0.9089
                 L=3   0.9715
                 L=4   0.9145
                 L=5   1.0152
                 L=6   1.0543
                 L=7   1.0573
                 L=8   0.8007
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[a] The value of k and the range of h are given in parentheses. Absent reflections are indicated by an asterisk, experimentally unobserved reflections by U, and systematic extinctions by an extra comma. For observed reflections the value of $10|F_o|$ and the standard error of $|F_o|$ are listed separated by a slant line. The standard error of $|F_o|$ is obtained from the standard error of $|F_o|^2$ by

$$\sigma|F_o| = \frac{[\sigma(F_o^2)/F_o^2]}{\sqrt{4 + [\sigma(F_o^2/2F_o^2]^2}}\, F_o$$

$F(0,0,0)$ is given as a reference point and is summed over the entire unit cell.

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(17) E. C. Lingafelter and J. Donohue, *Acta Cryst.*, **20**, 321 (1966).

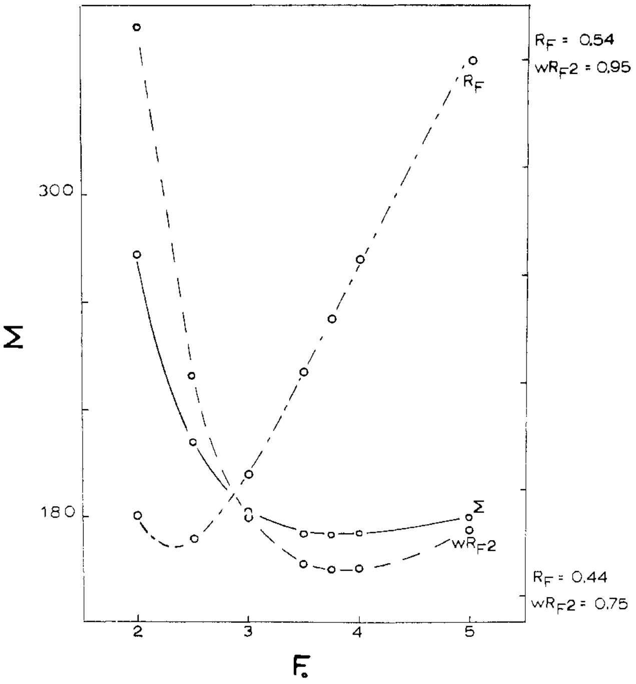

Figure 1.—Variation of the weighted sum of squares of residuals, $\Sigma w(|F_o| - |F_c|)^2$, denoted by Σ, and agreement factors R_F and wR_{F^2}, for different choices of $\langle |F_o| \rangle$. The minimum value in the sum of squares of residuals curve occurs at $\langle |F_o| \rangle$ = 3.75, which is 47% of the lowest readable value before the application of Lorentz and polarization factors.

Absent reflections are frequently omitted in refinements or are assigned one-half of the maximum observable in the appropriate region of the film. Neither of these procedures seems as satisfactory as either assigning an average value based upon the corresponding calculated structure factor or assigning an average value by minimizing the weighted sum of squares of residuals, $\Sigma w(|F_o| - |F_c|)^2$, for different choices of $\langle |F_o| \rangle$ for these absent reflections (or similarly for $|F|^2$ in place of $|F|$ if w is suitably modified). A test of this last procedure yielded a value of $\langle F_o \rangle$ = 3.75, which is 47% of the lowest readable value before the application of Lorentz and polarization factors. When the 301 reflections were included according to this prescription the final value of R_F was 0.195 for all observed and absent reflections. Figure 1 shows the weighted sum of squares of residuals and both weighted and unweighted agreement factors, all for absent reflections only, as functions of $\langle F_o \rangle$.

TABLE II

FINAL ATOMIC PARAMETERS

Atomic Positions in Fractions of the Unit Cell Edge

Atom	x	y	z
B(1)	0.2500	0.5689	0.0047
B(2)	0.1775	0.5228	0.1538
B(5)	0.1784	0.7729	0.0627
C(2′)	0.0881	0.3611	0.1960
H(1′)	0.2500	0.0062	0.4108
H(5′)	0.1185	0.6419	0.4993
H(7)	0.2500	0.9109	0.1355
H(8)	0.1456	0.7341	0.1944
H(9)	0.2500	0.5318	0.2638
H(10)	0.1093	0.1956	0.1370
H(11)	0.0363	0.3694	0.1111
H(12)	0.0714	0.3745	0.3080

Temperature Factors (Anisotropic[a] × 10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	T[c]
B(1)	42	209	202	0	0	−35	
B(2)	30	194	216	14	3	−17	
B(5)	45	223	216	10	−8	0	
C(2′)	40	274	271	−39	−5	5	
H(1′)	62	239	118				3.89
H(5′)	50	193	95				3.15
H(7)	54	207	102				3.38
H(8)[b]	0	0	0				0
H(9)	13	50	25				0.81
H(10)	120	462	228				7.54
H(11)	66	256	126				4.18
H(12)	104	400	197				6.54

Maximum Value of σ for Atomic Positions in Fractions of the Unit Cell Edge

Atom type	x	y	z
B	0.0005	0.0015	0.0012
C	0.0004	0.0009	0.0010
H(terminal)	0.0088	0.0171	0.0102
H(bridge)	0.0034	0.0142	0.0085

Maximum Value of σ for Temperature Factors

Atom type	β_{11}	β_{22}	β_{12}	β_{13}	β_{23}
B	5	27	8	7	15
C	3	17	7	7	13

[a] The thermal parameters are in the form exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. [b] For atom H(8) the determinant of the matrix of temperature factor components became negative, and hence all values of the temperature factors were reset to zero. [c] The isotropic temperature factor coefficients for the H atoms (T) were converted to anisotropic equivalents but were not further refined. The x parameters of B(1), H(1′), H(7), and H(9) and the β_{12} and β_{13} of B(1) are all restrained by symmetry and their standard deviations are zero. Equivalent positions for space group Pmcn are: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 - x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 + x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, \bar{y}, \bar{z}$; $^1/_2 - x, y, z$; $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$; $x, {}^1/_2 - y, {}^1/_2 + z$.

Discussion

Final parameters, based upon the 343 observed reflections, are given in Table II, disagreement factors are listed in Table III, and bond distances with their standard deviations computed from the full variance–covariance matrix are presented in Table IV. Corrections (Table IV) for thermal motion based upon the assumption that the second atom rides on the first are probably larger than those which would be obtained from motion of a rigid molecule, but our data do not justify such an exacting treatment. Bond angle standard deviations were calculated using the full variance–covariance matrix, but those listed in Table V are the maximum values for each type of bond angle in the expectation that the errors are not truly random. The molecule is shown in Figure 2, and the crystal structure in Figure 3.

In the molecule (Figure 2) the methyl groups are attached to adjacent basal B atoms which are 1.82 A apart, as compared with the three other B(basal)–B(basal) distances of 1.80 A. Thus there is no indication that the CH_3B-BCH_3 bond is abnormally strong compared with the HB–BH bonds of the molecule, or

TABLE III

DISAGREEMENT FACTORS[a] BASED ON F

Sin θ	R
0.00–0.40	0.11
0.40–0.50	0.10
0.50–0.60	0.08
0.60–0.65	0.08
0.65–0.70	0.12
0.70–0.75	0.14
0.75–0.80	0.12
0.80–0.85	0.15
0.85–0.90	0.17
0.90–1.00	0.15

Class	HKL	$0KL$	$H0L$	$HK0$	$H00$	$0K0$
All	0.11	0.14	0.10	0.10	0.08	0.20
$H = 2N$	0.11		0.10	0.11	0.08	
$H = 2N + 1$	0.11		0.09	0.10		
$K = 2N$	0.12	0.11		0.11		0.20
$K = 2N + 1$	0.10	0.17		0.10		
$L = 2N$	0.11	0.14	0.10			
$L = 2N + 1$	0.11	0.15				
$K + L = 2N$	0.10	0.14				
$K + L = 2N + 1$	0.12	0.14				
$L + H = 2N$	0.11		0.10			
$L + H = 2N + 1$	0.11		0.09			
$H + K = 2N$	0.12			0.10		
$H + K = 2N + 1$	0.10					
$H + K + L = 2N$	0.10					
$H + K + L = 2N + 1$	0.11					

$$R_F = \Sigma\big||F_o| - F_c|\big|/\Sigma|F_o| = 0.109$$
$$R_{F^2} = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.198$$
$$R_{wF^2} = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4]^{1/2} = 0.241$$

[a] Based on all observed reflections.

TABLE IV

BOND DISTANCES[a] AND STANDARD DEVIATIONS IN A

	Uncorrected	Corrected[b]	σ[c]
B(4)–B(5)	1.80	1.80	0.01
B(2)–B(5)	1.80	1.80	0.01
B(2)–B(3)	1.82	1.82	0.01
B(1)–B(5)	1.67	1.67	0.01
B(1)–B(2)	1.66	1.66	0.01
B(2)–C(2′)	1.57	1.55	0.01
B(1)–H(1′)	0.98	0.98	0.09
B(5)–H(5′)	1.09	1.11	0.06
B(5)–H(7)	1.42	1.44	0.07
B(2)–H(9)	1.35	1.38	0.05
B(5)–H(8)	1.29	1.32	0.04
B(2)–H(8)	1.46	1.50	0.04
C(2′)–H(10)	1.22	1.19	0.09
C(2′)–H(11)	1.01	1.02	0.08
C(2′)–H(12)	1.04	1.01	0.09

[a] Shortest intermolecular distances: B–B, 3.94; B–C, 4.04; C–C, 4.01; B–H, 3.13; C–H, 3.21; H–H, 2.87. [b] The first atom is assumed to be riding on the second. [c] The errors listed were obtained from the full variance–covariance matrix calculated during the final least-squares refinement of all position parameters and B and C temperature factors.

TABLE V

BOND ANGELES

Atoms	Degrees	σ
B(4)–B(5)–B(2)	90.4	0.5
B(3)–B(2)–B(5)	89.6	0.5
B(2)–B(1)–B(5)	64.5	1.0
B(2)–B(1)–B(3)	66.5	1.0
B(5)–B(1)–B(4)	65.2	1.0
B(1)–B(5)–H(5)	126.3	3.0
B(1)–B(2)–C(2′)	135.0	1.0
B(2)–C(2′)–H(10)	107.9	5.0
B(2)–C(2′)–H(11)	103.8	5.0
B(2)–C(2′)–H(12)	109.2	5.0
H(10)–C(2′)–H(12)	123.1	7.0
H(10)–C(2′)–H(11)	81.3	7.0
H(11)–C(2′)–H(12)	127.7	7.0
∠B(1)B(2)B(5)–B(5)B(2)H(8)[a]	203	3.0
∠B(1)B(2)B(3)–B(2)B(3)H(9)[a]	196	3.0
∠B(1)B(4)B(5)–B(4)B(5)H(7)[a]	194	3.0

[a] External dihedral angle.

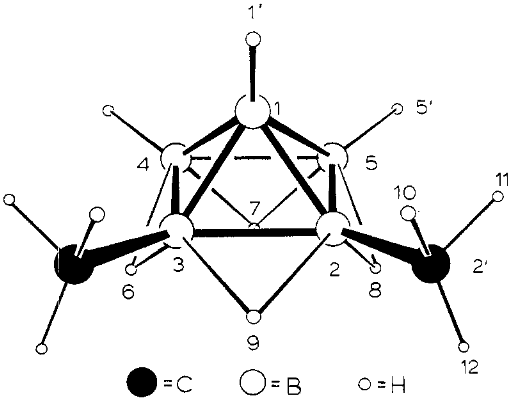

Figure 2.—The molecular structure and numbering scheme for $B_5H_7(CH_3)_2$.

compared with a similar distance[15,18] of 1.80 A in B_5H_9. Moreover, the B(basal)–B(apex) distances and the B(basal)–CH_3 distances are normal. The B(apex)–B(basal)–CH_3 angle of 135° in 2,3-$(CH_3)_2B_5H_7$ is in excellent agreement with the microwave value[18] of 136.2° in B_5H_9 and in reasonable agreement, within the large errors listed, with X-ray[16] and electron diffraction[19] studies. Although the B(basal)–C–H angles are close to tetrahedral values, the deviations of HCH angles from 109.5° are perhaps consistent with apparent errors associated with some torsional motion of the CH_3 group about the B–C axis. Nevertheless, the H(methyl) atoms are staggered with respect to the H(bridge) atoms. The external dihedral angles of 194, 196, and 203° in $(CH_3)_2B_5H_7$ are to be compared with the microwave value[18] of 196 ± 2° in B_5H_9. Perhaps the somewhat larger value of 203° is associated with the steric interactions which also prevent free rotation of the methyl group. As usual[4] all bonded distances to H are too short by about 0.1 A, but there is some uncertainty in the exact location of the H atoms as indicated by their large standard deviations. We first discuss these steric interactions on the assumption that all H atoms remain in the molecule during rearrangement.

These steric interactions may play a determinative role in the rearrangement of 1,2-$(CH_3)_2B_5H_7$ to 2,3-$(CH_3)_2B_5H_7$. If no such special features are present, the previous proposals[1–4] would predict a ratio of two parts of the 2,3 isomer (*cis*) to one part of the 2,4 iso-

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(18) H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, **22**, 262 (1954).

(19) K. Hedberg, M. E. Jones and V. Schomaker, *Proc. Natl. Acad. Sci. U. S.*, **38**, 679 (1952).

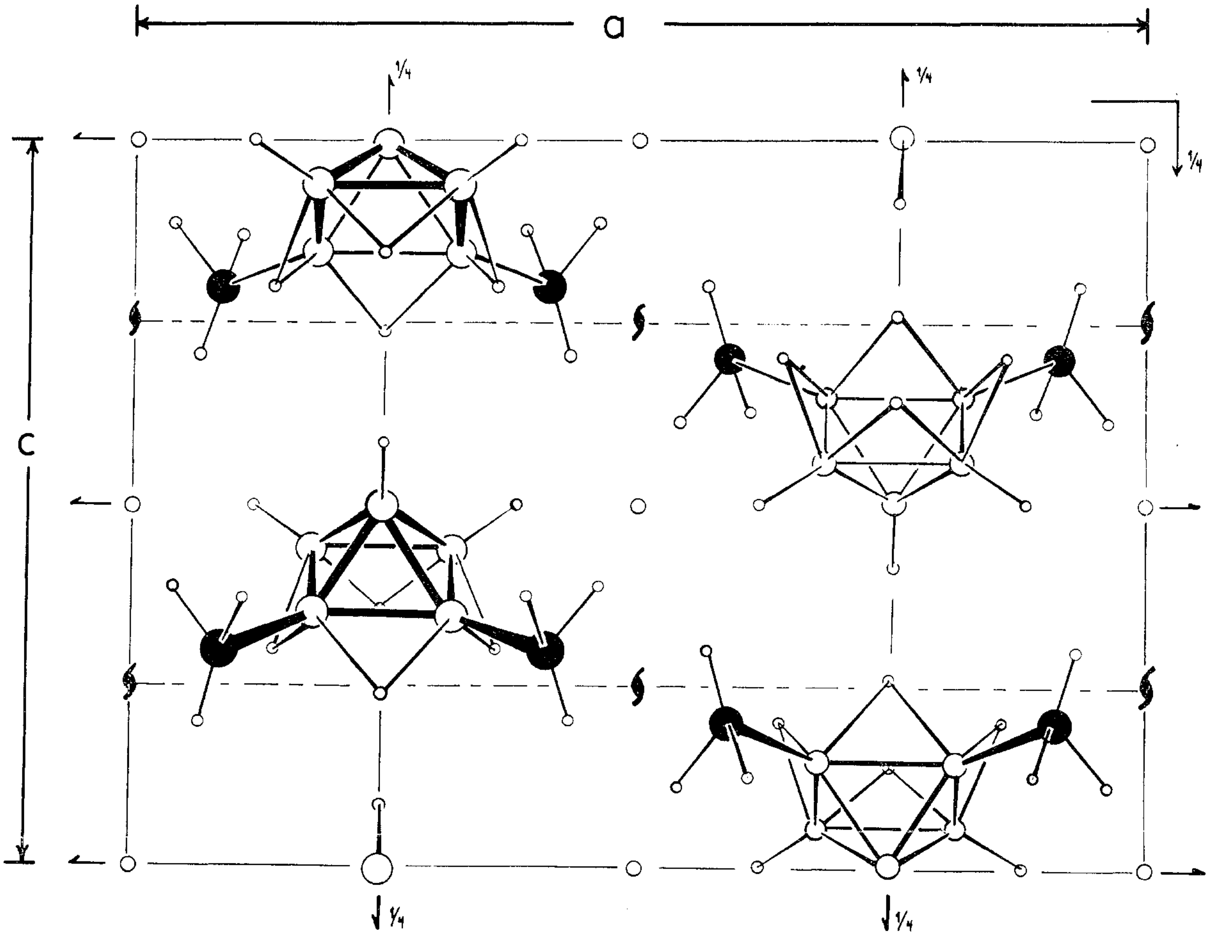

Figure 3.—The molecular packing as seen in the *h0l* projection. One unit cell is pictured.

mer (*trans*). Here, we comment on the details of probable H···H repulsions in a possible trigonal bipyramidal B_5 intermediate[20] (Figure 4). There are two ways in which the square base can change. If in Figure 4a 5–3 is contracted while 2–4 is expanded, the probable intermediate I in Figure 4b can then open as shown in Figure 4c to produce the 2,3 isomer. Models of this intermediate in which H atoms are placed nearly half-way between their starting and final positions indicate relievable steric problems for this pathway. On the other hand, if 2–4 is contracted while 5–3 expands intermediate II shown in Figure 4d is produced, which could then yield the 2,4 isomer; but if one assumes that H atoms are between starting and final values, one finds serious steric interactions. Idealized models were constructed for both intermediates assuming a distance of 1.9 A for the equatorial B–B distance. Even in the intermediate shown in Figure 4b the H(methyl)···H(bridge,face) contacts were almost as short as 2.0 A, but it is possible to relieve this interaction by moving the H(bridge,face) atoms back toward their original positions. In the intermediate of Figure 4d short contacts of 2.0 A also occur, but no reorientation of the methyl hydrogens and no reasonable movement of the bridge hydrogens removes the difficulty.

Let us now consider the possibility that one H^+ is lost in the formation of the intermediate so that the rearranging species is $(CH_3)_2B_5H_6^-$. Loss of H^+ from intermediate I could only improve this favorable steric situation, so this intermediate need not be considered further. However, the possibility of loss of H^+ from intermediate II requires more detailed examination. Any loss or rearrangement involving a terminal H atom from II is not likely because such a change would leave a lone pair near an electron-deficient framework, but, of course, this loss does not reduce the steric interference. Loss of a bridge H atom from II is more likely because then a BHB bond is merely converted to a BB bond. However, this change reduces interference only if one of the two bridge H atoms between apical B and equatorial $B(CH_3)$ of the intermediate is the H atom which is removed, and, even then, half of the original steric interaction remains. Suppose, however, that in addition to loss of one of these two bridge H atoms, the other bridge H atom is rearranged to a new location. The rearranged bridge H atom could become a terminal H atom, either on the equatorial B or on the apical B, or could occupy a new bridging position around the equator of the trigonal bypyramid. The first two cases result in BH_2 [or $BH(CH_3)$] groups, and although steric interference is probably relievable the concept of a BH_2 [or $BH(CH_3)$] group is without precedent among known closed polyhedral boron fragments. In the third case, there are two unique locations for a rearranged bridge H; although models show

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[20] R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

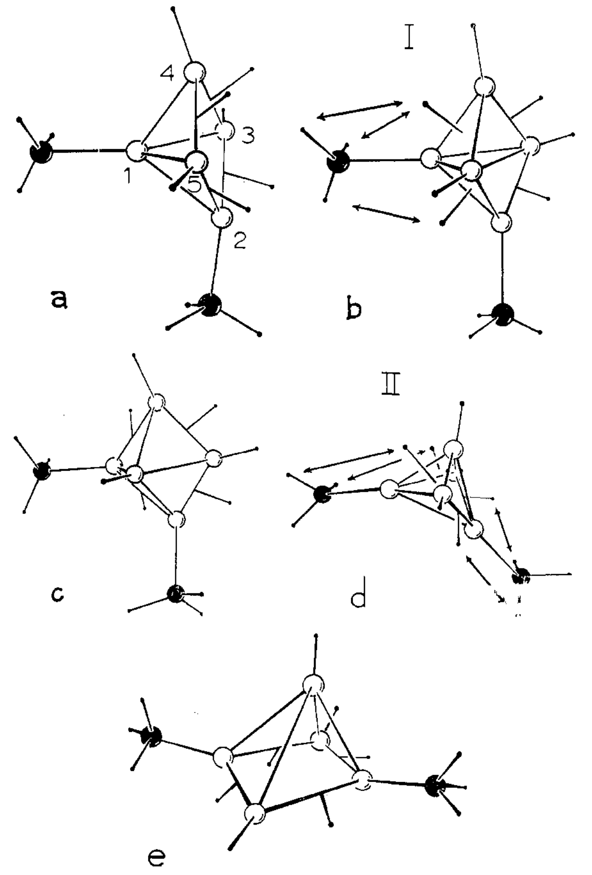

Figure 4.—The proposed rearrangement scheme. The path a → b → c results in the observed *cis*-substituted product. The path a → d → e is required for the unobserved *trans* product. Note that these intermediates retain the full complement of H atoms in the molecule, but that base catalysis may involve loss of H^+, and thermal rearrangement may involve intermolecular exchange.

little steric interference for either of these, the substantial H migration which is necessary for formation of such a model is perhaps possible, but is not in accord with the pathway which requires least motion of all atoms in the transformation.

It appears then that the steric interactions described for intermediate II can be completely relieved only if both of the bridge H atoms which bridge the equatorial B atom, also bonded to CH_3, and an apical B atom are eliminated, either by removal as H^+ or by relocation in the intermediate. If we require a minimum of atomic motion in the over-all rearrangement, elimination of these bridge H atoms seems unlikely. It seems quite plausible, then, that an intermediate somewhat like that in Figure 4b could form, leading only to the 2,3 isomer, but that the intermediate of Figure 4d cannot occur.

There remains the possibility that a base adduct of $(CH_3)_2B_5H_7$ is formed during the rearrangement, but the steric problems for an intermediate in this case are even greater than those discussed for $(CH_3)_2B_5H_7$ or $(CH_3)_2B_5H_6^-$.

The structural, and, to some extent, the mechanistic implications in the present work may also apply to the dibasal isomer obtained from the thermal rearrangement of 1,2-dimethylpentaborane. The base-catalyzed and thermally rearranged products have identical infrared spectra as well as identical ^{11}B and ^1H nmr spectra;[13] however, further studies are necessary before more conclusions can be drawn.

It may be of interest to search for such steric interactions in other boron hydrides which contain bridge H atoms and terminal H atoms substituted by alkyl or more bulky groups. A possible indication that steric interactions might occur even when no bridge H atoms are present might be deduced from the isolation[21] of C,3-dimethyl-1,2-dicarbaclovopentaborane(5), which has a trigonal-bipyramidal structure with one apex and one equatorial C atom and in which one CH_3 is on an equatorial B and the other is on one or the other of the C atoms. If the failure of this compound to rearrange to the presumably more stable 1,5 isomer (both C atoms at apices) is due to H···H interactions, then the molecule must be quite compact and probably somewhat flattened along the threefold axis of the idealized trigonal bipyramid. Indeed, a geometry of this kind is consistent with the bond orders computed[22] for $B_3C_2H_5$, but a detailed structural study is needed.

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(21) R. N. Grimes, *J. Am. Chem. Soc.*, **88**, 1070 (1966).

(22) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).