**Table IV.** Fractional Coordinates for $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCF_3)]_2\cdot 2CH_2Cl_2$[a]

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo(1) | 9685.4 (5) | 1258.5 (3) | 4516.8 (3) |
| Mo(2) | 9911.0 (5) | 1210.4 (3) | 5635.6 (3) |
| S(3) | 9472 (1) | 302 (1) | 5070 (1) |
| S(4) | 9880 (1) | 2127 (1) | 5092 (1) |
| O(5) | 8251 (4) | 1340 (3) | 4744 (2) |
| C(6) | 7996 (6) | 1335 (4) | 5211 (4) |
| O(7) | 8428 (4) | 1255 (3) | 5622 (2) |
| C(8) | 7007 (6) | 1392 (5) | 5291 (4) |
| F(9) | 6659 (8) | 834 (6) | 5318 (9) |
| F(10) | 6780 (8) | 1740 (8) | 5682 (6) |
| F(11) | 6617 (9) | 1685 (9) | 4872 (5) |
| S(12) | 9363 (2) | 2141 (1) | 3873 (1) |
| P(13) | 8840 (2) | 1480 (1) | 3396 (1) |
| S(14) | 8949 (1) | 641 (1) | 3773 (1) |
| O(15) | 9246 (5) | 1473 (3) | 2834 (3) |
| C(16) | 10168 (8) | 1303 (6) | 2775 (5) |
| C(17) | 10545 (8) | 1667 (6) | 2334 (5) |
| O(18) | 7880 (4) | 1656 (3) | 3229 (3) |
| C(19) | 7223 (7) | 1764 (6) | 3642 (5) |
| C(20) | 6541 (8) | 2185 (7) | 3426 (5) |
| S(21) | 9796 (2) | 2060 (1) | 6327 (1) |
| P(22) | 9495 (2) | 1380 (1) | 6854 (1) |
| S(23) | 9554 (1) | 555 (1) | 6457 (1) |
| O(24) | 10086 (5) | 1403 (3) | 7354 (2) |
| C(25) | 11031 (7) | 1325 (6) | 7310 (4) |
| C(26) | 11446 (9) | 1568 (7) | 7796 (5) |
| O(27) | 8620 ( 4) | 1498 (3) | 7153 (3) |
| C(28) | 7771 (8) | 1475 (7) | 6887 (6) |
| C(29) | 7355 (9) | 2100 (7) | 6917 (6) |
| N(30) | 10760 (4) | 1124 (3) | 4365 (3) |
| C(31) | 11666 (5) | 1117 (4) | 4318 (3) |
| C(32) | 12105 (6) | 598 (5) | 4093 (4) |
| C(33) | 13006 (6) | 609 (5) | 4073 (4) |
| C(34) | 13477 (6) | 1118 (5) | 4286 (4) |
| C(35) | 13036 (6) | 1639 (5) | 4510 (4) |
| C(36) | 12139 (6) | 1640 (4) | 4521 (4) |
| C(37) | 14463 (6) | 1111 (6) | 4274 (5) |
| N(38) | 11014 (5) | 1073 (3) | 5661 (3) |
| C(39) | 11927 (5) | 1035 (4) | 5706 (3) |
| C(40) | 12401 (6) | 509 (4) | 5554 (3) |
| C(41) | 13298 (6) | 530 (4) | 5588 (4) |
| C(42) | 13742 (6) | 1064 (5) | 5774 (4) |
| C(43) | 13237 (6) | 1587 (5) | 5929 (4) |
| C(44) | 12342 (6) | 1588 (4) | 5898 (4) |
| C(45) | 14724 (6) | 1082 (5) | 5794 (5) |
| Cl(46) | 5774 (4) | 5169 (2) | 1839 (2) |
| C(47) | 6887 (11) | 5029 (11) | 1947 (7) |
| Cl(48) | 7126 (3) | 4768 (2) | 2551 (2) |
| F(9) | 6734 (9) | 1121 (12) | 5745 (6) |
| F(10) | 6555 (9) | 1132 (15) | 4935 (8) |
| F(11) | 6821 (11) | 1978 (7) | 5342 (17) |

[a] Fractional coordinates are ×$10^4$.

recorded with a Varian XL 100 spectrometer at 40.5 MHz using $^1H$ decoupling and an external standard of 85% $H_3PO_4$. The infrared spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer using KBr pellets of the samples.

**$[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCF_3)]_2(\mu_4\text{-}S_2)$.** A sample of 1.0 g of the sulfhydryl-bridged compound was dissolved in $CH_2Cl_2$. To prevent decomposition, 0.10 mL of $CF_3CO_2H$ was added. Next, 0.5 mL of a freshly prepared 1.04 M $Br_2$ in $CH_2Cl_2$ solution was added. The solution color changed to a lighter orange. A large excess of *N*,*N*-dimethylaniline was added, causing the formation of a red color. The volume of the solution was reduced, and then a layer of ether was added carefully. Red crystals were produced in excess of a 50% yield and dried under a vacuum. Recrystallization was accomplished by using an ether/$CH_2Cl_2$ layering procedure. Anal. Calcd for $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCF_3)]_2(\mu_4\text{-}S_2)$: C, 30.4; H, 3.6; N, 3.0. Found: C, 30.6; H, 3.9; N, 2.8. Selected IR bands ($cm^{-1}$): 1639 (s), 1467 (m), 1388 (w), 1202 (s), 1153 (s), 1047 (m), 1003 (s), 959 (s), 854 (m), 820 (s), 790 (s). $^1H$ NMR ($CDCl_3$): $\delta$ 6.60 (4 H, q, aryl H), 4.0–4.4 (4 H, m, $OCH_2$), 2.08 (3 H, s, aryl $CH_3$), 1.31 and 1.23 (6 H, 2 t, $OCCH_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 114.3 (s).

**$[Mo_2(NC_6H_4CH_3)_2(S_2CN(i\text{-}C_4H_9)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCF_3)]_2(\mu_4\text{-}S)$.** After a 10-fold excess of $CF_3CO_2H$ was added to 0.60 mL of 0.19 M NaOH, the solution was evaporated to dryness under a vacuum. A sample of 0.10 g of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$ was added to the residue along with 15 mL of tetrahydrofuran. While the mixture was stirred, 0.14 mL of 0.40 M $Br_2$ was added. The color changed immediately to red-orange. After the mixture was stirred for 2 h, the solvent was evaporated under a vacuum, 20 mL of $CH_2Cl_2$ was added, and the mixture was filtered. Hexanes (15 mL) were added carefully to produce red-orange crystals in approximately 50% yield. Anal. Calcd for $[Mo_2(NC_6H_4CH_3)_2(S_2CN(i\text{-}C_4H_9)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CCF_3)]_2(\mu_4\text{-}S_2)$: C, 41.3; H, 5.1; N, 5.7. found: C, 41.2; H, 5.2; N, 5.4. Selected IR bands ($cm^{-1}$): 1642 (s), 1495 (s), 1254 (s), 1205 (s), 1154 (s), 819 (m), 732 (m), 443 (w), 430 (w). $^1H$ NMR ($CDCl_3$): $\delta$ 6.59 (4 H, q, aryl H), 3.74 (4 H, m, $CH_2$), 2.2–2.4 (2 H, m, CCH), 2.01 (3 H, s, aryl $CH_3$), 0.94 (12 H, m, $CCH_3$).

**X-ray Crystallography.** Cell dimensions, some of the details for the collection of the data, and final residuals are given in Table III. The methods used for the solution and refinement of the structure are available as supplementary material. Positional parameters for all non-hydrogen atoms can be found in Table IV.

**Supplementary Material Available:** Details of the solution and refinement of the structure, Tables SI and SII (fractional coordinates of the hydrogen atoms and anisotropic thermal parameters of all heavy atoms), and Tables SIII and SIV (all bond distances and angles) (7 pages); Table SV ($F_o$ and $F_c$) (11 pages). Ordering information is given on any current masthead page.

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# Stereochemistry of a 2,5-Disubstituted 1,4-Diazonia-2,5-diboratacyclohexane

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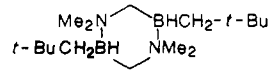
A small amount of co-subliming impurity was reported[1] to be formed in the synthesis of 1,1-dimethyl-1-azonia-3-boratacyclobutane from reaction of *tert*-butyllithium in pentane/hexane with $Me_3NCH_2BH_2NMe_3^+Cl^-$. This material was at that time recognized as a boron hydride derivative but was unidentified. Characterization of this substance, now, as 2,5-dineopentyl-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**) allows stereochemical features of the parent six-membered ring to be established.

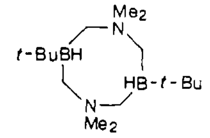
## Synthesis, Separation, and Characterization

With several scaled-up syntheses (for a total 2-g yield) of 1,1-dimethyl-1-azonia-3-boratacyclobutane, sufficient material was available for separation and identification of the impurity. Fractional recrystallization from methylene chloride or fractional vaporization gave two isomeric fractions with related mass spectral fragmentation and the same high mass peaks. The less soluble, lower vapor pressure fraction had a higher melting point of 156–158 °C; the more soluble, higher vapor pressure fraction had a much lower melting point of 59–60 °C. High-resolution mass spectra (Table I) show $P - 1$ peaks at $m/e$ 281 and 280 expected for a $C_{16}H_{40}N_2B_2$ parent composition. A nearby intense 211 peak, however, might mean that the higher masses are impurities. Under chemical ionization (with $NH_3$) conditions (Table I) the 100% peak is $m/e$ 281, and associated high fragments accord with the $C_{16}H_{40}N_2B_2$ parent of electron-ionization spectra. Elemental analyses also support such a composition.

Infrared data and low-field proton NMR data, along with synthesis conditions, would be compatible with six- or eight-membered heterocycles with neopentyl or *tert*-butyl substitution, respectively.



1



Detailed analysis of mass data and study of temperature dependence of the proton NMR spectrum accord with a six-membered

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**Table I.** Mass Spectral Data for 2,5-Dineopentyl-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane

| composition | formula mass | electron-ionizn[a] isomer mixture | | | chemical ionizn[a] cis isomer | | | cis isomer[b] | | | | | | trans isomer[b] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | intens | | sample 1[c] | | | sample 2[c] | | | | | |
| | | *m/e* | intens | Δ, mmass | *m/e* | obsd | calcd[d] | *m/e* | intens | Δ, mmass | *m/e* | intens | Δ, mmass | *m/e* | intens | Δ, mmass |
| $^{13}CC_{15}H_{39}N_2{}^{11}B_2$ | 282.3333 | 282.3363 | 0.6 | 3.3 | 282 | 16.9 | 18 | 282.3362 | 2.9 | | | | | | | |
| $C_{16}H_{39}N_2{}^{11}B_2$ | 281.3299 | 281.3317 | 4.5 | 1.7 | 281 | 100 | 100 | 281.3287 | 2.7 | −1.2 | 281.3309 | 4.0 | 1.0 | 281.3288 | 1.4 | −1.1 |
| $C_{16}H_{39}N_2{}^{11}B^{10}B$ | 280.3336 | 280.3408 | 2.0 | 7.2 | 280 | 59.4 | 59 | 280.3296 | 1.5 | −4.0 | 280.3344 | 1.6 | 0.8 | 280.3339 | 0.7 | 0.3 |
| $C_{16}H_{39}N_2{}^{10}B_2$ | | | | | 279 | 9.3 | 11 | | | | | | | | | |
| $C_{13}H_{33}N^{11}B_2$ | 225.2799 | 225.2726 | 10.0 | −7.3 | 225 | 1.0 | | 225.2768 | 5.3 | −3.1 | 225.2754 | 5.1 | −4.5 | 225.2751 | 2.3 | −7.8 |
| $C_{13}H_{32}N^{11}B_2$ | 224.2721 | 224.2726 | 35.0 | 0.5 | 224 | 4.4 | | 224.2766 | 37.8 | 4.5 | 224.2730 | 37.2 | 0.9 | 224.2732 | 14.8 | 1.2 |
| $C_{13}H_{32}N^{11}B^{10}B$ | 223.2757 | 223.2778 | 15.5 | 2.1 | 223 | 2.2 | | 223.2768 | 18.8 | 1.1 | 223.2760 | 18.0 | 0.3 | 223.2748 | 7.1 | −0.9 |
| $^{13}CC_{10}H_{29}N_2{}^{11}B_2$ | 212.2550 | 212.2550 | 11.7 | 0 | 212 | 2.0 | | 212.2578 | 12.8 | 2.8 | 212.2551 | 11.8 | 0.1 | 212.2553 | 4.6 | 0.3 |
| $C_{11}H_{29}N_2{}^{11}B_2$ | 211.2517 | 211.2518 | 100 | 0.1 | 211 | 16.6 | | 211.2576 | 100 | 5.8 | 211.2521 | 100 | 0.4 | 211.2522 | 39.5 | 0.5 |
| $C_{11}H_{29}N_2{}^{11}B^{10}B$ | 210.2553 | 210.2557 | 47.0 | 0.4 | 210 | 8.2 | | 210.2616 | 51.1 | 6.3 | 210.2553 | 48.3 | 0 | 210.2554 | 18.6 | 0.1 |
| $C_4H_{11}N^{11}B$ | 84.0984 | 89.0972 | 31.2 | −1.2 | | | | 84.0995 | 18.0 | 1.1 | 84.0990 | 46.9 | 0.6 | 84.0999 | 62.4 | 1.5 |
| $C_4H_{11}N^{10}B$ | 83.1021 | 83.1014 | 8.4 | −0.7 | | | | 83.0997 | 5.0 | −2.4 | 83.1026 | 11.4 | 0.5 | 83.1030 | 15.3 | 0.9 |
| $C_3H_9N^{11}B$ | 70.0828 | 70.0822 | 28.8 | −0.6 | | | | 70.0832 | 13.1 | 0.6 | 70.0831 | 53.1 | 0.3 | 70.0827 | 100 | 0.1 |
| $C_3H_9N^{10}B$ | 69.0864 | 69.0852 | 6 | −1.2 | | | | 69.0868 | 2.8 | 0.4 | 69.0865 | 11.7 | 0 | 69.0864 | 21.3 | 0 |

[a] Data from Battelle/Columbus. [b] Data from Midwest Center for Mass Spectrometry. [c] Two different samples from two different separations, run 2 years apart. [d] Intensity calculed from $0.90(P-1) + 0.10(P-2)$.

structure, but further confirmation was sought by oxidative hydrolysis of the alkyl substituents to the corresponding alcohol. A 50% recovery of neopentyl alcohol and no *tert*-butyl alcohol provided crucial support for the assignment as the cis/trans diastereomeric 2,5-dineopentyl-substituted six-membered heterocycle **1**.

Origin of the diastereomers in the cyclobutane synthesis is not completely established. Likely, cleavage of the cyclobutane by *tert*-butyllithium at the B–N link occurs to produce a functionalized borohydride salt, $Li^+\cdots{:}NMe_2CH_2BH_2CH_2\text{-}t\text{-}Bu^-$, followed by LiH loss and dimerization. This scheme finds experimental support in that *tert*-butyllithium does indeed react with the azoniaboratacyclobutane, even though no **1** is formed. The air-sensitive reaction product, probably the suggested aminoborohydride salt, however does give a 25% yield of the cis isomer of **1** by subsequent reaction with $Me_3NH^+I^-$. Isolation of but one isomer instead of both, as in the original synthesis, is possibly the result of a discrete new step and reagent. Clarification of both synthesis reactions is a matter of continuing research.

Both isomers appear to be stable indefinitely in air at room temperature (based on observations of samples stored for 8 years.) As reasonably might be expected from its lesser axial–axial alkyl contacts, the trans isomer is the preferred thermodynamic form. Brief thermolysis at 160 °C does not bring about change, but prolonged heating under vacuum at 160–170 °C for 6–7 h leads to complete cis to trans conversion. Isomerism is thus established unequivocally, and the chemical arguments for structure assignment are rid of any ambiguity stemming from questions of impurities and/or incomplete reaction.

## Experimental Section

Where required, standard vacuum-line procedures were employed.[2] A line equipped with Delmar-Urry O-ring joints and Teflon needle stopcocks, with pumping capability to $10^{-5}$ mmHg of noncondensable gas, provided for reactions, transfer, and sublimations. Melting points were measured in a Thomas-Hoover capillary melting point apparatus in open capillaries. Analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. Low-resolution NMR spectra were obtained with a Hitachi/Perkin Elmer R24B instrument. High-resolution NMR spectra and mass spectral data were obtained from regional instrumentation centers (see Acknowledgement) or Battelle/Columbus.

Synthesis of about 2 g of 1,1-dimethyl-1-azonia-3-boratacyclobutane was carried out in four batches following reported procedures.[1] Crude separation of the more volatile cyclobutane derivative from the cosubliming impurity was done by slow sublimation under high vacuum to 50 °C. From the lesser volatile residue, about 0.8 g of material subliming at 70 °C was collected as a mixture of byproduct and cyclobutane derivative. Purification of this byproduct fraction was done in batches, and a typical result is described. A 400-mg sample in 10 mL of methylene chloride was twice extracted with acidified water to remove by hydrolysis the cyclobutane derivative. The organic phase was separated and dried over $Na_2SO_4$. After solvent removal, fractional sublimation of the residue (280 mg) for 7 h at room temperature gave 110 mg of the cis isomer (softening 57–58 °C, mp 59–61 °C). Another 11 h of sublimation gave 40 mg of mixed isomers and 86 mg residue. Recrystallization of the residue from methylene chloride gave the trans isomer (150 °C sinter, mp 156–158 °C without decomposition).

Anal. Calcd for $C_{16}H_{40}N_2B_2$: C, 68.12; H, 14.29; N, 9.93. Found for the trans isomer: C, 68.23; H, 14.42; N, 9.69. Infrared data. (Mineral oil mulls, using Beckman 4240 spectrophotometer. Abbreviations: s = strong, m = moderate, w = weak, sh = shoulder, bd = broad. Peaks masked by mineral oil absorptions are not reported.)

Cis isomer: 2340 w bd (vw sh 2280, 2240, 2200, 2155), 1400 w, 1358 s, 1300 s (vw sh 1325, 1315, 1285, 1280), 1238 m, 1172 s (sh 1195 vw, 1185 w, 1160 vw), 1140 vw (doublet), 1128 vw bd, 1080 s (w sh 1095), 1024 vw, 1018 w, 972 m (vw sh 940, 945), 925 vw, 905 vw, 885 m, 830 s, 745 w, 728 w.

Trans isomer: 2350 w bd (vw sh 2410, 2330, 2310, 2275; w sh 2260, 2230), 2160 w, 1420 w, 1400 m, 1355 s, 1312 w, 1298 m, 1285 s, 1238 m (vw sh 1230), 1190 s (w sh 1175), 1135 w, 1118 m, 1090 s, 1022 w, 1005 m, 955 s (w sh 970; vw sh 935), 925 vw, 905 vw, 835 s (w sh 860), 765 w, 745 w, 720 vw. Proton NMR data are collected in Table II.

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(1) Warnock, G. F.; Miller, N. E. *Inorg. Chem.* **1979**, *18*, 3620.

(2) Shriver, D. F., *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

**Table II.** Proton NMR Data for **1**

| | | | chem shift, ppm (rel intens) | | | |
|---|---|---|---|---|---|---|
| $T$, °C | MHz/solvent | isomer | $NMe_2$ | $CH_2$(ring) | *t*-Bu | $CH_2$ |
| RT[d] | $60/CH_2Cl_2$ | cis[a] | 2.55, 2.35–2.40 (12.6) | 2.0, 1.7 bd m (3.6) | 0.75 (18) | |
| RT | $60/CH_2Cl_2$ | trans | 2.40 sh (12) | 1.8, 1.6 (6) | 0.75 (18) | |
| RT | $360/CS_2$[b] | cis[c] | 2.535, 2.330 (12) | 2.06 (1.7); 1.88, 1.84 (1.7) | 0.79 (17.4) | 0.14 (3.1) |
| −75 | $360/CS_2$[b] | cis | 2.6518, 2.4250, 2.4044, 2.2551 | 2.58–2.54 d, 1.93 m, 1.70–1.66 d, 1.54–1.50 d | 0.74 | 0.3 AB m, −0.06, −0.16 |
| RT | $360/CS_2$[b] | trans | 2.4060, 2.3684 (12) | 2.06 m (1.9)<br>1.73–1.68 d (1.8) | 0.78 (17.9) | 0.04, −0.18 (2.5) |
| −60 | $360/CS_2$[b] | trans | 2.4062, 2.3606 | 2.0 m 1.69–1.66 d | 0.75 | −0.06, −0.22 |

[a] With 16% trans impurity peaks. [b] Data from CSU Regional NMR Center. [c] Trans impurity peaks subtracted. [d] Key: RT, room temperature; bd, broad; s, singlet; d, doublet; m, multiplet.

Oxidative hydrolytic degradation was carried out to identify alkyl attached to boron after the ring was first labilized by iodination. A 33-mg sample (0.12 mmol) of isomer mixture was iodinated in 0.5 mL of $CHCl_3$ by addition of a solution of 35.1 mg (0.28 mmol) of iodine in 2 mL of $CHCl_3$ slowly until an orange color persisted (after almost all of the solution was added.) Solvent was removed under vacuum, and the residue was hydrolyzed and worked up in a modification of literature procedures.[3] It was dissolved in 0.6 mL of diglyme (bis(2-methoxyethyl)ether), and the solution was treated successively with 0.06 mL (0.18 mmol) of 3 M NaOH and 0.08 mL (0.7 mmol) of 30% hydrogen peroxide. The resulting orange-red mixture had a tacky oil present and was extracted with ether. The ether was washed until colorless with sodium sulfite solution and then analyzed by GLC using a 4 m × 1/4 in. glass (Deactiglas) column packed with Poropak-Q (80–140 mesh) at 175–180 °C in a Varian 3700 chromatograph using flame-ionization detection. Neopentyl alcohol was identified by comparison with standard mixtures of ether/alcohol and ether/alcohol/diglyme. No trace of *tert*-butyl alcohol was detected. Quantitation by comparison with prepared samples showed 9 mg (50%) neopentyl alcohol.

**Reaction of 1,1-Dimethyl-1-azonia-3-boratacyclobutane and *tert*-Butyllithium.** A slurry of 94 mg (1.11 mmol) of the azoniaboratacyclobutane in 3 mL of hexane did not react with 1.1 mmol of *tert*-butyllithium (0.65 mL of a 1.7 M solution in pentane) until 0.9 mmol of trimethylamine was added (under vacuum). Solution was effected in less than 1 h of stirring at room temperature under nitrogen. A white, air-sensitive solid remained when the volatiles were removed under vacuum, but no **1** was sublimed on heating to 60 °C. Neither was **1** liberated on dissolution of a small portion in water. When a hexane solution of the reactive intermediate was stirred with excess $Me_3NH^+I^-$, gas was evolved over a 10-h period. Filtration, followed by removal of solvent gave a solid residue from which 38 mg of **1** was sublimed at 70 °C. The product was identified as the cis isomer by its infrared spectrum: 24% yield; mp 61–64 °C.

**Cis to Trans Rearrangement.** A melting-point sample of the cis isomer, mp 61–64 °C was heated at 160–170 °C for 6 h in an evacuated capillary tube. On cooling, it melted at 156–158 °C and had an infrared spectrum identical with that of the trans isomer. Heating of a sample of the cis isomer briefly to 160 °C and immediately cooling did not noticeably change the melting point.

**Proton NMR Temperature Dependence.** Temperature dependence data at 360 MHz were obtained from the Regional NMR Center at Colorado State University for $CS_2$ solutions. $\Delta G^*$ was determined as 12.1 kcal/mol from coalescence temperatures (the downfield pair at −20 °C and the upfield pair at −25 °C) and the no-exchange separations of 82 and 54 Hz, respectively[4] {with the relationship $\Delta G^* = RT[23.765 + \ln T - \ln [2^{1/2}\pi(\Delta\nu)/2]]$}.

## Stereochemistry

The "parent" ring system for **1**, 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane,[5] in common with other valence-saturated six-membered rings, has a chair conformation, at least in the solid state,[6] and probably exists in solution as rapidly inverting conformers. Also like disubstituted cyclohexanes, the title compound was found to have cis/trans diastereomers (Figure 1). Because of the restrictions imposed from the heteroatom arrangement, the cis diastereomer is $C_1$ and presumedly chiral whereas the trans diastereomer is $C_i$ (assuming free rotation of neopentyls) and presumedly achiral. As is evident in Figure 1, the cis conformers are superimposable, so the ae $\rightleftharpoons$ ea equilibrium has no entropy of mixing term.

Assignment of the isolated fractions to cis/trans forms was based on melting points and the *N*-methyl proton resonance at low temperature. The nearly 100 °C difference in melting points would not be associated with the diastereomerism as such, but with the concomitant chirality and its effects on solid-state properties. Melting points are often lowered in a racemic modification,[7] so the lowest melting point isomer is assigned as the chiral cis conformers (that indicated in Figure 1 and the mirror image enantiomer.) Newman projections (Figure 2) of the cis/trans isomers shows fewer kinds of *N*-methyl environments for the trans-ee conformer, so the high melting isomer having the simplest *N*-methyl resonances at low temperature was assigned as the trans isomer, and thus the isomer assignments based on melting point and proton NMR are consonant.

Assignment of the *N*-methyl resonances in the −75 °C spectrum of the cis isomer to particular groups is difficult. A *tentative* but consistent assignment is ventured, based on the anisotropic shielding of C–C bonds.[8] This is conveyed in the numbering in Figure 3a. Examination of a model showed that the *tert*-butyl of the axial neopentyl group is so situated that the nearby axial *N*-methyl hydrogen (no. 4) is in its shielding zone and the nearby axial hydrogen is in the deshielding zone (and is perhaps the most deshielded methylene proton at 2.54/2.58 ppm). The methyl is assigned as no. 4, and the cis equatorial methyl, also in the shielded zone but not as close, is assigned as no. 3. If the most downfield resonance is assumed to be the other axial methyl because it is most like that in the unsubstituted ring in chemical shift (2.65 as compared to 2.56 ppm), the assignment is complete. Ring inversion at room temperature equilibrates cis methyl pairs (Figure 1). A similar argument would assign the trans isomer *N*-methyl resonances as equatorial upfield and axial downfield.

Temperature-dependent proton spectra at high field affirm the isomeric identification and demonstrate that the six-membered ring is in dynamic conformational equilibrium. The trans *N*-methyl doublet was unchanged to −60 °C (Figure 4), at which temperature the cis isomer has its ring inversion frozen; ee conformation of the neopentyl groups is assumed. The four different *N*-methyl environments possible for the cis isomer were observed at low temperature (−60 to −75 °C), as contrasted to two at room temperature (Figure 3). The 16% trans impurity present in the cis sample examined, along with the broad $CH_2$ peak near the downfield N-methyl, perturbed the line shape change from doublet to quartet (Figure 5).

$\Delta G^*$ for the ae $\rightleftharpoons$ ea inversion of the cis diastereomer was calculated from coalescence temperatures and peak separations under no exchange.[3] Coalescence of the downfield pair of resonances was estimated at −20 °C while that of the upfield pair was estimated at −25 °C, and no-exchange peak separations were 82 and 54 Hz, respectively. The discernment of which peaks were coalescing was difficult since the inner pair are so close. The alternate assignments of pairings 1/3 and 2/4 versus 1/2 and 3/4 gave errors of 7.4 and 1.4 Hz total, respectively, in the centroids of the chemical shift of the singlets at room temperature. The

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(3) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1959**, *81*, 6423.

(4) Bovey, F. *Nuclear Magnetic Resonance Spectroscopy*; Academic: New York, 1969; p 190.

(5) Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1196.

(6) Hseu, T. H.; Larsen, L. A. *Inorg. Chem.* **1976**, *14*, 336.

(7) Eilel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 43–49.

(8) Reference 4, pp 77–78.

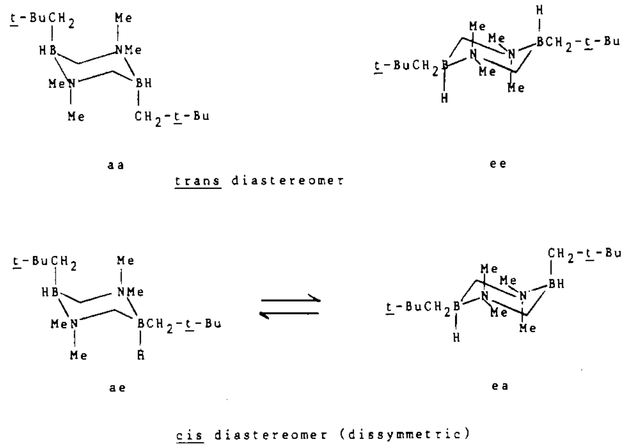

**Figure 1.** Diastereomers of **1**.

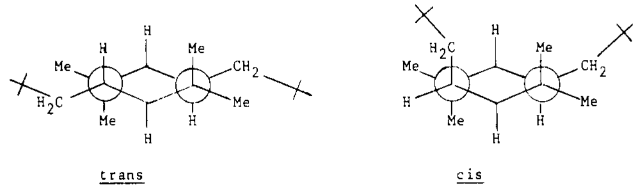

**Figure 2.** Newman projections of diastereomers.

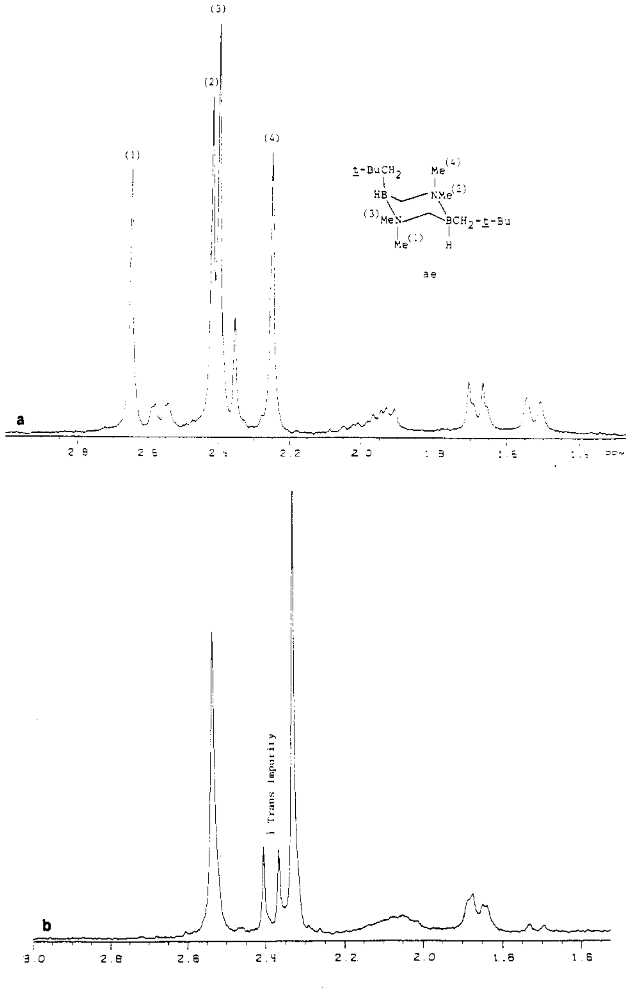

**Figure 3.** 360-MHz $^1H$ NMR spectra: (a) *cis*-$(Me_3CCH_2BHCH_2NMe_2)_2$ at -65 °C/$CS_2$; (b) *cis*-$(Me_3CCH_2BHCH_2NMe_2)_2$ at 25 °C/$CS_2$.

latter pairing seems more reasonable in view of the better fit and the agreement with the tentative peak assignments. The calculated $\Delta G^* = 12.1$ kcal/mol compares with that of the similar 1,1,4,4-tetramethylcyclohexane[9] [$\Delta H^* = 13.3$ kcal/mol, $\Delta S^* = 9.1$ eu/mol, $\Delta G^*(-62\ °C) = 11.4$ kcal/mol].

Boron-bonded methylene proton NMR data for the cis isomer similarly show four separate multiplet signals at -75 °C: two doublets centered at 2.56 ppm and 1.52 ppm coalescing to the very broad 2.06 ppm resonance at room temperature and one

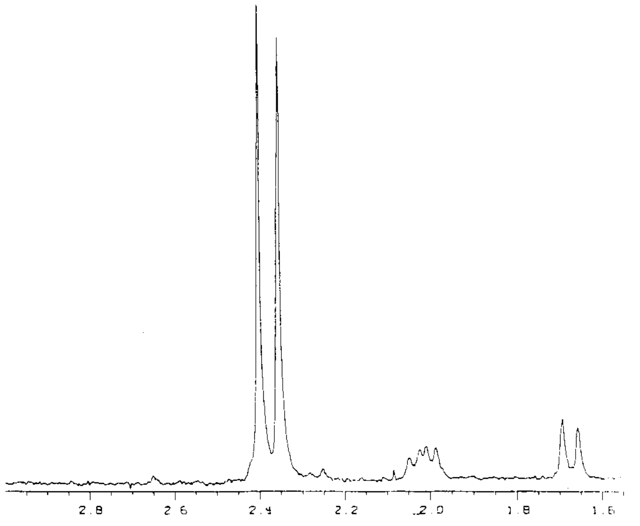

**Figure 4.** 360-MHz $^1H$ NMR spectrum of *trans*-$(Me_3CCH_2BHCH_2NMe_2)_2$ at -60 °C/$CS_2$.

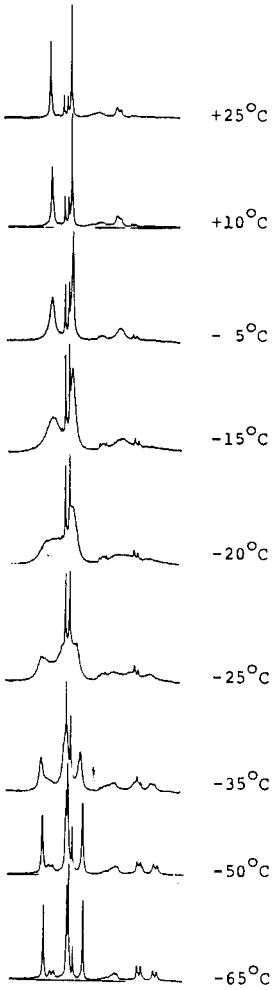

**Figure 5.** 360-MHz $^1H$ NMR spectra showing the temperature dependence of *cis*-$(Me_3CCH_2BHCH_2NMe_2)_2$.

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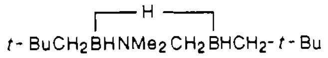
(9) Murray, R. W.; Kaplan, M. L. *Tetrahedron* **1967**, *23*, 1575.

doublet centered at 1.68 ppm and a 1.93 ppm complex multiplet coalescing to the doublet of doublets signal at 1.84/1.88 ppm. The resonances are inherently broadened by the boron quadrupole and spin splittings. Other small, broad multiplets in the region near TMS are presumedly associated with the methylene protons of the neopentyls. Two resonances at −0.06 and −0.72 ppm are present in the trans isomer, and three multiplets, one looking like AB splitting, are present in the cis isomer at −75 °C: 0.3 (0.40, 0.36, 0.28, 0.24 ppm AB pattern), −0.06, and −0.16 ppm, coalescing to a very broad resonance at 0.14 ppm at room temperature. Taken together, these observations suggest an AB methylene pattern for the axial neopentyl methylene of the cis isomer and a less defined multiplet for the equatorial methylene.

The neopentyl methyl resonance shift is slightly temperature dependent, even in the nonexchanging trans isomer, moving about 0.03 ppm upfield on cooling.

The stereochemistry of the isomers allows a better understanding of the high resolution mass spectral data of the separated isomers (Table I). Significantly, the 100% peaks are different, being the 211 peak for the cis isomer and the 70 peak for the trans isomer. The one neopentyl group on the cis isomer that is axial (at the time of fragmentation) would have strong contact with axial groups and should be more easily lost than the equatorial groups on the trans isomer, whence the high 211 (parent less neopentyl) of the cis isomer. A stable structure, probably cyclic, may be inferred for the 223/224 fragment because of its significant intensity. One, with hydrogen bridging over the gap from the lost $CH_2NMe_2$ moiety, satisfies the valencies believably:



$t\text{-}BuCH_2BHNMe_2CH_2BHCH_2\text{-}t\text{-}Bu$

## Conclusion

Characterization of two diastereomers of the dineopentyl-substituted BCN-sequenced heterocycle and study of the temperature dependent proton resonance spectrum of the cis isomer establish firmly the dynamic nature of the ring system, a feature that previously was a matter of conjecture. Additionally, the substituted ring is found to be robust toward atmospheric conditions and toward ring opening at room temperature. The cis isomer rearranges to the thermodynamically favored trans isomer, but only after prolonged heating at 160–170 °C. Possibilities are therefore promising that other 2,5-disubstituted diastereomers may be made and separated, and these possibilities would allow investigation of whether substitution reactions at boron proceed with or without retention. Finally, a synthesis of 2,5-dialkyl-substituted six-membered BCN-sequenced heterocycles is uncovered.

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**Registry No.** **1**-*cis*, 114492-12-5; **1**-*trans*, 114530-91-5; $H_2BCH_2N(Me)_2CH_2$, 71371-27-2.

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# Additions and Corrections

1986, Volume 25

**Ahmad Moini, Roberta Peascoe, Philip R. Rudolf, and Abraham Clearfield***: Hydrothermal Synthesis of Copper Molybdates.

Page 3783. In Table II the *y* positional parameter for Mo2 should read 0.70979 (6) instead of 0.79079 (6).—Abraham Clearfield