

The  $^{13}\text{C}$  spectra assigned to the 2c and 1b positions overlap, but can be separated by a formalism based on differences in  $^{13}\text{C}$ - $^{11}\text{B}$  heteronuclear couplings. The relative areas of the resolved spectra indicate that  $33 \pm 5\%$  of the carbon atoms have  $^{13}\text{C}$ - $^{11}\text{B}$  couplings that can be interpreted only as 1b lattice sites. The spectrum of the 1b carbon indicates axially symmetric shielding, in agreement with the threefold rotational symmetry at the site. Also, the magnitude and orientation of the chemical shielding anisotropy are comparable to that of other unsaturated carbon species with axially symmetric shielding, such as acetylene and inorganic acetylides. The  $^{13}\text{C}$  NMR spectrum interpreted as carbon in 2c lattice positions is broadened by much stronger  $^{13}\text{C}$ - $^{11}\text{B}$  dipolar couplings and has about one-third the chemical shielding anisotropy as the 1b carbons. Although it is not possible to extract the precise chemical shielding components, the spectrum is consistent with the threefold symmetry of the 2c site.

The isotropic shifts of the spectra resolved and identified on the basis of the spin-echo data are  $\sim -85$  and  $\sim -2$  ppm, for the 1b and 2c carbon species, respectively. Thus, although the conventional  $^{13}\text{C}$  NMR spectra are completely overlapped, the spectra acquired while the sample was spinning at the "magic angle" will yield two resolved peaks at the isotropic shifts. The relative areas of the peaks at  $-85$  and  $-2$  ppm, adjusted to compensate for the differences in chemical anisotropy at each site,<sup>25</sup> would indicate the distribution of carbon among the 1b and 2c sites.

**Acknowledgment.** The analysis of the spin-echo data benefited from discussions with Dean Douglass.

**Registry No.** B<sub>12</sub>C<sub>3</sub>, 12069-32-8.

(25) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

## Use of Nuclear Magnetic Resonance To Investigate Bonding Interactions between Quadrupolar Nuclei. Boron-Boron Spin-Spin Coupling Constants in Linked Polyhedral Borane and Carborane Cages<sup>1,2</sup>

John A. Anderson,<sup>3a</sup> Robert J. Astheimer,<sup>3b</sup> Jerome D. Odom,<sup>\*3a</sup> and Larry G. Sneddon<sup>\*3b,4</sup>

Contributions from the Departments of Chemistry, University of South Carolina, Columbia, South Carolina 29208, and University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received September 28, 1983

**Abstract:** High-field boron-10 and boron-11 NMR has been used to observe boron-boron coupling in two-center, two-electron, boron-boron bonds linking coupled-cage boranes and carboranes. The values of  $J_{\text{B}^{11}\text{B}}$  were found to range from 151 to  $\sim 79$  Hz: 3:3'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>, 151 Hz; 1:1'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>, 149 Hz; 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub>, 137 Hz; 1:3'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>, 124 Hz; 1:2'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>, 112 Hz; 2:1'-[1-(CH<sub>3</sub>)B<sub>5</sub>H<sub>7</sub>][B<sub>5</sub>H<sub>8</sub>], 112 Hz; 3:5'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>,  $\geq 100$  Hz; and 2:2'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>,  $\sim 79$  Hz. To aid in the determination of the coupling, noninteractive solvents, elevated temperatures, and resolution-enhancement techniques were employed, and the utility of these techniques in analyzing the NMR line shapes of coupled quadrupolar nuclei is discussed. The boron-11 NMR spectrum of 3:5'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub> is shown to be of special interest since it was demonstrated that the unusual line shapes of the resonances arising from the linked borons are due to second-order effects resulting from strong homonuclear coupling between the two borons. It also has been shown that Kroner and Wrackmeyer's correlation between the magnitude of  $J_{\text{BB}}$  and the s character of an orbital can be used to calculate the s orbital character of the hybrid orbitals involved in the exopolyhedral boron-boron linkages. Values were found to range from 40.7% s ( $\sim \text{sp}^{1.5}$ ) for B<sub>3,3'</sub> in 3:3'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub> to 31.8% s ( $\sim \text{sp}^{2.2}$ ) for B<sub>2,2'</sub> in 2:2'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>. Intracage boron-boron spin-spin coupling in both 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> and in the coupled cage boranes and carboranes was also observed and is discussed.

The tremendous impact that nuclear magnetic resonance spectroscopy has had in all areas of chemistry is well recognized. With the advent of Fourier transform methods in NMR spectroscopy and the widespread use of "broad-band" FT spectrometers, an increasing number of nuclei are being studied. An inspection of the nuclear properties of the elements reveals that 87 of 116 magnetically active isotopes have a nuclear spin value,  $I$ , greater than  $1/2$  (i.e., are quadrupole nuclei).<sup>5,6</sup> The principal

difficulty in NMR studies of quadrupolar nuclei is that, owing to relaxation effects, line widths can be very large, preventing the extraction of useful information that is commonly obtained in studies of spin  $1/2$  nuclei. Perhaps because of the lack of experimental data and the complexities of the systems, theoretical studies of the NMR line shapes of quadrupolar nuclei spin-spin coupled to other quadrupolar nuclei have been lacking. However, there is an increasing recognition among chemists that modern sample and data manipulation techniques provide an effective means to study many of these chemically interesting quadrupolar nuclei.

Boron possesses two magnetically active nuclei, both of which are quadrupolar ( $^{10}\text{B}$ ,  $I = 3$ , 20%;  $^{11}\text{B}$ ,  $I = 3/2$ , 80%). The utility of  $^{11}\text{B}$  NMR spectroscopy in studies of boron hydrides, carboranes, and other boron-containing compounds is well documented.<sup>7,8</sup>

(1) Part 7 of "High Resolution Boron-11 Nuclear Magnetic Resonance Spectroscopy". For Part 6 see: Stampf, E. J.; Garber, A. R.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 6550-6554.

(2) Taken in part from the thesis of J. A. Anderson, submitted to the Department of Chemistry in partial fulfillment of the requirements for the Ph.D. degree.

(3) (a) University of South Carolina. (b) University of Pennsylvania.

(4) Alfred P. Sloan Foundation Fellow.

(5) Harris, R. K.; Mann, B. E., Eds. "NMR and the Periodic Table"; Academic Press: New York, 1978.

(6) Brevard, C.; Granger, P. "Handbook of High Resolution Multinuclear NMR"; John Wiley and Sons: New York, 1981.

(7) Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

(8) Noth, H.; Wrackmeyer, B. "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds"; Spinger-Verlag: Berlin, 1978.

Table I. Spin-Spin Coupling Constants in Two-Center, Two-Electron BB Bonds

compd	$J_{11B^{11}B}$ , Hz
3:3'-[2,4-C <sub>2</sub> B <sub>5</sub> H <sub>6</sub> ] <sub>2</sub>	151 <sup>a</sup>
1:1'-[B <sub>5</sub> H <sub>8</sub> ] <sub>2</sub>	149 <sup>a</sup>
2:2'-[1,5-C <sub>2</sub> B <sub>3</sub> H <sub>4</sub> ] <sub>2</sub>	137 <sup>a</sup>
2:2',3':1'-[1,5-C <sub>2</sub> B <sub>3</sub> H <sub>4</sub> ]- [1',5'-C <sub>2</sub> B <sub>3</sub> H <sub>3</sub> ]- [1'',5''-C <sub>2</sub> B <sub>3</sub> H <sub>4</sub> ]	135 <sup>b</sup> B <sub>2</sub>
2':2-[1',5'-C <sub>2</sub> B <sub>3</sub> H <sub>4</sub> ]- [1,6-C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ]	131, <sup>c</sup> 126 <sup>d</sup>
1-(Cl <sub>2</sub> B) <sub>2</sub> H <sub>6</sub>	~124 <sup>e</sup>
1:3'-[2,4-C <sub>2</sub> B <sub>5</sub> H <sub>6</sub> ] <sub>2</sub>	124 <sup>a</sup> B <sub>3</sub> ' (120 <sup>a</sup> B <sub>1</sub> )
1-(Cl <sub>2</sub> B)-2-ClB <sub>5</sub> H <sub>7</sub>	~122 <sup>e</sup>
1:5'-[2,4-C <sub>2</sub> B <sub>5</sub> H <sub>6</sub> ] <sub>2</sub>	119, <sup>c</sup> ~109 <sup>f</sup>
1:2-[B <sub>5</sub> H <sub>8</sub> ] <sub>2</sub>	115 <sup>a</sup> B <sub>1</sub> , (110 <sup>a</sup> B <sub>2</sub> ') 106 <sup>f</sup>
2:1'-[1-(CH <sub>3</sub> )B <sub>5</sub> H <sub>7</sub> ][B <sub>5</sub> H <sub>8</sub> ]	121 <sup>a</sup> B <sub>1</sub> ' (103 <sup>a</sup> B <sub>2</sub> )
1:2-[B <sub>10</sub> H <sub>13</sub> ] <sub>2</sub>	~105 <sup>g</sup>
3:5'-[2,4-C <sub>2</sub> B <sub>5</sub> H <sub>6</sub> ] <sub>2</sub>	~100 <sup>a</sup>
2:2'-[B <sub>5</sub> H <sub>8</sub> ] <sub>2</sub>	~79 <sup>a</sup>
B <sub>2</sub> [N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>	75 <sup>h</sup>

<sup>a</sup> This work. <sup>b</sup> Measured from broad resonance, ref 19. <sup>c</sup> Re-measured from original spectrum, by using the separation of the inner two members of the quartet. <sup>d</sup> Reference 19. <sup>e</sup> Reference 18. <sup>f</sup> Reference 16. <sup>g</sup> Reference 17. <sup>h</sup> Reference 15.

making boron-11 probably the most widely studied quadrupolar nucleus. The first experimental determination of boron-boron spin-spin coupling was reported<sup>9</sup> in 1971 for the apical to basal borons in pentaborane (9). Since that time the determination of coupling constants in polyboranes and carboranes has become relatively routine.<sup>10</sup> Boron-boron coupling interactions in boranes have been shown to depend upon the particular bonding situation<sup>11</sup> of the boron atoms involved and, at least in some instances, on substituent effects.<sup>12</sup> In general, the magnitude of the coupling constant between bonded boron atoms appears to be linearly related to the fractional s character of the bonding orbitals.<sup>13,14</sup> However, experimental verification of this postulate has been hampered by the paucity of coupling constants which have been determined for two-center, two-electron, boron-boron bonds. Kroner and Wrackmeyer predicted<sup>14</sup> a value of 78.7 Hz for  $J_{11B^{11}B}$  in the hypothetical molecule B<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>, and Bachmann et al. calculated<sup>15</sup> a value of 75 Hz for  $J_{11B^{11}B}$  in B<sub>2</sub>[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> on the basis of the <sup>10</sup>B NMR spectrum of the compound at high temperature. Boron-boron coupling constants have also been recently observed in two-center, two-electron bonds between boron atoms joining borane<sup>16-19</sup> and carborane<sup>16,19</sup> cages, with values ranging in magnitude from 105 to 126 Hz (Table I).

Since a number of synthetic methods have now been developed<sup>17-20</sup> for the formation of boron-boron-linked multicage bo-

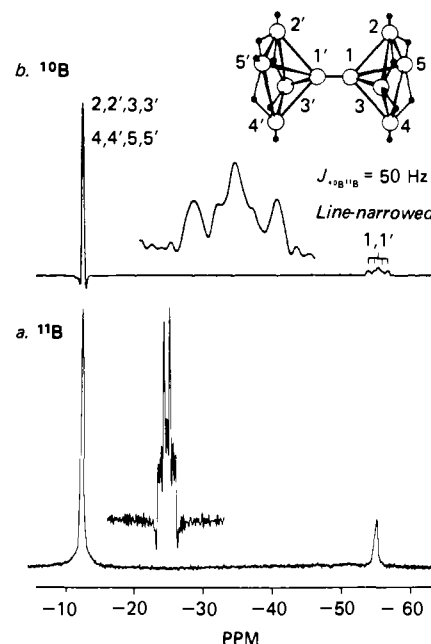


Figure 1. Proton-spin-decoupled, boron NMR spectra of 1:1'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>. (a) 25.69-MHz <sup>11</sup>B NMR spectrum at 35 °C in C<sub>6</sub>D<sub>6</sub>. An expansion is shown of the resonance (line narrowed, 67 °C) arising from the basal borons. ( $J_{11B_1,11B_2} = 17.7$  Hz,  $J_{11B_2,10B_1} = 6.3$  Hz). (b) 42.99-MHz <sup>10</sup>B NMR spectrum at 50 °C in *n*-heptane. An expansion is shown of the B<sub>1,1'</sub> resonance.

ranes and carboranes, a large selection of these compounds are now available. This offers an excellent opportunity to obtain boron-boron coupling constants in two-center, two-electron, boron-boron bonds in a variety of cage bonding configurations. We have now undertaken a detailed NMR study of a series of such compounds, and the results are reported herein.

### Experimental Section

**Instrumental Work.** The boron NMR spectra were obtained on a Bruker WH-400 NMR spectrometer operating at 128.4 (<sup>11</sup>B) or 42.99 MHz (<sup>10</sup>B), a Bruker WH-360 NMR spectrometer operating at 115.5 MHz (<sup>11</sup>B), or an IBM NR-80 NMR spectrometer operating at 25.69 MHz (<sup>11</sup>B). Standard broad-band proton noise-modulated decoupling was used throughout. Standard variable-temperature accessories were employed with an estimated accuracy of ±0.5 °C. Field-frequency lock was provided by locking to the deuterium resonance of benzene-*d*<sub>6</sub> either as the solvent in 10-mm tubes or by spinning a 5-mm sample tube containing the compound, dissolved in an appropriate solvent, placed coaxially inside a 10-mm tube containing benzene-*d*<sub>6</sub> in the annular space between the two tubes.

The compounds studied were dissolved either in benzene-*d*<sub>6</sub>, pentane, hexane, or heptane. Sample concentrations ranged from 3% to ca. 10%

(9) Odom, J. D.; Ellis, P. D.; Walsh, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 3529-3530.

(10) See, for example: ref 8, Chapter 8.

(11) Stampf, E. J.; Garber, A. R.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 6550-6554.

(12) Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1978**, *12*, 681-685.

(13) Onak, T.; Leach, J. B.; Anderson, S.; Frisch, M. J.; Marynick, D. J. *Magn. Reson.* **1976**, *23*, 237-248.

(14) Kroner, J.; Wrackmeyer, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2283-2290.

(15) Bachmann, F.; Noth, H.; Pommerening, H.; Wrackmeyer, B. *J. Magn. Reson.* **1979**, *34*, 237-248.

(16) Astheimer, R. J.; Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1108-1109.

(17) Boocock, S. K.; Cheek, Y. M.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 1430-1437.

(18) Gaines, D. F.; Heppert, J. A.; Coons, D. E.; Jorgenson, M. W. *Inorg. Chem.* **1982**, *21*, 3662-3665.

(19) Astheimer, R. J.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 1928-1934.

(20) (a) Grimes, R. N.; Wang, F. E.; Lewin, R.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1961**, *47*, 996-998. (b) Grimes, R. N.; Lipscomb, W. N. *Ibid.* **1962**, *48*, 496-499. (c) Dobson, J.; Maruca, R.; Schaeffer, R. *Inorg. Chem.* **1970**, *9*, 2161-2166. (d) Gaines, D. F.; Iorns, T. V.; Clevenger, E. N. *Ibid.* **1971**, *10*, 1096-1097. (e) Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1976**, 95-96. (f) Plotkin, J. S.; Astheimer, R. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 4155-4163. (g) Gaines, D. F.; Jorgenson, M. W.; Kulzick, M. A. *J. Chem. Soc., Chem. Commun.* **1979**, 380-381. (h) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182. (i) Dobson, J.; Gaines, D.; Schaeffer, R. *J. Am. Chem. Soc.* **1965**, *87*, 4072-4074. (j) Greenwood, N. N.; Kennedy, J. D.; Spalding, T. R.; Taylorson, D. J. *J. Chem. Soc., Dalton Trans.* **1979**, 840-846. (k) Brown, G. M.; Pinson, J. W.; Ingram, L. L., Jr. *Inorg. Chem.* **1979**, *18*, 1951-1956. (l) Boocock, S. K.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S.; Staves, J. J. *J. Chem. Soc., Dalton Trans.* **1980**, 790-796. (m) Burg, A. B.; Reilly, T. *J. Inorg. Chem.* **1972**, *11*, 1962-1964. (n) Dobbie, R. C.; Distefano, E. W.; Black, M.; Leach, J. R.; Onak, T. *J. Organomet. Chem.* **1976**, *114*, 233-238. (o) Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 2644-2650. (p) Williams, R. E.; Gerhart, F. J.; Hickey, G. I.; Ditter, J. F. *U.S.C.F.S.T.I., AD Rep.* **1969**, No. 693314. (q) Janovsek, Z.; Hermanek, S.; Plessek, J.; Stibr, B. *Collect. Czech., Chem. Commun.* **1974**, *39*, 2363-2373. (r) Zbynek, J.; Plessek, J.; Stibr, B.; Hermanek, S. *Ibid.* **1983**, *48*, 228-231. (s) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886-2891. (t) Corcoran, E. W., Jr.; Sneddon, L. G., to be submitted for publication.

Table II.  $^{11}\text{B}$  NMR Parameters for the Dimers of  $\text{B}_5\text{H}_6$ 

compd	$J_{^{11}\text{B}^{11}\text{B}}^a$		$\delta_{\text{base}}^b$	$\delta_{\text{apex}}^b$
	base-to-apex <sup>c</sup>	exopolyhedral		
1:1'-[ $\text{B}_5\text{H}_8$ ] <sub>2</sub>	17.7 ± 0.6 <sup>e</sup>	149.3 ± 3.7 <sup>d,f</sup> ( $\text{B}_1\text{-B}_1'$ )	-13.2 <sup>e</sup>	-55.4 <sup>e</sup>
1:2'-[ $\text{B}_5\text{H}_8$ ] <sub>2</sub>	17.6 ± 2.4 <sup>g</sup> ( $\text{B}_{2,3,4,5}$ ; $\text{B}_{3',4',5}'$ )	109.6 ± 2.4 <sup>g</sup> ( $\text{B}_2\text{-B}_1$ ) 115.0 ± 2.4 <sup>g</sup> ( $\text{B}_1\text{-B}_2'$ )	-3.6 <sup>g</sup> ( $\text{B}_2'$ ) -12.6 <sup>g</sup> ( $\text{B}_{2,3,4,5}$ ; $\text{B}_{3',4',5}'$ ) -13.4 <sup>g</sup> ( $\text{B}_4'$ )	-50.7 <sup>g</sup> ( $\text{B}_1'$ ) -56.2 <sup>g</sup> ( $\text{B}_1$ )
2:2'-[ $\text{B}_5\text{H}_8$ ] <sub>2</sub>	20.5 ± 2.0 <sup>h</sup> ( $\text{B}_{3,3',4,4'}$ ) 21.3 ± 2.0 <sup>h</sup> ( $\text{B}_{4,4'}$ )	79.4 ± 1.4 <sup>d,f</sup> ( $\text{B}_2\text{-B}_2'$ )	-11.0 <sup>h,i</sup> ( $\text{B}_{2,2'}$ ) -11.6 <sup>h</sup> ( $\text{B}_{4,4'}$ ) -12.6 <sup>h</sup> ( $\text{B}_{3,3',4,4'}$ )	-51.2 <sup>h</sup>

<sup>a</sup> In Hz. <sup>b</sup> Chemical shifts reported in ppm with respect to external  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in benzene- $d_6$ ; a positive sign denotes a shift to higher frequency (lower field); assignments of the boron resonances are in parentheses. <sup>c</sup> Measured from the basal resonance in all cases. <sup>d</sup> Determined from the  $^{10}\text{B}$  spectrum, then converted to  $J_{^{11}\text{B}^{11}\text{B}}$  by multiplying  $J_{^{11}\text{B}^{10}\text{B}}$  by  $\gamma^{11}\text{B}/\gamma^{10}\text{B} = 2.98$ . <sup>e</sup>  $^{11}\text{B}$  [ $^1\text{H}$ ] at 25.69 MHz in benzene- $d_6$  at 67 °C. <sup>f</sup>  $^{10}\text{B}$  [ $^1\text{H}$ ] at 42.99 MHz in *n*-heptane at 50 °C. <sup>g</sup>  $^{11}\text{B}$  [ $^1\text{H}$ ] at 128.4 MHz in *n*-pentane at 74 °C. <sup>h</sup>  $^{11}\text{B}$  [ $^1\text{H}$ ] at 128.4 MHz in benzene- $d_6$  at 74 °C; in *n*-heptane the chemical shifts are -10.4, -11.1, -12.1, and -51.3 ppm, respectively. <sup>i</sup>  $^{10}\text{B}$  [ $^1\text{H}$ ] at 42.99 MHz in *n*-heptane at 74 °C. <sup>j</sup> Chemical shift is -11.1 ppm at ambient temperature in benzene- $d_6$ .

by volume, except for 2,4- $\text{C}_2\text{B}_5\text{H}_7$ , which was 20%. All samples were freeze-pump-thaw degassed and sealed under dynamic vacuum.

The precision of individual  $J_{\text{BB}}$  values is given in the tables. Chemical shifts are reported in parts per million (ppm) with respect to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in benzene- $d_6$  and were obtained by sample replacement. A positive chemical shift denotes a resonance to lower shielding (higher frequency). Chemical shifts are estimated to be accurate to better than 0.1 ppm. Computer enhancement of the spectra to improve resolution was employed by utilization of the Bruker or IBM supplied Lorentz-to-Gauss line-shape transformation<sup>21</sup> and by zero filling.

The boron spin-lattice relaxation times ( $T_1$ ) were measured by the Freeman-Hill modification of the inversion-recovery pulse sequence<sup>22</sup> ( $T-90^\circ-\tau-180^\circ-\tau-90^\circ$ ), where  $T$  is the recycle time. The  $90^\circ$  pulse width was 10  $\mu\text{s}$ . Twenty-five values of  $\tau$  were used in the  $T_1$  determinations, and the values of the peak intensities were used in a nonlinear three-parameter least-squares fit<sup>23</sup> of the data on an IBM PC. The  $T_1$  determinations are estimated to be accurate to  $\pm 10\%$ . Spectral simulations in this work were performed with the Bruker/IBM-supplied PAN-IC.81 program on an Aspect 2000A computer.

**Materials.** The compounds 2:2'-[1,5- $\text{C}_2\text{B}_3\text{H}_4$ ]<sub>2</sub> and 2:2',3':2''-[1,5- $\text{C}_2\text{B}_3\text{H}_4$ ][1',5'- $\text{C}_2\text{B}_3\text{H}_3$ ][1'',5''- $\text{C}_2\text{B}_3\text{H}_4$ ] were synthesized using hot/cold gas-phase pyrolysis techniques described elsewhere.<sup>19</sup> All other coupled boranes or carboranes studied were products of gas-phase mercury-photosensitized photolyses, also previously described.<sup>20f</sup> The compounds 2:1'-[1-( $\text{CH}_3$ ) $\text{B}_5\text{H}_7$ ][ $\text{B}_5\text{H}_8$ ] and 2:2'-[1-( $\text{CH}_3$ ) $\text{B}_5\text{H}_7$ ][ $\text{B}_5\text{H}_8$ ] were synthesized from the copolyolysis of a 70%  $\text{B}_5\text{H}_9$ /30% 1-( $\text{CH}_3$ ) $\text{B}_5\text{H}_8$  mixture.

## Results

**1:1'-[ $\text{B}_5\text{H}_8$ ]<sub>2</sub>.** The  $^1\text{H}$ -decoupled  $^{11}\text{B}$  NMR spectrum (Figure 1a) at 25.69 MHz at ambient probe temperature ( $\sim 35^\circ\text{C}$ ) of this compound in  $\text{C}_6\text{D}_6$  displays two resonances with chemical shifts corresponding to those reported previously<sup>20c</sup> (Table II). Although the basal boron resonance normally appears as a singlet, resolution enhancement of the spectrum reveals a slightly collapsed quartet with an average  $J_{^{11}\text{B}_1^{11}\text{B}_{2,3,4,5}} = 16.7 \pm 1.2$  Hz. Increasing the temperature of the sample and subsequent resolution enhancement of the resulting spectrum (expansion, Figure 1a) yielded a  $J_{^{11}\text{B}_1^{11}\text{B}_{2,3,4,5}} = 17.7 \pm 0.6$  Hz. Additionally, three of seven resonances due to  $^{11}\text{B}$ - $^{10}\text{B}$  spin-spin coupling were visible with an average  $J_{^{11}\text{B}^{10}\text{B}} = 6.3$  Hz. In neither spectrum was resolvable coupling observed in the resonance of the apical borons. A determination of  $^{11}\text{B}$  spin-lattice relaxation times ( $T_1$ ) yielded values of 35.4 ms for the basal borons and 94.7 ms for the apical borons at 35 °C.

The  $^1\text{H}$ -decoupled  $^{10}\text{B}$  NMR spectrum (42.99 MHz) of the compound at 50 °C in *n*-heptane (Figure 1b) exhibits a singlet for the resonance of the basal borons and a broad multiplet for the apical boron resonance. Resolution enhancement (expansion, Figure 1b) reveals that this multiplet is a slightly collapsed quartet (peak separations: 36.6, 50.0, and 35.4 Hz, respectively) su-

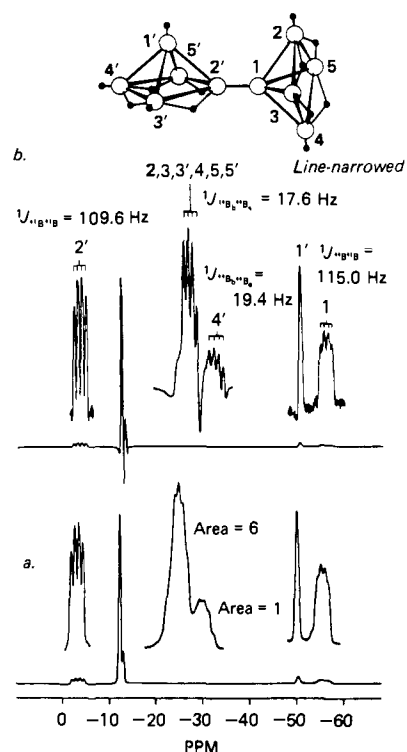


Figure 2. Proton-spin-decoupled, 128.4-MHz  $^{11}\text{B}$  NMR spectra of 1:2'-[ $\text{B}_5\text{H}_8$ ]<sub>2</sub> at 74 °C in *n*-pentane. Spectrum b is line narrowed. Expansions are shown of all resonances.

perimposed on a singlet (due to the symmetrical  $^{10}\text{B}$ - $^{10}\text{B}$  apical isotopomer). By use of the separation of the inner two lines of the quartet, a  $J_{^{11}\text{B}_1^{11}\text{B}_1'} = 149.3$  Hz can be calculated for the boron atoms joining the two cages.

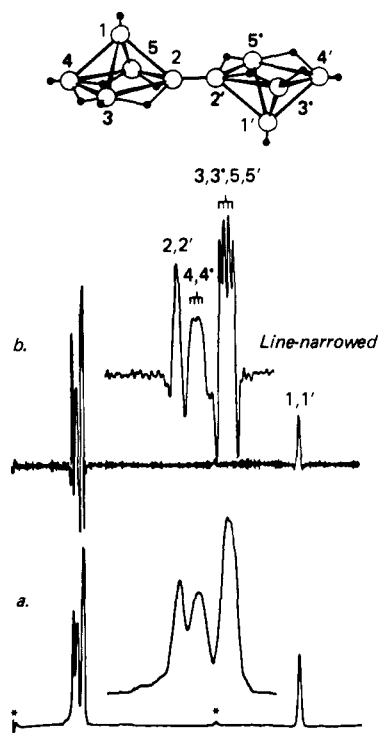
**1:2'-[ $\text{B}_5\text{H}_8$ ]<sub>2</sub>.** The  $^1\text{H}$ -decoupled  $^{11}\text{B}$  NMR spectrum (128.4 MHz) of this compound in *n*-pentane at 74 °C (Figure 2a) is identical with that reported previously<sup>16,20d</sup> except that the resonance arising from the 2,3,3',4,4',5,5' borons has been resolved into two resonances with relative intensities 6:1. The resonance of area 1 can be assigned to the unique basal 4' boron atom. Assignments and chemical shifts are given in Table II. Resolution enhancement of this spectrum (Figure 2b) resulted in well-resolved quartets for the resonances of boron 2' ( $J_{^{11}\text{B}_1^{11}\text{B}_2'} = 109.6$  Hz), 2,3,3',4,5,5' ( $J_{^{11}\text{B}_1^{11}\text{B}_2} = 17.6$  Hz), 4' ( $J_{^{11}\text{B}_1^{11}\text{B}_4'} = 19.4$  Hz), and 1 ( $J_{^{11}\text{B}_1^{11}\text{B}_1'} = 115$  Hz).

**2:1'-[1-( $\text{CH}_3$ ) $\text{B}_5\text{H}_7$ ][ $\text{B}_5\text{H}_8$ ].** The 115.5-MHz  $^1\text{H}$ -coupled  $^{11}\text{B}$  NMR spectrum of this compound (pentane, 25 °C) exhibits four resonances: -4.2 ppm, quartet,  $J_{^{11}\text{B}_1^{11}\text{B}_1'} = 102.9 \pm 2$  Hz ( $\text{B}_2$ ); -12.4 ppm, doublet,  $J_{\text{B-H}} = 160$  Hz ( $\text{B}_{2,3',4,5,5'}$ ,  $\text{B}_{3,5}$ ,  $\text{B}_4$ ); -42.1 ppm, singlet ( $\text{B}_1$ ); -56.2 ppm, quartet,  $J_{^{11}\text{B}_1^{11}\text{B}_2} = 120.6 \pm 2$  Hz ( $\text{B}_1'$ ). Resolution enhancement of the proton-spin-decoupled resonance at -12.4 ppm allows the assignment of the three overlapping basal

(21) Braoudakis, G.; Gerothanassis, I. P.; Lauterwein, J. J. *Magn. Reson.* **1983**, *52*, 288-293.

(22) Martin, M. L.; Delpuech, J.-J.; Martin, G. J. "Practical NMR Spectroscopy"; Heyden and Son Ltd.: London, 1980; p 256.

(23) Sass, M.; Ziessow, D. J. *Magn. Reson.* **1977**, *25*, 263-276.

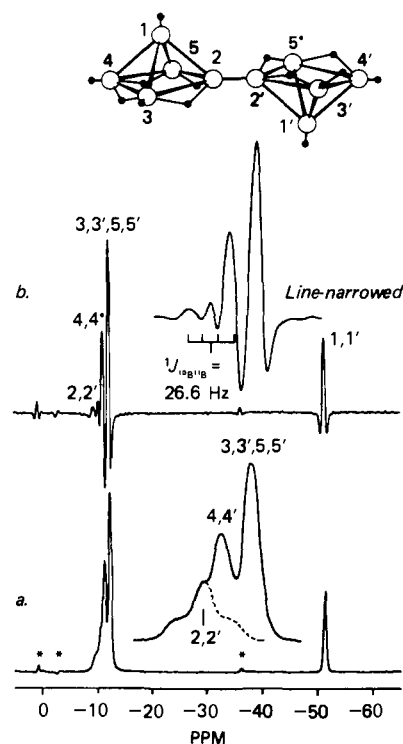


**Figure 3.** Proton-spin-decoupled, 128.4-MHz  $^{11}\text{B}$  NMR spectra of  $2:2'-[\text{B}_5\text{H}_8]_2$  at  $74^\circ\text{C}$  in *n*-heptane. Spectrum b is line narrowed. Expansions are shown of the low-field resonances (\* = impurities).

resonances:  $\text{B}_{3,5}$  at  $-11.7$  ppm,  $\text{B}_{2',3',4',5'}$  at  $-12.4$  ppm with  $J_{^{11}\text{B}_1,^{11}\text{B}_2} = 17.3 \pm 1.2$  Hz, and  $\text{B}_4$  at  $-13.0$  ppm. The average value for the exopolyhedral boron-boron coupling constant is  $111.7$  Hz.

$2:2'-[\text{B}_5\text{H}_8]_2$ . The  $^{11}\text{B}$  NMR spectrum (128.4 MHz) of this compound in  $\text{C}_6\text{D}_6$  at  $30^\circ\text{C}$  is the same as that reported previously.<sup>20d,24</sup> However, when the temperature is raised to  $74^\circ\text{C}$  in either  $\text{C}_6\text{D}_6$  or *n*-heptane (Figure 3a) the most deshielded resonance ( $-11.2$  ppm) is resolved into two resonances, a relatively broad singlet ( $-11.0$  ppm) and a broad multiplet ( $-11.6$  ppm). Comparison of the  $^1\text{H}$ -coupled  $^{11}\text{B}$  spectrum to the  $^1\text{H}$ -decoupled spectrum (both at  $74^\circ\text{C}$  in  $\text{C}_6\text{D}_6$ ) leads to the following assignments:  $-11.0$  ppm,  $\text{B}_{2,2'}$ ;  $-11.6$  ppm,  $\text{B}_{4,4'}$ ;  $-12.6$  ppm,  $\text{B}_{3,3',5,5'}$  (Table II), contrary to a previous assignment<sup>25</sup> based on the more indirect technique of partially relaxed Fourier transform  $^{11}\text{B}$  NMR.<sup>26</sup> Resolution enhancement of the  $74^\circ\text{C}$  ( $\text{C}_6\text{D}_6$ ) spectrum (Figure 3b) yields  $J_{^{11}\text{B}_1,^{11}\text{B}_4} = 21.3 \pm 2.0$  Hz for the multiplet at  $-11.6$  ppm and  $J_{^{11}\text{B}_1,^{11}\text{B}_3} = 20.5 \pm 2.0$  Hz for the resonance at  $-12.6$  ppm.

In the  $^{10}\text{B}$  NMR spectrum (Figure 4a) (42.99 MHz) of this compound (heptane,  $74^\circ\text{C}$ ) the most deshielded resonance ( $2,2'$  borons) appears to be a broad "triplet" (confirming the assignment above) with the most shielded component of the triplet coincidental with the resonance at  $-11.1$  ppm (assigned to the  $4,4'$  borons). Resolution enhancement of the  $^{10}\text{B}$  spectrum (Figure 4b) results in better resolution of the two most deshielded components of this broad "triplet" with the most shielded component remaining under the  $4,4'$  boron resonance. If the assumption is made that the most deshielded portion of this "triplet" is the lowest field component of a quartet and that the second and third components lie underneath the center portion of the triplet (which is due to primarily to the resonance of the isotopomer with  $^{10}\text{B}$  atoms in both the 2 and  $2'$  positions), then the separation between these two "triplet" components ( $39.9$  Hz) multiplied by two and divided by three should represent a good estimate of  $J_{^{10}\text{B}_1,^{10}\text{B}_2}$ . This value is  $26.6$  Hz corresponding to a  $J_{^{11}\text{B}_1,^{11}\text{B}_2} = 79.4$  Hz.



**Figure 4.** Proton-spin-decoupled, 42.99-MHz  $^{10}\text{B}$  NMR spectra of  $2:2'-[\text{B}_5\text{H}_8]_2$  at  $74^\circ\text{C}$  in *n*-heptane. Spectrum b is line narrowed. Expansions are shown of the low-field resonances (\* = impurities).

$2:2'-[1-(\text{CH}_3)\text{B}_5\text{H}_7]_2$ . The  $^{11}\text{B}$  NMR spectrum of this compound ( $^1\text{H}$  coupled,  $25^\circ\text{C}$  in pentane) confirms the previously published assignment<sup>20f</sup> ( $32.1$  MHz). Aided by the resolution-enhanced proton-spin-decoupled spectrum, the  $\text{B}_{3,3',5,5'}$  resonance can unambiguously be assigned at  $-11.3$  ppm, with  $J_{\text{B-H}} = 149.3$  Hz and  $J_{^{11}\text{B}_1,^{11}\text{B}_3} = 19.1 \pm 1.9$  Hz. The  $\text{B}_{2,2'}$  (singlet) and  $\text{B}_{4,4'}$  (doublet) resonances are coincidentally overlapped at  $-10.0$  ppm, preventing the determination of  $J_{^{11}\text{B}_1,^{11}\text{B}_2}$  by  $^{10}\text{B}$  NMR spectroscopy.

$2:2'-[1-(\text{CH}_3)\text{B}_5\text{H}_7][\text{B}_5\text{H}_8]$ . The  $^{11}\text{B}$ -coupled  $^{11}\text{B}$  spectrum of this compound exhibits three resonances: a broad multiplet centered at approximately  $-11.3$  ppm, a singlet at  $-42.8$  ppm, and a doublet at  $-51.4$  ppm,  $J_{\text{B-H}} = 175.9$  Hz, of relative intensity 8:1:1, respectively. The  $^1\text{H}$ -decoupled, resolution-enhanced  $^{11}\text{B}$  spectrum at  $74^\circ\text{C}$  in pentane of the downfield multiplet exhibits a singlet at  $-10.4$  ppm assigned to the  $2,2',4$  boron resonances, a partially collapsed quartet at  $-11.0$  ppm assigned to the  $4'$  boron resonance, and two well-resolved overlapping quartets at  $-11.8$  and  $-12.1$  ppm, giving the semblance of a 1:1:2:2:1:1 sextet. These quartets are assigned to the 3,5 and  $3',5'$  boron resonances ( $J_{^{11}\text{B}_1,^{11}\text{B}_3} = 19.0 \pm 2.0$  Hz and  $J_{^{11}\text{B}_1,^{11}\text{B}_3'} = 19.5 \pm 2.0$  Hz). The  $^1\text{H}$ -coupled spectrum allows easy identification of the  $\text{B}_1$  resonance ( $-42.8$  ppm) and the  $\text{B}_1'$  resonance ( $-51.4$  ppm).

Due to sample limitations a determination of the boron-boron coupling constant between the 2 and  $2'$  boron atoms was not possible by  $^{10}\text{B}$  NMR.

$1:3'-[2,4-\text{C}_2\text{B}_3\text{H}_6]_2$ . The  $^{11}\text{B}$  NMR spectrum of this compound ( $^1\text{H}$  decoupled, resolution enhanced,  $74^\circ\text{C}$ , hexane) (Figure 5) confirms the previously published assignment<sup>20f</sup> ( $32.1$  MHz) and also resolves the quartet assigned to the  $\text{B}_3$  resonance ( $7.1$  ppm) and three lines of the quartet assigned to  $\text{B}_1$  ( $-17.1$  ppm). The  $^{11}\text{B}$ - $^{11}\text{B}$  coupling constant derived from the resonance of  $\text{B}_1$  is  $123.7 \pm 2.9$  Hz and that derived from the  $\text{B}_3$  resonance is  $119.9 \pm 2.9$  Hz (Table III).

$3:3'-[2,4-\text{C}_2\text{B}_3\text{H}_6]_2$ . The  $^{11}\text{B}$  NMR spectrum of this compound ( $^1\text{H}$  decoupled, resolution enhanced, *n*-heptane,  $61^\circ\text{C}$ ) (Figure 6) confirms the previous assignment<sup>20f</sup> and in addition reveals intracage boron-boron spin-spin coupling between the  $1,1',7,7'$  boron atoms and the  $5,5',6,6'$  boron atoms. Each of the

(24) Rietz, R. R.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1972**, *11*, 1242-1244.

(25) Rietz, R. R.; Schaeffer, R. *J. Am. Chem. Soc.* **1973**, *95*, 4580-4582.

(26) Allerhand, A.; Clouse, A. O.; Rietz, R. R.; Roseberry, T.; Schaeffer, R. *J. Am. Chem. Soc.* **1972**, *94*, 2445-2448.

Table III.  $^{11}\text{B}$  NMR Parameters for 2,4- $\text{C}_2\text{B}_5\text{H}_7$  and Selected Coupled Dimers

compd	$^1J_{^{11}\text{B}^{11}\text{B}}$ <sup>a</sup>		$\delta_{^{11}\text{B}}$ <sup>b</sup>	
	base-to-apex	exopolyhedral	base	apex
2,4- $\text{C}_2\text{B}_5\text{H}_7$	$9.2 \pm 0.5^{c,d}$ ( $\text{B}_1\text{-B}_5$ ) <sup>e</sup> $9.7 \pm 0.5^{c,d}$ ( $\text{B}_5\text{-B}_1$ )		$6.7^f$ ( $\text{B}_3$ ) <sup>g</sup> $3.6^f$ ( $\text{B}_{5,6}$ ) <sup>g</sup>	$-22.1^f$ ( $\text{B}_{1,7}$ ) <sup>g</sup>
1:3'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ] <sub>2</sub>		$119.9 \pm 2.9^h$ ( $\text{B}_{3'}\text{-B}_1$ ) $123.7 \pm 2.9^h$ ( $\text{B}_1\text{-B}_{3'}$ )	$8.0^h$ ( $\text{B}_3$ ) <sup>i</sup> $7.1^h$ ( $\text{B}_{3'}$ ) <sup>i</sup> $5.3^h$ ( $\text{B}_{5,6}$ ) <sup>i</sup> $4.6^h$ ( $\text{B}_{5',6'}$ ) <sup>i</sup>	$-17.1^h$ ( $\text{B}_1$ ) <sup>i</sup> $-18.5^h$ ( $\text{B}_7$ ) <sup>i</sup> $-21.4^h$ ( $\text{B}_{1',7'}$ ) <sup>i</sup>
3:3'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ] <sub>2</sub>	$9.8 \pm 0.6^{j,k}$ ( $\text{B}_1\text{-B}_5$ ) $9.3 \pm 0.6^{j,k}$ ( $\text{B}_5\text{-B}_1$ )	$151.4 \pm 3.6^l$	$9.5^m$ ( $\text{B}_{3,3'}$ ) <sup>i</sup> $5.0^m$ ( $\text{B}_{5,6,5',6'}$ ) <sup>i</sup>	$-21.1^m$ ( $\text{B}_{1,7,1',7'}$ ) <sup>i</sup>
3:5'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ] <sub>2</sub>		$\geq 100^{n,o}$	$\sim 10.8^{n,o}$ ( $\text{B}_3$ ) <sup>i</sup> $8.0^o$ ( $\text{B}_{3'}$ ) <sup>i</sup> $\sim 6.2^{n,o}$ ( $\text{B}_{5'}$ ) <sup>i</sup> $5.5^o$ ( $\text{B}_{6'}$ ) <sup>i</sup> $4.9^o$ ( $\text{B}_{5,6}$ ) <sup>i</sup>	$-21.0^o$ ( $\text{B}_{1,7,1',7'}$ ) <sup>i</sup>

<sup>a</sup> In Hz. <sup>b</sup> Chemical shifts reported in ppm with respect to external  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in benzene- $d_6$ ; a positive sign denotes a shift to higher frequency (lower field); assignments of the boron resonances are in parentheses. <sup>c</sup> Reported as the average separation between peaks in the septet (due to coupling to two chemically shift equivalent  $^{11}\text{B}$ 's). <sup>d</sup> Estimated as  $\leq 15$  Hz in ref 13. <sup>e</sup> The first boron listed is the resonance in which the coupling was measured; the second boron is the boron to which the first is spin-spin coupled. <sup>f</sup>  $^{11}\text{B}$  { $^1\text{H}$ } at 25.69 MHz in *n*-hexane at ambient probe temperature. <sup>g</sup> Assignments as in ref 13. <sup>h</sup>  $^{11}\text{B}$  { $^1\text{H}$ } at 128.4 MHz in *n*-hexane at 74 °C. <sup>i</sup> Assignments consistent with ref 20f. <sup>j</sup>  $^{11}\text{B}$  { $^1\text{H}$ } at 25.69 MHz in *n*-heptane at 61 °C. <sup>k</sup> Reported as the average separation between the five resolved peaks of the septet. <sup>l</sup>  $^{10}\text{B}$  { $^1\text{H}$ } at 42.99 MHz in *n*-heptane at 62 °C;  $J_{^{10}\text{B}^{11}\text{B}}$  was determined, then converted to  $J_{^{11}\text{B}^{11}\text{B}}$  by multiplying by  $\gamma^{11}\text{B}/\gamma^{10}\text{B} = 2.98$ . <sup>m</sup>  $^{11}\text{B}$  { $^1\text{H}$ } at 128.4 MHz in *n*-heptane at 74 °C. <sup>n</sup> Estimate based on line shape simulations of a strongly coupled AB system ( $I = 3/2$ ) using the Bruker-supplied PANIC program; see text. <sup>o</sup>  $^{11}\text{B}$  { $^1\text{H}$ } at 128.4 MHz in *n*-hexane at 74 °C.

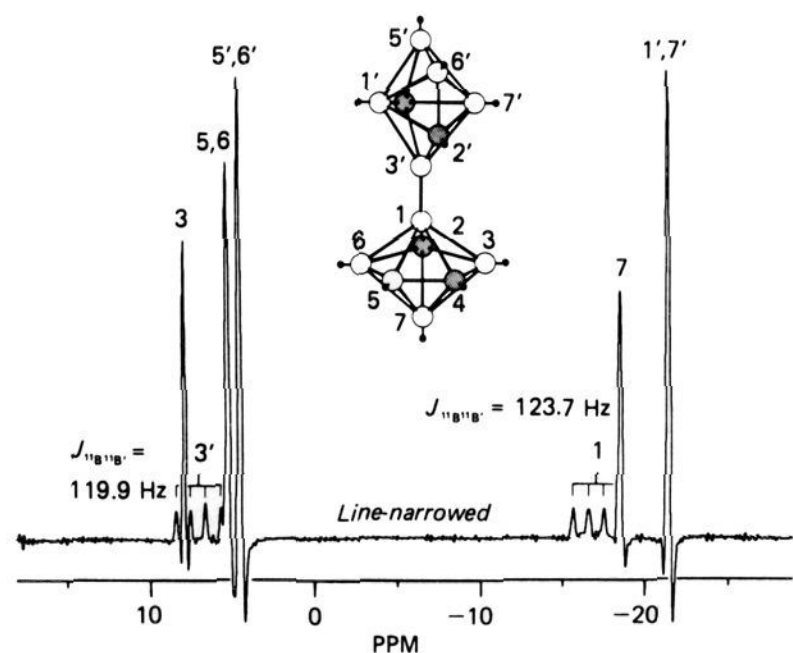


Figure 5. Proton-spin-decoupled, 128.4-MHz  $^{11}\text{B}$  NMR spectrum (line narrowed) of 1:3'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ]<sub>2</sub> at 74 °C in hexane.

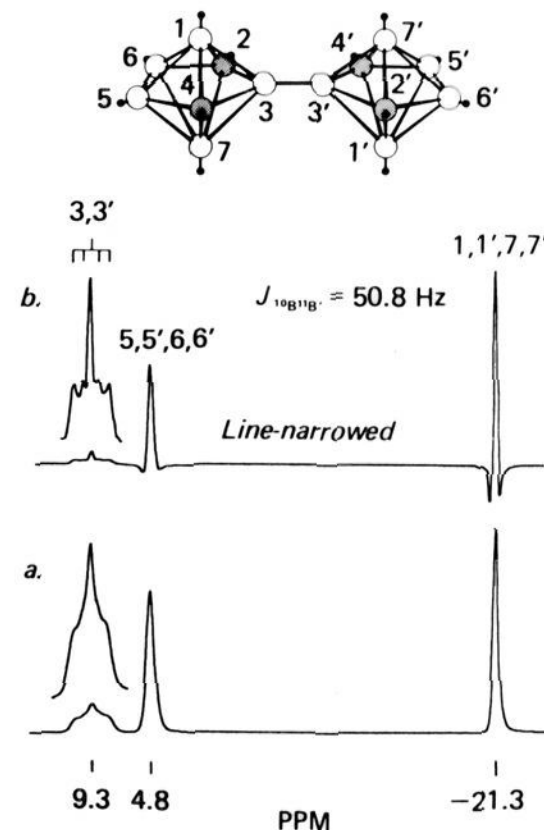


Figure 7. Proton-spin-decoupled, 42.99-MHz  $^{10}\text{B}$  NMR spectrum of 3:3'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ]<sub>2</sub> at 62 °C in *n*-heptane. Spectrum b is line narrowed. Expansions are shown of the low-field ( $\text{B}_{3,3'}$ ) resonance.

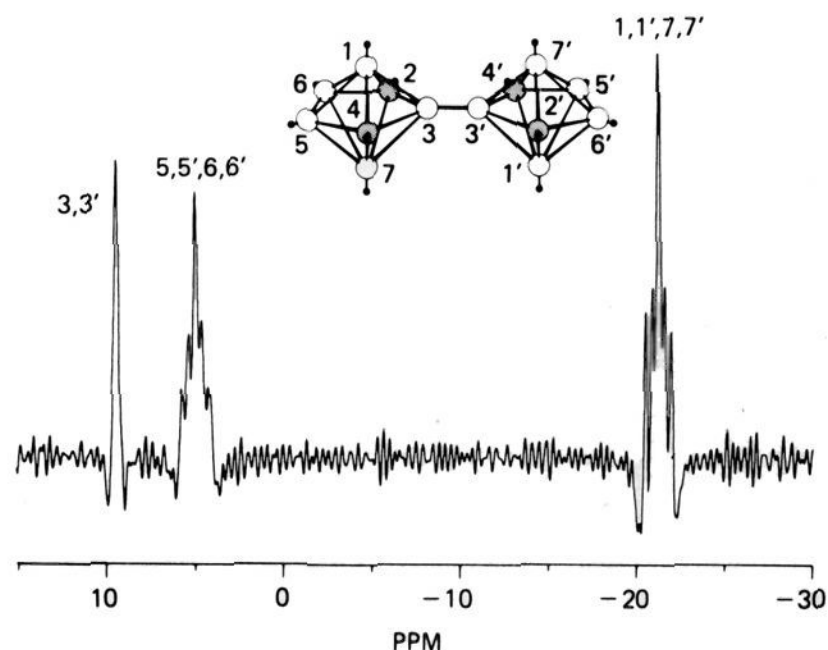


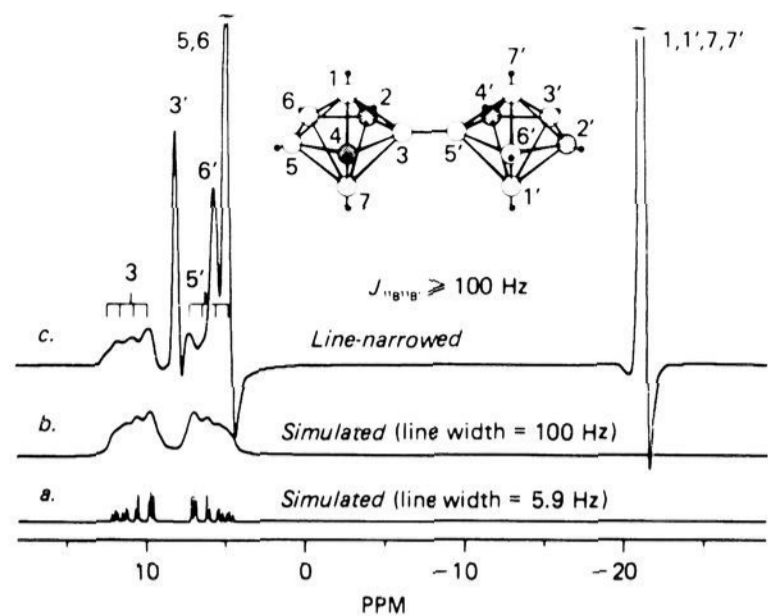
Figure 6. Proton-spin-decoupled, 25.69-MHz  $^{11}\text{B}$  NMR spectrum (line narrowed) of 3:3'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ]<sub>2</sub> at 61 °C in *n*-heptane ( $J_{^{11}\text{B}^{11}\text{B}} = 9.5$  Hz).

resonances is a five-line multiplet which presumably are the five inner lines of a septet arising from spin coupling to two equivalent

boron atoms. The  $J_{^{11}\text{B}^{11}\text{B}}$  value is  $9.5 \pm 0.6$  Hz, compared to a value of  $J_{^{11}\text{B}^{11}\text{B}}$  of 9.5 Hz for 2,4- $\text{C}_2\text{B}_5\text{H}_7$  measured under identical conditions.

The 42.99-MHz  $^{10}\text{B}$  spectrum ( $^1\text{H}$  decoupled, resolution enhanced, heptane, 62 °C) (Figure 7) was obtained in order to determine the coupling constant between the 3 and 3' boron atoms. The resonance assigned to these nuclei consists of a well-resolved quartet (due to  $^{11}\text{B}$ - $^{10}\text{B}$  coupling), superimposed on a single sharp peak (due to the symmetrical  $^{10}\text{B}$ - $^{10}\text{B}$  isotopomer). If the separation of the inner two lines of the quartet is taken as the value of  $J_{^{10}\text{B}^{11}\text{B}}$ , then  $J_{^{11}\text{B}^{11}\text{B}} = 151.4 \pm 3.6$  Hz.

**3:5'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ]<sub>2</sub>.** The previously published 32.1-MHz  $^{11}\text{B}$  spectrum<sup>20f</sup> of this molecule did not allow clear identification of either the 3 or 5' boron resonances, although all other resonances were assigned. The 128.4-MHz  $^{11}\text{B}$  spectrum ( $^1\text{H}$  decoupled, resolution enhanced, hexane, 74 °C) (Figure 8c) confirms the previous assignment as well as allowing the assignment of the 3 and 5' resonances ( $\delta_3 \cong 10.3$  ppm and  $\delta_{5'} \cong 6.2$  ppm). A con-



**Figure 8.** (a) Simulated  $^{11}\text{B}$  NMR spectrum ( $\Delta\delta = 615$  Hz,  $J = 100$  Hz and line width = 5.9 Hz) for the 3 and 5' boron resonances in 3:5'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ] $_2$ . (b) Simulated  $^{11}\text{B}$  NMR spectrum with line broadening (line width = 100 Hz). (c) Proton-spin-decoupled, 128.4-MHz  $^{11}\text{B}$  NMR spectrum (line narrowed) of 3:5'-[2,4- $\text{C}_2\text{B}_5\text{H}_6$ ] $_2$  at 74 °C in hexane.

sideration of the chemical shift difference ( $\Delta\delta$ ) between the resonance of borons 3 and 5', and an expected coupling constant of greater than 100 Hz, gives a value of  $\Delta\delta/J \cong 6$ , which could lead to second-order effects in these resonances. A line simulation program with spectral parameters  $\Delta\delta = 615$  Hz,  $J = 100$  Hz, and half-height line width = 5.9 Hz gives the spectrum, shown in Figure 8a, for a relatively strongly coupled spin  $3/2$ -spin  $3/2$  case. Deliberate line broadening (100 Hz) gives excellent agreement (Figure 8b) with the experimental line shapes for the resonance of boron 3 and what can be seen for the resonance of boron 5'. Owing to the uncertainty in the exact chemical shifts and the amount of line broadening which should be taken into account, a boron-boron coupling  $\geq 100$  Hz can only be estimated.

The 42.99-MHz  $^{10}\text{B}$  NMR spectrum of this molecule yielded no additional information.

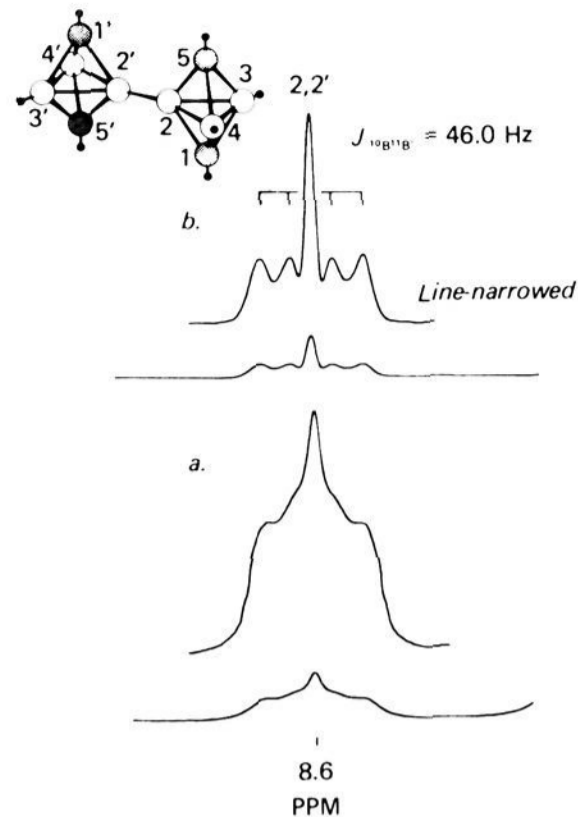
**2:2'-[1,5- $\text{C}_2\text{B}_3\text{H}_4$ ] $_2$ .** The 42.99-MHz  $^{10}\text{B}$  spectrum of this molecule ( $^1\text{H}$  decoupled, resolution enhanced, heptane, 74 °C) shows two resonances consistent with the previously reported  $^{11}\text{B}$  spectrum.<sup>20m-o</sup> However, the resonance of relative area = 2, assigned to the 2,2' borons is a well-resolved quartet superimposed on a sharp singlet (Figure 9b). If the separation between the two inner lines of the quartet is taken as  $J_{10\text{B}_2^{11}\text{B}_2}$ , then  $J_{11\text{B}_2^{11}\text{B}_2} = 137.1 \pm 2.9$  Hz.

**2:2',3':2''-[1,5- $\text{C}_2\text{B}_3\text{H}_4$ ][1',5'- $\text{C}_2\text{B}_3\text{H}_3$ ][1'',5''- $\text{C}_2\text{B}_3\text{H}_4$ ].** The 115.5-MHz  $^{11}\text{B}$  NMR spectrum of this molecule ( $^1\text{H}$  decoupled, heptane) exhibits two broad singlet resonances at 8.3 ( $\text{B}_{2,3'}$  and  $\text{B}_{2,2''}$ ) and 2.3 ppm ( $\text{B}_{3,4,3'',4''}$  and  $\text{B}_{4'}$ ) in agreement with the previously reported  $^{11}\text{B}$  spectrum<sup>20o</sup> at 32.1 MHz. However, the 2.3 ppm resonance (a broad doublet in the  $^1\text{H}$ -coupled spectrum) exhibits an upfield shoulder centered at 1.6 ppm assigned to  $\text{B}_{4'}$ .

The 42.99-MHz  $^{10}\text{B}$  NMR spectrum of the 8.3 ppm resonance ( $^1\text{H}$  decoupled, heptane, resolution enhanced, 74 °C) is split into a complex multiplet. It was not possible to determine a boron-boron coupling constant for the spectrum, owing to the unresolved overlap of the  $\text{B}_{2,3'}$  and  $\text{B}_{2,2''}$  resonances.

## Discussion

Several theoretical and empirical treatments of NMR line shapes for spin  $1/2$  nuclei spin-spin coupled to quadrupolar nuclei<sup>27-29</sup> have appeared. For a nucleus spin-spin coupled to a boron-11 ( $I = 3/2$ ), the multiplet may occur as a sharp, well-resolved quartet, a single line, or in intermediate stages between these two extremes depending upon the value<sup>28,30</sup> of the quantity  $2\pi JT_1$ , where  $J$  is the spin-spin coupling constant between the



**Figure 9.** Proton-spin-decoupled, 42.99-MHz  $^{10}\text{B}$  NMR spectra of the  $\text{B}_{2,2'}$  resonance of 2:2'-[1,5- $\text{C}_2\text{B}_3\text{H}_4$ ] $_2$  at 74 °C in n-heptane. Spectrum b is line narrowed.

two nuclei and  $T_1$  is the spin-lattice relaxation time of the nucleus scalar coupled to the  $^{11}\text{B}$  nucleus under observation. When  $2\pi JT_1$  is greater than 10, the multiplet will be a well-resolved 1:1:1:1 quartet; at a value of  $10^{1/2}$  the multiplet will only be slightly collapsed, and at values of  $0.1^{1/2}$  the multiplet will become a singlet. Owing to this effect of quadrupolar relaxation on the line shapes of  $^{11}\text{B}$  spectra, it is often difficult to extract exact coupling constants.

The experimentally measurable  $J_{11\text{B}^{11}\text{B}}$  values in this study were in most cases determined from the peak separations of the inner two lines of the quartets. An inspection of the theoretical line shapes for nuclei spin-spin coupled to quadrupolar nuclei<sup>27-29</sup> shows that, for the  $I = 3/2$  case, the outer lines decay much more rapidly than the inner lines as quadrupolar relaxation becomes more dominant. In fact, the outer-line positions move toward the center of the multiplet relatively rapidly and the two inner lines remain more or less in a fixed position as the fine structure collapses. Therefore, the inner-line separation most accurately measures the coupling constant in the absence of a tedious total line-shape analysis using relaxation data.

In those cases where the two coupled  $^{11}\text{B}$  nuclei were chemical shift equivalent, the  $J_{11\text{B}^{11}\text{B}}$  was calculated by an experimental measurement of the boron-10-boron-11 coupling constant in the  $^{10}\text{B}$  spectrum and then multiplying by the ratio of the gyromagnetic ratios,  $\gamma^{11}\text{B}/\gamma^{10}\text{B} = 2.98$ .

The spin-lattice relaxation time,  $T_1$ , is dominated by quadrupolar relaxation as given by the expression<sup>31</sup>

$$\frac{1}{T_1} = \left(\frac{3}{40}\right) \left(\frac{2I+3}{I^2(2I-1)}\right) \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2qQ}{h}\right)^2 \tau_c \quad (1)$$

where  $I$  is the nuclear spin of the quadrupolar nucleus,  $\eta$  is the asymmetry parameter,  $eQ$  is the nuclear quadrupole moment, and  $\tau_c$  is the correlation time for molecular reorientation of the nucleus. The simplest expression for the correlation time  $\tau_c$  is given<sup>32</sup> by

$$\tau_c = 4\pi\xi a^3/3kT \quad (2)$$

where  $\xi$  is the viscosity in poise,  $a$  is the radius of the molecule (assumed to be spherical), and  $T$  is the absolute temperature. Since the line shape is dependent upon the magnitude of  $2\pi JT_1$ , then it follows that if one has a means of increasing the spin-lattice

(27) Pople, J. A. *Mol. Phys.* **1958**, *1*, 168-174.

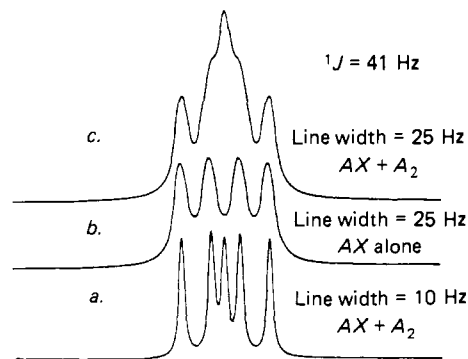
(28) Bacon, J.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3063-3069.

(29) Suzuki, M.; Kubo, R. *Mol. Phys.* **1963**, *7*, 201-209.

(30) Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 1401-1405.

(31) Abragam, A. "Principles of Nuclear Magnetism"; Clarendon Press: Oxford, 1961; p 314.

(32) In ref 31, p 300.



**Figure 10.** PANIC simulations of the A portion of an AX spin system, with  $A = {}^{10}\text{B}$  and  $X = {}^{11}\text{B}$ .

relaxation time, thus increasing the value of  $2\pi J T_1$ , the line shape may have more structure and a more accurate value of the coupling constant may be obtained. It can easily be seen from the above expression that an increase in the temperature as well as a decrease in the viscosity of the solvent should increase the resolution of the multiplet obtained. In several cases we have been able to accomplish this by changing the solvent from toluene or benzene, to pentane, hexane, or heptane, and by raising the temperature to  $\sim 74^\circ\text{C}$ . In most cases this was performed in conjunction with a "resolution enhancement"<sup>33</sup> by Gaussian multiplication<sup>23,34</sup> of the free induction decay prior to Fourier transformation.

To ascertain whether the multiplet in the apical  ${}^{10}\text{B}$  resonance of  $1:1'-[\text{B}_5\text{H}_8]_2$  is due to resolvable  ${}^{10}\text{B}-{}^{11}\text{B}$  coupling between the apical boron atoms, the value of  $2\pi J T_1$  was determined ( $J_{10\text{B}^{11}\text{B}} = 50\text{ Hz}$ ;  $T_1({}^{11}\text{B}_1) = 82.8\text{ ms}$ ). The value obtained, 26, indicates that the expected multiplet should be a completely resolved 1:1:1:1 quartet. However, the value of  $2\pi J T_1$  for the  ${}^{11}\text{B}-{}^{10}\text{B}$  base-to-apex coupling ( $J_{10\text{B}^{11}\text{B}_2} = 5.9\text{ Hz}$ ;  $T_1({}^{11}\text{B}_2) = 30.2\text{ ms}$ ) was determined to be 1.1, showing that partial collapse (a "doublet" structure) of this anticipated fine structure should produce only "broadening" of the individual members of the quartet. This apparent broadening will arise since the most abundant of the isotopomers with  ${}^{10}\text{B}$  in an apical position will have four equivalent  ${}^{11}\text{B}$ 's in the basal position producing a 13-line pattern<sup>35</sup> with a 5.9-Hz separation between peaks (in the ideal case of being first order and completely resolved). The collapse of this 13-line multiplet due to the intermediate value of  $2\pi J T_1$  paired with the small coupling constant will combine to produce broad, essentially featureless peaks<sup>36</sup> in the well-resolved 1:1:1:1  ${}^{10}\text{B}-{}^{11}\text{B}$  quartet, as well as a broadened resonance for the  ${}^{10}\text{B}-{}^{10}\text{B}$  singlet. Further reflection shows that this situation will be even further complicated by the large number of isotopomers with varying numbers of  ${}^{10}\text{B}$  isotopes in the basal positions. The isotopomers with only one  ${}^{10}\text{B}$  in the two possible apical positions could have an additional complication by being a complex spin system, i.e., the A portion of an  $\text{X}_4\text{AYX}_4'$  system. (Of course, the additional possible coupling constants, e.g.,  $J_{\text{AX}'}$ , will be vanishingly small and hence completely collapsed, but the magnetic inequivalence could conceivably introduce asymmetry into the line shapes.)

Some of the general overall features of this type of system can be crudely simulated as follows: only two types of isotopomers will contribute to the  ${}^{10}\text{B}$  signal intensity—the  ${}^{10}\text{B}-{}^{11}\text{B}$  unsymmetrically, apically substituted and the  ${}^{10}\text{B}-{}^{10}\text{B}$  symmetrically, apically substituted molecules. (The  ${}^{11}\text{B}-{}^{11}\text{B}$  apically substituted molecules will not contribute to the  ${}^{10}\text{B}$  spectrum of the apical

resonance). This assumes, as shown above, that only the apical  ${}^{10}\text{B}-{}^{11}\text{B}$  coupling is resolved and all other coupling is essentially collapsed and can be considered, for ease in simulation, as only adding equal amounts of line width to all resolvable resonances. The overall multiplet intensities of the  ${}^{10}\text{B}-{}^{11}\text{B}$  quartet relative to the  ${}^{10}\text{B}-{}^{10}\text{B}$  singlet will be in a 0.89 to 0.11 ratio normalized to an individual line intensity of 1:1:1:1 for the quartet and a unit intensity for the singlet. As Figure 10a illustrates, the addition of a 1:1:1:1 quartet with  $J = 41\text{ Hz}$  to a singlet of intensity 1 results in essentially a 1:1:1:1:1 five-line pattern when the individual line widths are 10 Hz. Whereas adding the same quartet and singlet utilizing a line width of 25 Hz results in a broad "triplet" (Figure 10c) very similar in shape to the actual  ${}^{10}\text{B}$  spectrum of the apical resonance in  $1:1'-[\text{B}_5\text{H}_8]_2$  (Figure 1b). This "triplet" structure was seen in the  ${}^{10}\text{B}$  spectrum in all cases where the two sites of the exopolyhedral attachment between the two cages were chemically shift equivalent in the  ${}^{11}\text{B}$  spectrum.

In a recent paper<sup>14</sup> Kroner and Wrackmeyer investigated boron-hydrogen and boron-boron coupling constants in diboranes, polyboranes, and carboranes via CNDO/S and ab initio calculations and found that these coupling constants can be consistently interpreted on the basis of density matrix changes. More specifically, a good correlation of the reduced coupling constant,  ${}^1K_{11\text{B}^{11}\text{B}}$ , with the charge density bond order matrix,  $p^2_{\text{B}_{(2\text{s})}\text{B}_{(2\text{s})}}$ , was obtained. Using Kroner and Wrackmeyer's data and the expression for the reduced<sup>37</sup> coupling constant

$${}^1K_{\text{AB}} = (1/h)(2\pi/\gamma_{\text{A}})(2\pi/\gamma_{\text{B}})J_{\text{AB}} \quad (3)$$

one can derive the following

$$J_{11\text{B}^{11}\text{B}} (\text{Hz}) = 1056.7p^2_{11\text{B}_{(2\text{s})}^{11}\text{B}_{(2\text{s})}} - 23.882 \quad (4)$$

$$p^2_{11\text{B}_{(2\text{s})}^{11}\text{B}_{(2\text{s})}} = (9.463 \times 10^{-4})J_{11\text{B}^{11}\text{B}} + 0.0226 \quad (5)$$

These expressions now provide the basis to examine the data with regard to consistency of the magnitude of the boron-boron coupling constant and the s-orbital character of the boron-boron bond. This, of course, assumes that the Fermi contact term dominates<sup>38,39</sup> the spin-spin coupling mechanism.

By use of the experimentally determined value of 149.3 Hz for  $J_{11\text{B}^{11}\text{B}}$  in  $1:1'-[\text{B}_5\text{H}_8]_2$ , a calculated value for  $p^2_{11\text{B}_{\text{apex}(2\text{s})}^{11}\text{B}_{\text{apex}(2\text{s})}}$  of 0.1637 is obtained, which leads to a %  $s$  ( ${}^{11}\text{B}_{\text{apex}(2\text{s})}$ ) = 40.5%, or a hybridization<sup>40</sup> of the apical borons of roughly  $\text{sp}^{1.5}$ . A similarly derived value of  $p^2_{11\text{B}_{\text{apex}(2\text{s})}^{11}\text{B}_{\text{base}(2\text{s})}}$  by using the experimental  $J_{11\text{B}^{11}\text{B}}$  value of 112.0 Hz in  $1:2'-[\text{B}_5\text{H}_8]_2$  gives 0.1284. If it is assumed that the %  $s$  character is constant for the exopolyhedrally bonded apical boron atom in both  $1:1'-[\text{B}_5\text{H}_8]_2$  and  $1:2'-[\text{B}_5\text{H}_8]_2$ , then a value for %  $s$  ( $\text{B}'_{\text{base}(2\text{s})}$ ) is 31.8% and a hybridization of  $\text{sp}^{2.2}$  is calculated for the basal boron ( $\text{B}_2$ ) orbital involved in the bond between the two cages of  $1:2'-[\text{B}_5\text{H}_8]_2$ . If we now assume that the %  $s$  character in the apical and basal borons is relatively constant, the values which we have obtained above can be used to calculate a boron-boron coupling constant in  $2:2'-[\text{B}_5\text{H}_8]_2$  of 82.7 Hz. It is gratifying to see that this value agrees extremely well with the experimentally determined value of  $79.4 \pm 1.4\text{ Hz}$ . Kroner and Wrackmeyer also predicted<sup>14</sup> a very similar value (78.7 Hz) for  $J_{11\text{B}^{11}\text{B}}$  for the two nominally  $\text{sp}^2$ -hybridized boron atoms in  $\text{B}_2(\text{CH}_3)_4$  (the  $p^2$  value gives a calculated hybridization of  $\text{sp}^{2.2}$ ).

(37) Harris, R. K. In "NMR and the Periodic Table"; Harris, R. K.; Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 1, p 9.

(33) Clouse, A. O.; Moody, D. C.; Rietz, R. R.; Roseberry, T.; Schaeffer, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 2496-2501.

(34) (a) Ernst, E. *Adv. Magn. Reson.* **1966**, *2*, 1-135. (b) Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337-340. (c) Lindon, J. C.; Ferrige, A. G. *Ibid.* **1979**, *36*, 277-280.

(35) The expected intensities would be 1:4:10:20:31:40:44:40:31:20:10:4:1.

(36) Since to our knowledge no explicit theoretical line-shape studies for quadrupolar nuclei coupled to other quadrupolar nuclei have illustrated the various states of collapse with discrete figures, this particular line-shape behavior can only be extrapolated by examining the theoretical line shapes for quadrupolar nuclei as the value of  $I$  becomes progressively larger. For example, see ref 29.

(38) (a) Fri, K.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1216-1226. (b) Lynden-Bell, R. M.; Sheppard, N. *Proc. R. Soc. London, Ser. A* **1962**, *A269*, 385-403. (c) Litchman, W. M.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6775-6776. (d) Weylshen, R. E. *Annu. Rep. NMR Spectrosc.* **1977**, *7*, 246-291.

(39) Maciel, G. E. In "N. M. R. Spectroscopy of Nuclei Other than Protons"; Axenrod, T.; Webb, G. A., Eds.; John Wiley: New York, 1974; pp 187-218.

(40) %  $s = (p^2)^{1/2} \times 100$ ,  $\lambda_i^2 = (100\% - \% s) / \% s$ , and %  $p = \lambda_i^2 / (1 + \lambda_i^2) \times 100$ , where  $\lambda_i$  is the hybridization parameter;<sup>41</sup>  $\lambda_i = 0$  for pure  $s$  and  $\lambda_i \rightarrow \infty$  for pure  $p$ .

(41) Bingel, W. A.; Luttke, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 899-990.

In examining this relationship between the % *s* character and the boron–boron spin–spin coupling constant, it should be noted that the good agreement obtained above allows the use of the experimentally determined coupling constants to estimate the hybridization of the boron atoms or, conversely, to use theoretically derived orbital electron densities to get some idea of the magnitude of the boron–boron coupling constant.

For example, Gaines et al.<sup>18</sup> recently reported the first compounds containing a trigonal boron moiety  $\sigma$ -bonded to a boron in boron hydride clusters, 1-(Cl<sub>2</sub>B)B<sub>3</sub>H<sub>8</sub> and 1-(Cl<sub>2</sub>B)-2-ClB<sub>3</sub>H<sub>7</sub>. Boron-11 NMR spectra of these two compounds provided  $J_{\text{B}_1\text{B}_2}$  values of  $\sim 124$  Hz for 1-(Cl<sub>2</sub>B)B<sub>3</sub>H<sub>8</sub> and  $\sim 122$  Hz for 1-(Cl<sub>2</sub>B)-2-ClB<sub>3</sub>H<sub>7</sub>. If it is assumed that the boron atom in the -BCl<sub>2</sub> moiety is hybridized sp<sup>2</sup> and also that the value of sp<sup>1.5</sup> for the apical boron obtained from 1:1'-[B<sub>3</sub>H<sub>8</sub>]<sub>2</sub> is still valid, a calculated  $J_{\text{B}_1\text{B}_2}$  value of 118.8 Hz is obtained. On the basis of the assumptions used and the approximate experimental values reported, the agreement between the calculated and experimental values appears to be very good.

Similarly, a recent statement that the  $J_{\text{B}_1\text{B}_2}$  value of 105 Hz determined in 1:2'-[B<sub>10</sub>H<sub>13</sub>]<sub>2</sub> is a normal value expected for a two-center, two-electron, B–B bond with the borons having sp<sup>3</sup> hybridization<sup>17</sup> appears to be incorrect. In fact, a calculation of the type described above gives a boron–boron coupling constant of 42.2 Hz for two boron atoms bonded by sp<sup>3</sup> hybridized orbitals. Conversely, with use of the 105-Hz experimental value, an average hybridization of the boron atoms of sp<sup>1.9</sup> can be calculated.

The % *s* character of the coupled boron atoms in 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub> calculated from the observed  $J_{\text{BB}'}$  (137 Hz) is 39%, or a hybridization of sp<sup>1.6</sup>. Fehlner has recently studied 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub> using photoelectron spectroscopy and has proposed a significant  $\pi$ -type interaction across the exopolyhedral B–B bond.<sup>200</sup> Thus, we would also expect, on the basis of the calculated low *p* character of the exopolyhedral  $\sigma$ -bond, that *p*-orbital electron density is available for  $\pi$ -type bonding. Likewise, for the mixed-cage compound<sup>19</sup> 2':2-[1',5'-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>][1,6-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>] a hybridization of sp<sup>1.7</sup> is calculated for the exopolyhedral  $\sigma$ -bond contribution from B2, and we would predict a similar barrier to rotation as observed above by Fehlner for 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub>.

By use of the experimental coupling constants, from Table I with eq 5, the % *s* character of each boron hybrid orbital in the exopolyhedral bonds of 3:3'-, 1:3'-, and 1:5'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub> can be determined as follows: B1 = 34.3%; B3 = 40.7%; and B5 = 39.4%. Use of eq 4 predicts a value of 145.8 Hz for  $J_{\text{BB}'}$  in 3:5'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub>, which is only in fair agreement with the experimental estimate of  $\geq 100$  Hz. Likewise, the predicted  $J_{\text{BB}'}$  value for 1:1'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub> is 100 Hz and for 5:5'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub> is 140.4 Hz.

The <sup>11</sup>B NMR spectrum of 3:5'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub> deserves special comment. As mentioned above a consideration of the chemical shift difference between B3 and B5' and a reasonable estimate of the boron–boron coupling constant lead one to conclude that the spectrum should display second-order effects due to strong homonuclear boron–boron coupling. Even though magnetic nonequivalence of two boron nuclei has been observed to affect the line shape of a <sup>1</sup>H-coupled boron spectrum,<sup>42</sup> to our knowledge this is the first time that second-order effects due to a strong homonuclear coupling between two quadrupolar nuclei have been clearly observed in a <sup>1</sup>H-decoupled boron spectrum. A dearth of published theoretical works<sup>43</sup> on the effect of strong homonuclear coupling on line shapes of quadrupolar nuclei hinders attempts to extract a more exact value of the coupling constant (and <sup>11</sup>B chemical shifts) from line shape simulations of 3:5'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub>. For this reason extended iteration of the <sup>11</sup>B spectrum using the PANIC program was not performed, and the reported values are only approximate. It is possible the the use of higher

rank coupling as described by Siddall<sup>43</sup> is applicable here and that the theory of Pyper<sup>44</sup> for calculating NMR line shapes of spin 1/2 nuclei coupled to quadrupolar nuclei should be extended to quadrupolar nuclei coupled to other quadrupolar nuclei. Clearly further work is needed in this area. The <sup>10</sup>B spectrum of this multiplet, which should be first order for <sup>10</sup>B–<sup>11</sup>B coupling (though the <sup>10</sup>B–<sup>10</sup>B isotopomer would still be strongly coupled), is very broad and essentially featureless.

A previous study<sup>11</sup> has estimated that  $J_{\text{B}_1\text{B}_2}$  in the closed three-center, two-electron BBB bond of B<sub>3</sub>H<sub>7</sub>·CO is 11 Hz. This value is similar to the values determined in this study for  $J_{\text{B}_1\text{B}_2}$  in 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> (9.2, 9.7 Hz) and in the two cages of 3:3'-[2,4-C<sub>2</sub>B<sub>3</sub>H<sub>6</sub>]<sub>2</sub> (9.3, 9.8 Hz). Examination of the localized valence structure<sup>45</sup> for 2,4-C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> shows that B<sub>5</sub> and B<sub>6</sub> are joined in a symmetrical closed three-center, two-electron BBB bond with B<sub>1</sub>, further implying that  $J_{\text{BB}}$  in a closed three-center, two-electron bond is small.

It is interesting to note that recently Morris and co-workers<sup>46</sup> have measured  $J_{\text{BB}}$  values in the series of neutral B<sub>3</sub>H<sub>7</sub>(NR<sub>*n*</sub>H<sub>3-*n*</sub>) compounds where R = CH<sub>3</sub> and *n* = 0, 1, 2, and 3 and in the anionic compounds [B<sub>3</sub>H<sub>7</sub>(X)]<sup>-</sup> where X = Cl, NCS, and (N-C)BH<sub>3</sub>. These compounds should also contain closed three-center, two-electron bonds; however the values of  $J_{\text{BB}}$  are larger and fall in the range of 16.5–21.0 Hz. This apparent contradiction can be understood in terms of evidence presented by these workers that the skeletal bonding in at least some of these compounds could have substantial contributions from two-center, two-electron bonds which would increase the value of  $J_{\text{BB}}$ . It should be noted that these values (16.5–21.0 Hz) bracket the value<sup>12</sup> of the base-to-apex  $J_{\text{BB}}$  of 19.4 Hz in pentaborane(9) whose localized valence structure<sup>45</sup> can be described as a resonance hybrid of two two-center, two-electron bonds and a three-center, two-electron bond forming four equivalent bonds between the four equivalent basal borons and the apical boron.

It has been established from molecular orbital calculations<sup>45b,47</sup> and from reactivity studies<sup>48,49</sup> of carboranes and the boron hydrides that the electronic character of an apical boron is quite different from a basal boron. Typically apical borons display larger boron–hydrogen coupling constants than do basal borons, reflecting the supposedly larger % *s* hybridization of boron in the boron–hydrogen bond of the apical borons. From the experimentally observed  $J_{\text{BH}}$  values for a variety of boranes and carboranes, a set of S<sub>*B*</sub>-orbital populations have been derived and were found to correlate well with those obtained from theoretical calculations.<sup>13,14</sup> Although rigorous theoretical calculations for the compounds in this study are not yet available, the % *s* character of the exopolyhedral boron–boron bonds reported above do generally correlate well with those values derived from  $J_{\text{B-H}}$  of the parent compounds. The largest value among the B<sub>3</sub>H<sub>9</sub> dimers is found for 1:1'-[B<sub>3</sub>H<sub>8</sub>]<sub>2</sub> ( $J_{\text{BB}'}$  = 149.3 Hz) between two apical borons, while the smallest value is found in 2:2'-[B<sub>3</sub>H<sub>8</sub>]<sub>2</sub> ( $J_{\text{BB}'}$  = 79.4 Hz), between two basal borons. This is, in fact, the same ordering of magnitudes found for apical and basal  $J_{\text{BH}}$  values<sup>50</sup> in B<sub>3</sub>H<sub>9</sub>. The high *s*-orbital character of the exopolyhedral boron–boron bond in 1:1'-[B<sub>3</sub>H<sub>8</sub>]<sub>2</sub> should also allow significant interactions involving *p* orbitals on the two apical borons, such as has been proposed<sup>200</sup> for 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub>. Indeed, a theoretical calculation<sup>51</sup> has shown that the *p* orbitals not involved in the

(44) (a) Pyper, N. C. *Mol. Phys.* **1971**, *21*, 977–988. (b) Harris, R. K.; Pyper, N. C. *Ibid.* **1975**, *29*, 205–223.

(45) (a) Lipscomb, W. N. *Acc. Chem. Res.* **1973**, *6*, 257–262. (b) Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1972**, *94*, 8692–8699. (c) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *Ibid.* **1977**, *99*, 6226–6237.

(46) Jacobsen, G. B.; Morris, J. H.; Reed, D. J. *Chem. Res., Synop.* **1983**, 42–43.

(47) Switkes, E.; Epstein, I. R.; Tossell, J. A.; Stevens, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1970**, *92*, 3837–3846.

(48) (a) Olsen, R. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5072–5075. (b) Onak, T.; Dunks, G. B.; Beaudet, R. A.; Poynter, R. L. *Ibid.* **1966**, *88*, 4622–4625.

(49) Onak, T. "Organoborane Chemistry"; Academic Press: New York, **1975**; pp 196–198.

(50) In ref 7, p 100.

(42) Farrar, T. C.; Johannesen, R. B.; Coyle, T. D. *J. Chem. Phys.* **1968**, *49*, 281–285.

(43) (a) Siddall, T. H., III; Flurry, R. L., Jr. *J. Magn. Reson.* **1980**, *39*, 487–497. (b) Siddall, T. H., III; Flurry, R. L., Jr. *J. Inorg. Nucl. Chem.* **1981**, *43*, 659–662. (c) Siddall, T. H., III; Flurry, R. L., Jr. *J. Magn. Reson.* **1981**, *43*, 357–372. (d) Siddall, T. H., III *J. Phys. Chem.* **1982**, *86*, 91–96.



exopolyhedral boron-boron  $\sigma$  bond of 1:1'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub> are oriented in a fashion suitable for multiple bonding. However, on the basis of the observed<sup>20a</sup> boron-boron bond distance of 1.74(6) Å it was concluded that no such  $\pi$ -type interactions are present.

The % *s* character at boron in the exopolyhedral boron-boron bonds as calculated above from eq 4 for the possible dimers of 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> are B3 (40.7%)  $\cong$  B5 (39.4%) > B1 (34.3%). The exopolyhedral % *s* character for the boron atoms in 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> may be calculated from the experimental values<sup>52</sup> of  $J_{BH}$  with the relationship<sup>52,53</sup> % *s* = 0.312 $J_{BH}$ , but the same ordering is not obtained: B3 (57%,  $J_{BH}$  = 182 Hz)  $\cong$  B1 (56%,  $J_{BH}$  = 179 Hz) > B5 (52%,  $J_{BH}$  = 169 Hz). In both cases, however, boron atom B3 has the highest *s* character. This is consistent with the higher electronegativity of the two neighboring carbons relative to boron which increases the p-orbital contribution of the B3 atom toward the cage B-C bonds, thereby increasing the s-orbital contribution of these borons toward the exopolyhedral bonds.<sup>52</sup> An additional observation is that the largest coupling constants ( $J_{BB'}$  and  $J_{BH}$ ) in these cage compounds involve boron atoms (B3 in 2,4-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, B1 in B<sub>5</sub>H<sub>9</sub>) which can be described as having fractional closed three-center, two-electron bonding in the skeletal bonds<sup>45a</sup> to the rest of the cage.

In summary, it has been shown that Kroner and Wrackmeyer's correlation<sup>14</sup> of  $J_{BB'}$  with the degree of *s* character of the hybrid orbitals involved in the boron-boron bond can be empirically

extended to boron-boron 2-center, 2-electron bonds. Large values of  $J_{BB'}$  in the boron-boron linked boron hydride and carborane cages are found to be attributable to high degrees of *s* character in the hybrid orbitals involved in the exopolyhedral 2-center, 2-electron, boron-boron bond. Likewise, small values of  $J_{BB'}$  are indicative of low *s* character as in the various three-center, two-electron intracage<sup>11,46</sup> boron-boron-boron bonds. This correlation now provides a probe of the various bonding situations of boron based on experimentally determined spin-spin coupling constants and, in special cases, allows a determination of the hybridization of a boron in a particular bond with a reasonable degree of confidence.

**Acknowledgment.** J.A.A. and J.D.O. gratefully acknowledge financial support from the National Science Foundation (CHE80-13694) and valuable assistance from Dr. Ron Garber in obtaining the relaxation time measurements and Dr. P. D. Ellis for the  $T_1$  program. R.J.A. and L.G.S. thank the National Science Foundation and the Army Research Office for support. The use of the facilities of the University of South Carolina Regional NMR Center, funded by the National Science Foundation (CHE82-07445), is also gratefully acknowledged. J.D.O. thanks Dr. R. E. Williams for the gift of 2,5-C<sub>2</sub>B<sub>5</sub>H<sub>7</sub>.

**Registry No.** 1:1'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>, 71595-75-0; 1:2'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>, 31831-99-9; 2:1'-[1-(CH<sub>3</sub>)B<sub>5</sub>H<sub>7</sub>][B<sub>5</sub>H<sub>8</sub>], 89017-48-1; 2:2'-[B<sub>5</sub>H<sub>8</sub>]<sub>2</sub>, 28775-81-7; 2:2'-[1-(CH<sub>3</sub>)B<sub>5</sub>H<sub>7</sub>]<sub>2</sub>, 71605-80-6; 2:2'-[1-(CH<sub>3</sub>)B<sub>5</sub>H<sub>7</sub>][B<sub>5</sub>H<sub>8</sub>], 89017-49-2; 1:3'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>, 70480-12-5; 3:3'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>, 59419-84-0; 3:5'-[2,4-C<sub>2</sub>B<sub>5</sub>H<sub>6</sub>]<sub>2</sub>, 70513-48-3; 2:2'-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sub>2</sub>, 60569-26-8; 2:2',3':2''-[1,5-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>][1'',5''-C<sub>2</sub>B<sub>3</sub>H<sub>4</sub>], 74501-91-0; B, 7440-42-8.

(51) Moore, E. B., Jr. *J. Am. Chem. Soc.* **1963**, *82*, 676-679.

(52) Onak, T.; Wan, E. *J. Chem. Soc., Dalton Trans.* **1974**, 665-669.

(53) Williams, R. E.; Harmon, K. M.; Spielmann, R., *J. OTS, AD* **1964**, No. 603782.

## Electron Density Superposition Errors in Ethynyllithium

Steven M. Bachrach and Andrew Streitwieser, Jr.\*

*Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received July 25, 1983*

**Abstract:** Typical ab initio calculations with modest basis sets of organolithium and related compounds juxtapose an electron-deficient center having many functions (lithium) and an electron-rich center with function deficiencies (carbanion), a situation that leads to superposition errors in both energy and electron density. Electron density study of ethynyllithium exemplifies the problem and shows that such errors are minimized by proper use of diffuse functions in the basis; diffuse functions are more effective in reducing electron density superposition errors than polarization functions (d orbitals).

### 1. Introduction

Much discussion in the recent literature has centered on the nature of the carbon-lithium bond, particularly with the growing use of organolithium reagents in organic synthesis. Schleyer and co-workers have argued that the C-Li bond, though largely ionic, contains significant covalent character supplied through lithium p orbitals.<sup>1</sup> This conclusion was drawn from structural aspects and Mulliken populations of various organolithium compounds. The structures of organolithium compounds have the unusual property of lithium atoms bridging anionic centers in an effort

to minimize the electrostatic energy. Since Schleyer found definite Mulliken population in Li p orbitals and Mulliken bond population involving Li p orbitals, he concluded that Li p orbitals are used to describe the covalent bonding in organolithium compounds.

The Streitwieser group, on the other hand, has maintained that the C-Li bond is predominantly ionic and bases their argument on integrated spatial electron populations (ISEP).<sup>2</sup> ISEP differs from Mulliken populations in that ISEP assigns electrons to regions of space regardless of where the basis functions are centered; Mulliken populations assign electrons to atoms by determining the number of electrons in each basis function centered on each atom, totally neglecting the spatial extent of these functions.

There exists general agreement that organolithium compounds may be essentially viewed as simply ion pairs. The carbon of the

(1) (a) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527. (b) Kos, A. J.; Schleyer, P. v. R. *Ibid.* **1980**, *102*, 7928. (c) Apeloig, Y.; Clark, T.; Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R. *Isr. J. Chem.* **1980**, *20*, 43. (d) Kos, A. J.; Jemmis, E. D.; Schleyer, P. v. R.; Gleiter, R.; Fischbach, V.; Pople, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4996. (e) Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 448. (f) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. (g) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617. **Added in Proof:** Professor Schleyer now believes (personal communication) that the C-Li bond is essentially ionic.

(2) (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Klein, J.; Kost, D.; Schriver, G. W.; Streitwieser, A., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.