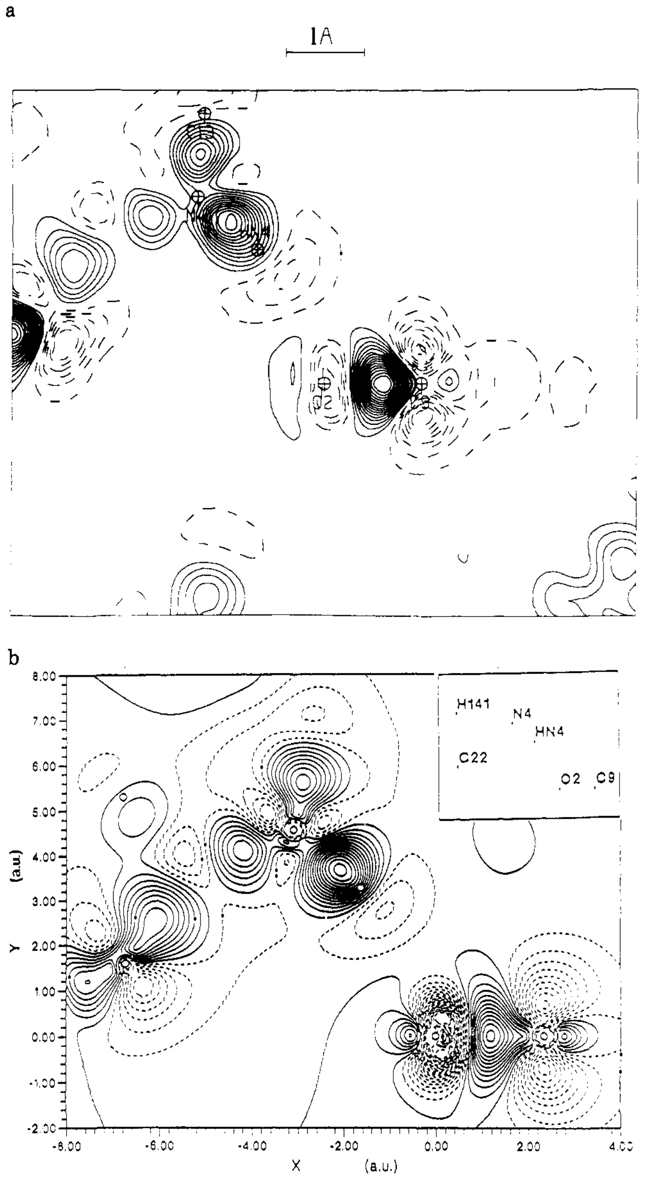

Figure 3. Deformation density in the plane defined by the C9–O2···N4 atoms (*β* turn). (a) Experimental dynamic model map; contours as in Figure 2a. (b) Theoretical map; contours as in Figure 2b.

formation density in the plane containing the N4, O2, and C9 atoms, respectively obtained from the enkephalin experimental model (Figure 3a) and from the SCF calculation on the fragment (Figure 3b). The O2 oxygen lone pairs do not show up on this map, due to the orientation of the C9–N2 and C9–C1 bonds (both represented by CH bonds in the model fragment) in a plane practically perpendicular to the figure. H(N4) is then faced to a region of density depopulation around O2, a situation which does not agree with the standard hydrogen-bond concept. An investigation of the electrostatic potential derived from the experimental charge distribution,[8a] however, suggests that an electrostatic interaction remains possible. As a matter of fact, the electrostatic potential around the O2 atom has not a "rabbit ear" shape[8] but rather an almost spherical "skull" shape (see Figure 6a,b in ref 8a). Calculations are now being carried out on other model fragments of the molecule in order to investigate, in connection with the experimental electron distribution, the various forms of hydrogen bonding between the enkephalin molecule and the three molecules of crystallization water. An investigation of the topological properties of the Laplacian of the total charge density, either theoretical[9] or experimental,[10] could also help in locating the nonbonded charge concentrations responsible for the formation of hydrogen bonds.

Acknowledgment. The quantum chemical calculations have been carried out on the CRAY-2 computer of the Centre de Calcul Vectoriel de la Recherche (Palaiseau, France), through a grant of computer time from the CCVR.

Registry No. Leu-enkephalin, 58822-25-6.

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(10) (a) Stewart, R. F. In *Application of Charge Density Research to Chemistry and Drug Design*; Jeffrey, G. A., Piniella, J. F., Eds.; NATO ASI Series, Physics; Plenum: New York, 1991; Vol. 250, pp 63–101. (b) Bianchi, R.; Destro, R.; Gatti, C.; Merati, F. *Ibid.*; p 339. (c) Bianchi, R.; Destro, R.; Merati, F. *Ibid.*; p 340. (d) Souhassou, M.; Li, N. American Crystallographic Meeting, Toledo, OH, July 1991.

Boron–Boron Double Bonding in the Species $[B_2R_4]^{2-}$: Synthesis and Structure of $[\{(Et_2O)Li\}_2\{Mes_2BB(Mes)Ph\}]$, a Diborane(4) Dianion Analogue of a Substituted Ethylene

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Compounds of boron are characterized by an enormous range of structural types that often possess features rarely found among derivatives of other elements. Accordingly, research on their chemical properties has been prominent for more than three decades.[1] Nonetheless, there remain numerous classes of boron compounds that are, at present, either unknown or only partially understood. For example, there is relatively little structural information available for compounds that have bonds of multiple character between two boron centers,[2-4] nor have compounds of the general formula $(MBR_2)_n$ (M = alkali metal, R = organo group, n = 1, 2, 3...) been well characterized experimentally.[5] In

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(1) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(2) Structural data appears to be confined to transition metal complexes of heterocycles that incorporate B_2 or B_3 units. B–B distances as low as 1.563 Å have been observed in such complexes. See in the following references: Robinson, W. T.; Grimes, R. N. *Inorg. Chem.* **1975**, *14*, 3056. Herberich, G. E.; Hessner, B.; Hostalek, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 642. Herberich, G. E.; Hessner, B.; Hostalek, M. *J. Organomet. Chem.* **1988**, *355*, 473. Davis, J. H.; Sinn, E.; Grimes, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 4784. A series of uncomplexed three-membered rings with B–B distances as low as 1.58 Å have been reported: Dirschl, F.; Hanecker, E.; Nöth, H.; Rattay, W.; Wagner, W. *Z. Naturforsch.* **1986**, *41b*, 32. van Bonn, K.-H.; Schreyer, P.; Paetzold, P.; Boese, R. *Chem. Ber.* **1988**, *121*, 1045. Meyer, H.; Schmidt-Lukasch, G.; Baum, G.; Massa, W.; Berndt, A. *Z. Naturforsch.* **1988**, *43b*, 801.

(3) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 870. Berndt, A.; Klusik, H.; Schlüter, K. *J. Organomet. Chem.* **1981**, *222*, C25. These papers describe the preparation and the solution EPR spectra of the tetraalkyldiborane(4) radical anions $[B_2R_4]^{\bullet-}$, e.g., (R = $CH_2(t\text{-Bu})$, which presumably have multiple B–B character. A two-electron reduction of B_2R_4 was not reported.

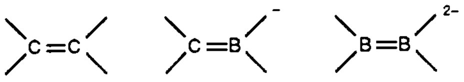
(4) The existence in solution of species of the type $[B_2Ar_4]^{\bullet-}$ (Ar = $C_6H_4(4\text{-}NMe_2)$) has been postulated in the following reference: Leffler, J. E.; Watts, G. B.; Tanigaki, T.; Dolan, E.; Miller, D. S. *J. Am. Chem. Soc.* **1970**, *92*, 6825.

(5) Compounds of formula $MB(C_4H_9)_2$ (M = alkali metal) have been implicated in the reduction of $ClB(C_4H_9)_2$ by Na/K alloy: Auten, R. W.; Kraus, C. A. *J. Am. Chem. Soc.* **1952**, *74*, 3398. For further information on the reduction of diorganoboron halides by Li, Na/K, or Mg, see the following references: Köster, R.; Benedikt, G. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 515. Köster, R.; Benedikt, G.; Grassberger, M. A. *Justus Liebigs Ann. Chem.* **1968**, *719*, 187.

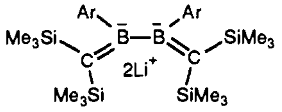
this paper, the synthesis and structure of the species $[\{(Et_2O)Li\}_2\{Mes_2BB(Mes)Ph\}]$ (**1**), which (a) corresponds to the formula $[Li(Et_2O)BR_2]_2$ and (b) has a B–B double bond, are now described.

The title compound was synthesized by stirring $Mes_2BB(Mes)Ph$[6] (**2**) with excess lithium powder in an ether/hexane mixture. Filtration and recrystallization from Et_2O afforded **1** as red crystals in good yield. ^{11}B NMR solution studies indicated a chemical shift difference of over 70 ppm between **1** (+24.7 ppm) and **2** (+99 ppm). A single-crystal X-ray crystallographic study afforded the structure illustrated in Figure 1. Clearly, the precursor **2** has been twice reduced to form a contact ion triple with two ether-solvated lithium cations. The major structural features of **1** are best illustrated by a comparison of its structural parameters with those of **2**,[8] as shown in Table I. The most dramatic changes upon reduction involve the closure of the angle between the boron planes from 79.1° to 7.3° and the contraction of the B(1)–B(2) bond length from 1.706 (12) to 1.636 (11) Å. Other notable differences are the longer (~0.06 Å) B–C bonds and the smaller (6–11°) C–B–C angles of **1**. There are also changes in the torsion angles subtended by the aromatic rings. In particular, the plane of the C(1) ring becomes almost parallel (torsion angle 6.3°) to the plane containing the B(1) atom. As Figure 1 shows, the structure of **1** includes two ether-solvated Li^+ cations. Each lithium interacts to varying degrees with the boron and carbon centers. The closest Li···B contacts involve Li(2)···B(2) (2.339 (16) Å) and Li(2)···B(1) (2.360 (13) Å). Li(2) also interacts with the carbon atoms C(1) (2.426 (15) Å), C(2) (2.321 (16) Å), and C(16) (2.472 (15) Å). The Li(1) center is less strongly bound (2.497 (15) Å for Li(1)···B(1) and 2.395 (15) Å for Li(1)···B(2)) to the boron centers but is more strongly associated with the carbon centers, as exemplified by the Li(1)···C distances of 2.276 (15) Å for C(7), 2.342 (15) Å for C(12), and 2.176 (15) Å for C(25). Li(1) and Li(2) are 1.09 and 1.73 Å distant from, and on the opposite sides of, the averaged $B_2\{C(ipso)\}_4$ plane. In addition, the Li(1)B(1)B(2)Li(2) array forms an irregular butterfly shape (fold angle 158.8°) such that the angles between the Li(1)B(1)B(2) and Li(2)B(1)B(2) planes and the averaged $B_2\{C(ipso)\}_4$ plane are 29.2 and 50.4°.

The structural details above suggest two obvious interpretations based upon idealized models. The first views the molecule as isoelectronic to the corresponding ethylene derivatives, as depicted schematically by the following sequence in which CH_2 is replaced by BH_2^- moieties.



Several features of the structure of **1** are in accordance with this view. The molecule has an almost planar core composed of two boron and four ipso carbon atoms. Moreover, the B–B bond is shortened by about 0.07 Å. In addition, the CBC angles are less than 120°, in agreement with the multiple character of the B–B bond. The B–B distance, however, is not as short as that expected[9,10] for a "normal" B–B double bond (1.5–1.53 Å). Most probably, the presence of adjacent negative charges on the boron centers results in B–B bond elongation due to the Coulombic repulsion. A comparison of the B–B distance in **1** with that observed in the interesting dianion **3**[11] is thus most apt.



Ar = Mes or 2,3,5,6-Me_4C_6H

3

This compound, which can be considered to have a single bond between two negatively charged borons, has a B–B distance of 1.859 (8) Å. In other words, the B–B bond in **1** is over 0.22 Å (~12%) shorter. By this criterion, at least the term "double bond" is justified for the B–B interaction in **1**.

A second possible interpretation of the structure involves a diborane model in which the bridging hydrogens are replaced by lithiums. Thus, the structure of **1** may be compared to that of $(HBMes_2)_2$,[12] wherein the B···B separation is 1.851 (3) Å with B–C distances of 1.602 (3) Å and CBC angles of 123.2 (1)°. These values underline the dramatic structural changes that take place when the bridging hydrogens are replaced by the more electropositive lithiums. The molecule **1** thus corresponds to an original model[13] proposed for B_2H_6 which viewed it as an ethylene-like $[H_2BBH_2]^{2-}$ fragment with two H^+ ions embedded in the π-electron cloud.

An additional noteworthy feature of **1** is its stoichiometry, which corresponds to that of the lithium derivative $[Li(Et_2O)BR_2]_2$. No compounds corresponding to the general formula MBR_2 (M =

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[6] (a) The synthetic method described here is based upon that reported in the following references: Biffar, W.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 56; Schluter, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 57. With cooling in a dry ice/acetone bath and rapid stirring, $B_2(OMe)_4$[6b] (0.99 g, 6.8 mmol) in pentane (40 mL) was added by a double-tipped needle to a slurry of LiMes (2.65 g, 21 mmol) in pentane (50 mL). The mixture was allowed to warm to room temperature overnight. Filtration and volume reduction of the filtrate gave, upon cooling overnight in a −20 °C freezer, $Mes_2BB(Mes)OMe$ as colorless crystals: yield 1.53 g, 55%; ^1H NMR (C_6D_6) δ 6.63 (s, 4 H), 6.56 (s, 2 H) 3.34 (s, 3 H (OMe)), 2.16 (s, 12 H, OMe), 2.01 (s, 6 H), 2.0 (s, 3 H), 1.95 (s, 6 H); ^{11}B NMR (C_6D_6) δ 98, 59. $Mes_2BB(Mes)OMe$ (1.15 g, 2.8 mmol) in pentane (50 mL) was added dropwise to a rapidly stirred slurry of LiPh (0.38 g, 4 mmol) in pentane (30 mL) with cooling in a dry ice/acetone bath. The mixture was allowed to warm to room temperature overnight and then filtered. Reduction in volume of the filtrate to ~30 mL gave, upon cooling in a −20 °C freezer, the product $Mes_2BB(Mes)Ph$ (**2**) as colorless crystals: yield 1.03 g, 80%; mp 171–173 °C; ^1H NMR (C_6D_6) δ 7.61 (d, 2 H), 7.11 (t, 3 H), 6.75 (s, 6 H), 2.22 (s, 12 H), 2.16 (s, 3 H), 2.12 (s, 6 H), 2.04 (s, 6 H); ^{11}B (C_6D_6) δ 99. The title compound **1** was synthesized by the dropwise addition of $Mes_2BBMes(Ph)$ (0.71 g, 1.53 mmol) in hexane (30 mL) to lithium powder (0.035 g, 5 mmol) in Et_2O (50 mL) cooled in a dry ice/acetone bath. The mixture was stirred for 1 h and then allowed to reach room temperature within 2 h. Stirring for an additional 3 h gave a red solution. Filtration and removal of solvents under reduced pressure gave a dark red solid. This was redissolved in warm Et_2O (30 mL). Filtration and cooling in a −20 °C freezer overnight gave the product $[\{(Et_2O)Li\}_2\{Mes_2BB(Mes)Ph\}]$, **1**, as dark red crystals: yield 0.67 g, 70%; mp 82–84 °C; ^{11}B NMR (Et_2O, C_6D_6) δ 24.7. (b) Brotherton, R. J.; McCloskey, A. L.; Boone, J. L.; Manasevit, H. M. *J. Am. Chem. Soc.* **1960**, *82*, 6245.

[7] Crystal data for **1** with Mo Kα radiation (λ = 0.71069 Å), *T* = 130 K; monoclinic *Pn*, *a* = 8.917 (2) Å, *b* = 17.379 (4) Å, *c* = 12.222 (3) Å, β = 92.89 (2)°, *Z* = 2; 2349 data with $I > 3\sigma(I)$, *R* = 0.073. One of the ether molecules (O(1)) is disordered between two sites of occupancy 75% and 25%. The site of greatest occupancy is shown in Figure 1.

[8] (a) Moezzi, A. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. Unpublished data. Full details of this structure will be published in a full account of this work. It represents the first[8b] crystal structure of a tetraorganodiborane(4). (b) Professor Berndt has informed us that the structure of $(Me_3Si)_2CH(Dur)BB(Dur)CH(SiMe_3)_2$ (Dur = 2,3,5,6-Me_4C_6H) has been determined by his group. The B–B distance is 1.739 (7) Å. Berndt, A.; Allwohn, J. Unpublished work.

[9] The radius of three-coordinate boron is about 0.85 Å,[10a] which affords a value of ~1.7 Å for a B–B single bond between trigonal planar boron atoms. By analogy with carbon systems, where the distance in ethylene is 0.2 Å shorter than that in ethane,[10b] a B–B double bond distance of 1.5 Å may be estimated. Another estimate of the B–B double bond length may be obtained by subtracting 10% from the single bond distance, which affords a value of 1.53 Å. Pauling cites the double bond radius of boron as 0.76 Å, in other words, 1.52 Å for a B–B double bond: Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1944. Boron–boron bonds as short as ca. 1.6 Å have been reported for binary metal borides: Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; p 1052. For a recent theoretical treatment of the electronic properties of such compounds, see the following reference: Meyer, R. M.; Hoffmann, R. *Chem. Mater.* **1991**, *3*, 547.

[10] (a) Values given for the radius of boron vary considerably (from about 0.8 to 0.9 Å).[1b] A value of 0.85 Å, however, is usually consistent with structural data for three-coordinate boron. The B–B distance seen in **2** bears out this value. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 18.

[11] Pilz, M.; Allwohn, J.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1030.

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[13] Wiberg, E. Z. *Anorg. Allg. Chem.* **1928**, *173*, 199. Pitzer, K. S. *J. Am. Chem. Soc.* **1945**, *67*, 1126.

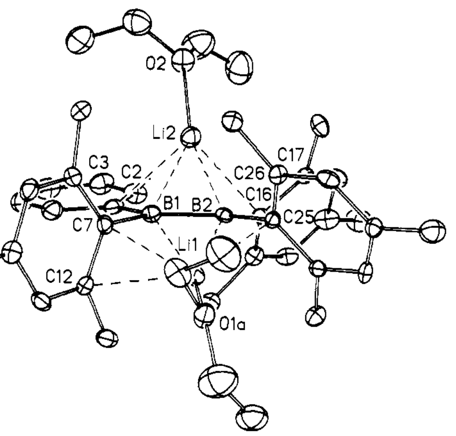

Figure 1. Computer-generated thermal ellipsoid plot of **1**. Some important bond distances (angstroms) and angles (degrees) not given in the text or Table I are as follows: Li(1)–O(1a) = 1.962 (15), Li(1)–O(1b) = 1.927 (22), Li(2)–O(2) = 1.918 (15); B(2)–B(1)–C(1) = 124.6 (4), B(2)–B(1)–C(7) = 125.8 (6), B(1)–B(2)–C(16) = 122.2 (6), B(1)–B(2)–C(25) = 128.8 (6). Interplanar angles between the averaged planes at the following atoms are as follows: B(1) and C(1), 6.3°; B(1) and C(7), 86.8°; B(2) and C(16), 56.8°; B(2) and C(25), 56.6°.

Table I. Selected Bond Distances (Å) and Angles (deg) in **1** and **2**

	1	**2**
B(1)–B(2)	1.636 (11)	1.706 (12)
B(1)–C(1)	1.613 (11)	1.565 (12)
B(1)–C(7)	1.648 (7)	1.579 (11)
B(2)–C(16)	1.642 (10)	1.576 (9)
B(2)–C(25)	1.643 (11)	1.586 (12)
C(1)–B(1)–C(7)	109.5 (5)	115.1 (7)
C(10)–B(2)–C(25)	108.9 (6)	119.8 (6)
angle between B(1) and B(2) planes	7.3	79.1

alkali metal, R = organo group) have been structurally characterized to date. The contrast between **1** and the structures of the dimeric lithium salts of alkyls, aryls, amides, phosphides, or alkoxides further emphasizes the unique structural features observed in **1**.[14]

Finally, it is notable that calculations[15] on the parent compound $Li_2B_2H_4$ show that it is planar and thermodynamically very stable and has a B–B distance of 1.613 Å. An alternative configuration, in which the Li^+ ions are disposed above and below the $B_2H_4^{2-}$ plane, has a B–B distance of 1.629 Å and is 14.9 kcal mol^{-1} less stable. Clearly, the agreement between the theoretical and structural data for **1** is very good. Further calculations on the energy of the π-bonding and the rotation barrier in **1** are in progress.[16]

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support and Professors T. L. Allen, W. H. Fink, and R. Hoffmann for useful discussions. We also thank Professor A. Berndt for making data available to us prior to publication.

Registry No. 1, 139199-40-9; **2**, 139199-38-5.

Supplementary Material Available: Tables of data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (10 pages); listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Three-Dimensional Microscopic ^1H NMR Imaging of Rigid Polymers

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We report the first application of ^1H nuclear magnetic resonance (NMR) to obtain three-dimensional (3-D) spatially resolved images of a rigid polymer. The technique, which has been demonstrated on a polycarbonate sample, uses MREV-8 multiple-pulse homonuclear decoupling[1,2] in combination with 3-D back-projection.[3-6] The image provides a 3-D map of the proton content within the specimen to a spatial resolution of $150_x \times 150_y \times 150_z$ μm^3. The reconstructed surface-rendered image is a reasonably accurate reproduction of the specimen's complex topology.

The inherently broad line widths associated with homonuclear dipolar interactions of abundant proton spins in solids have hampered the rapid development of NMR imaging techniques for materials. Only within the last several years have effective imaging strategies been implemented to overcome broadening effects in rigid, protonated solids. Several techniques for proton NMR imaging of solids have been demonstrated,[6-15] but only in linear (1-D) or planar (2-D) fashion. Spatial discrimination in the third dimension has been difficult to achieve due to the inherently short proton transverse relaxation times (T_2s) in solids. This rapid decay of magnetization has precluded the use of spatial encoding methods, which are commonly used in liquids.[16,17]

Recent work in our laboratory has focused on the use of multiple-pulse coherent averaging of homonuclear broadened lines, which is applied in conjunction with back-projection techniques to obtain 3-D spatially encoded images of proton density. The

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[§] Dow Chemical Company.

[∥] Chemistry Division, Argonne National Laboratory.

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