10 ml of acetone and added to a 100-ml three-necked round-bottomed flask equipped with a Teflon stirring bar, reflux condenser, and a dropping funnel containing a solution of 2.14 g (12.7 mmol) of ethynylcarborane in 25 ml of acetone. A gas bubbler was connected to the flask and a rapid stream of O_2 was bubbled through the solution as the ethynylcarborane solution was added dropwise over a 30-min period. Oxygen was bubbled through the reaction mixture for an additional 2 hr, and then the contents of the flask was poured into 100 ml of ice-cold 3 *M* HCl and extracted with four 100-ml portions of pentane. The pentane extracts were combined, dried over anhydrous $MgSO_4$, and evaporated to dryness. The resulting brown solid was chromatographed on a 1 × 10 in. silica gel column and eluted with hexane to afford 1.10 g (3.29 mmol, 51.7%) of white product, mp 315–317° dec. *Anal.* Calcd for $B_{20}C_8H_{22}$: B, 64.69; C, 28.72; H, 6.58. Found: B, 64.84; C, 28.92; H, 6.24.

Acknowledgments. The authors are indebted to Dr. R. J. Wiersema for the 80.5-MHz ^{11}B nmr spectra and electrochemical measurements and to Professor M. Kubota for helpful discussions. This work was supported in part by the Office of Naval Research and the National Science Foundation under Grant GP-14372X1, to whom we express our thanks.

Resolution of the Accidental Degeneracy in the Spectrum of 2-[2′-Pentaboran(9)yl]pentaborane(9) by Application of Partially Relaxed Fourier Transform Boron-11 Nuclear Magnetic Resonance Spectroscopy[1]

Richard R. Rietz and Riley Schaeffer*

Contribution No. 2186 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received February 16, 1973*

Abstract: The accidental degeneracy in the 70.6-MHz ^{11}B nmr spectrum of 2-[2′-pentaboran(9)yl]pentaborane(9) has been resolved by obtaining a series of partially relaxed Fourier transform (PRFT) spectra. The increased resolution reveals one singlet and three doublets, in accord with the predicted C_{2h} structure.

Structural studies using nmr are often hampered in the case of quadrupolar nuclei by overlap of the broad resoances. Line-narrowing techniques have been shown to be useful where significant chemical shift differences occur.[2] We describe here resolution of overlapping resonances in a case where little chemical shift difference is present.

The molecule chosen for study arises from slow decomposition of liquid pentaborane(9) at room temperature[3] or the hot–cold, flow-quench pyrolysis of gaseous B_5H_9 in the presence of diborane(6) at 140°.[4] The major product in both reactions is 2-[2′-pentaboran(9)-yl]pentaborane(9), 2,2′-$(B_5H_8)_2$.[5] Mass spectra and nmr studies suggest a structure comprised of two B_5H_8 units connected by a boron–boron bond (see Figure 1).

Our recently presented high-field pmr and ^{11}B nmr spectra of 2,2′-$(B_5H_8)_2$[6] support this structure based on the B_5H_9 model. However, neither spectrum displays the expected reduction in molecular symmetry from C_{4v} for B_5H_9 to C_{2h} for 2,2′-$(B_5H_8)_2$. The pmr spectrum of 2,2′-$(B_5H_8)_2$ nearly overlies that of B_5H_9; for the small range of proton chemical shifts, interference from ^{10}B–H septets and nuclear quadrapole broadening (^{11}B, $I = {}^3/_2$; ^{11}B, $I = 3$) cause accidental overlap of the ^{11}B–H quartets.[6] The high-field ^{11}B nmr spectrum of 2,2′-$(B_5H_8)_2$ closely resembles that of B_5H_9, but fails to show the splitting for the different types of basal boron atoms that has been reported for other 2-substituted B_5H_8 derivatives.[7]

Experimental Section

Details of the nmr apparatus,[8] the specific application of the PRFT technique[9] to ^{11}B nmr spectroscopy,[10] and the preparation and purification of 2,2′-$(B_5H_8)_2$[3,4] have been described elsewhere. Spectra were run on a 20% v/v solution in *n*-pentane.

Results and Discussion

Our previously reported high-field, continuous-wave ^{11}B nmr spectrum[6] of 2,2′-$(B_5H_8)_2$ is identical with that shown in Figure 2A. The high-field doublet of intensity 2 is easily assigned to the apical 1,1′ boron atoms by analogy to pentaborane(9). The low-field resonances of intensity 8 must be attributed to the accidental overlap of an expected B(2,2′) singlet ($I = 2$), a B-(3,3′,5,5′) doublet ($I = 4$), and a B(4,4′) doublet ($I = 2$). Attempts to improve the resolution by varying the solvent, concentration, or temperature failed. Noise-modulated proton decoupling and artificial line-narrowing experiments[2] were also unsuccessful.

Despite the small chemical shift differences for three

---

[1] Studies of Boranes. XXXV; for paper XXXIV of this series, see R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, in press.

[2] A. O. Clouse, D. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 2496 (1973).

[3] D. F. Gaines, T. V. Iorns, and E. N. Clevenger, *Inorg. Chem.*, **10**, 1096 (1971).

[4] J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).

[5] Named and numbered under the new rules appearing in *Inorg. Chem.*, 7, 1945 (1968).

[6] R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **11**, 1242 (1972).

[7] (a) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967); (b) A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 1407 (1968); (c) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

[8] A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

[9] R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

[10] A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **94**, 2445 (1972).

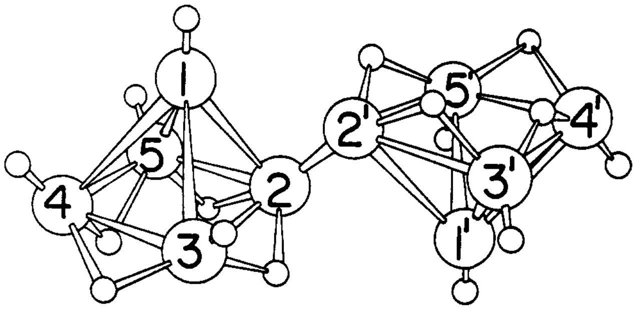


Figure 1. Proposed structure of 2-[2'-pentaboran(9)yl]pentaborane(9), 2,2'-$(B_5H_8)_2$.

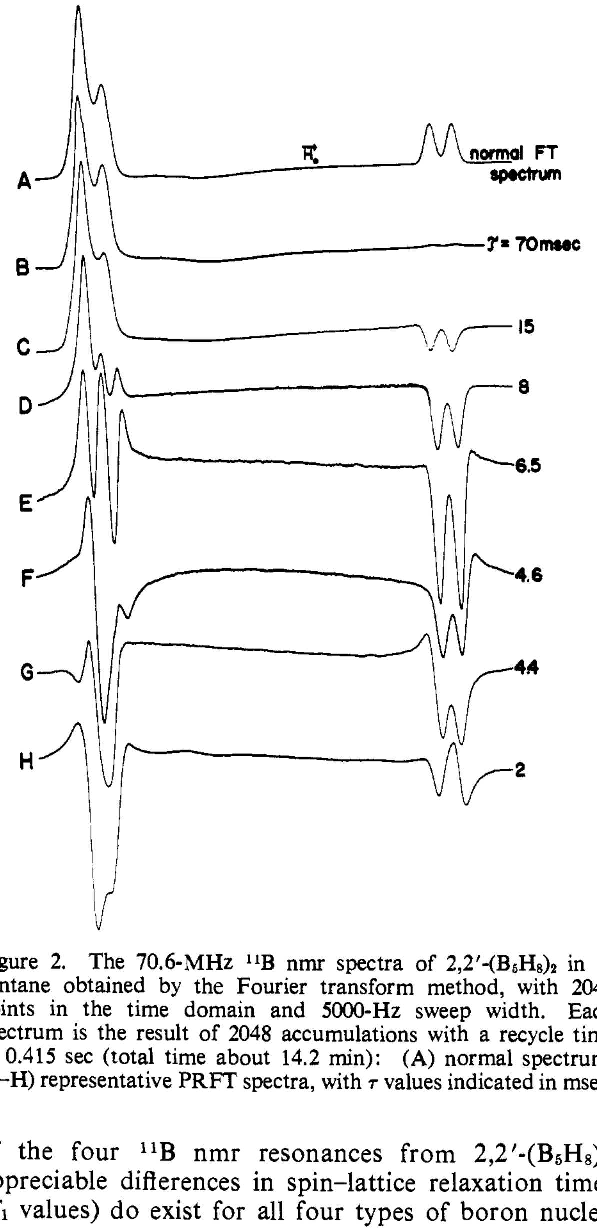


Figure 2. The 70.6-MHz ^{11}B nmr spectra of 2,2'-$(B_5H_8)_2$ in *n*-pentane obtained by the Fourier transform method, with 2048 points in the time domain and 5000-Hz sweep width. Each spectrum is the result of 2048 accumulations with a recycle time of 0.415 sec (total time about 14.2 min): (A) normal spectrum, (B–H) representative PRFT spectra, with τ values indicated in msec.

of the four ^{11}B nmr resonances from 2,2'-$(B_5H_8)_2$, appreciable differences in spin–lattice relaxation times (T_1 values) do exist for all four types of boron nuclei. We have shown before that the PRFT technique can exploit such differences in T_1 values to extract heretofore unobservable lines in the ^{11}B nmr spectrum of *n*-B_9H_{15}.[10] We show here the application of the PRFT method to the ^{11}B nmr spectral ambiguity presented for 2,2'-$(B_5H_8)_2$.

In short, selection of the appropriate interval τ between the 180° pulse and 90° pulse such that $\tau = T_1 \ln 2$ will cause the amplitude (A) of a particular resonance to appear "nulled" (*i.e.*, $A = 0$) with respect to the equilibrium amplitude (A_0) as measured in the normal FT spectrum.[11]

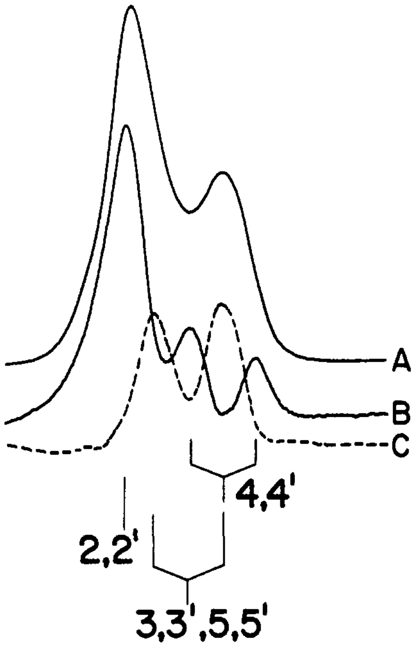


Figure 3. Blowup of low-field resonances of 2,2'-$(B_5H_8)_2$: (A) normal spectrum, (B) PRFT spectrum at τ = 8 msec, (C) "difference" spectrum of Figure 3A minus Figure 3B. Assignments of the resonances are given below the peaks. Chemical shifts and coupling constants (δ, ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (J, Hz)) are: B(2,2'), +8.5 (— —); B(3,3',5,5'), +10.7 (135); B(4,4'), +11.6 (135); and B(1,1'), +50.4 (175).

$$A = A_0[1 - 2 \exp(\tau/T_1)]$$

For example, at τ 70 msec (Figure 2B) the resonances attributed to B(1,1') are nulled. In a set of overlapping resonances arising from several nuclei of varying relaxation times, τ is chosen to null a particular resonance and simplify the spectra.[12]

A series of ^{11}B PRFT spectra for 2,2'-$(B_5H_8)_2$ is shown in Figure 2. The most informative PRFT spectrum results when τ 8 msec (Figure 2D). The B(3,3',5,5') doublet of intensity four at δ +10.7 ppm has been nulled. In this experiment the singlet from B(2,2') and the doublet from B(4,4') have appreciably shorter relaxation times and are completely resolved. B(2,2') and B(4,4') are nulled at τ 5 and 1.5 msec, respectively (neither spectra shown). The remaining PRFT spectra represent experiments in which $\tau \neq T_1 \ln 2$ for any nuclei. Consequently, the resultant spectra are the sums of the amplitudes of the positive and negative resonances involved. The T_1 values obtained are $T_1(1,1') = 100.0 \pm 5.0$, $T_1(2,2') = 2.15 \pm 0.2$, $T_1(3,3',5,5') = 11.4 \pm 0.2$, and $T_1(4,4') = 7.15 \pm 0.2$ msec.

We note that the order of *relative* spin–lattice relaxation times, T_1[B–H(apical)] ≫ T_1[B–H(terminal)] > $T_1(BH_2)$ > T_1(B − B), applies to all the common boron hydrides and carboranes we have observed;[13]

---

[11] (a) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954); (b) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 64.

[12] A more detailed explanation is given in ref 10.

[13] Molecules which have been observed to fit this trend are B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{18}, *n*-B_9H_{15}, $B_{10}H_{14}$, *n*-$B_{18}H_{22}$, 2,4-$B_5C_2H_7$, 1,7-$B_7C_2H_9$, 1,2-$B_8C_2H_{10}$, 1,6-$B_8C_2H_{10}$, 2,3-$B_9C_2H_{11}$, and 5,6-$B_8C_2H_{12}$.

however, excepting the generally longer *relative* relaxation times for apical boron nuclei (regardless of chemical shift), we caution against spectral and structural assignments by this method.

Since B(2,2′) and B(4,4′) have different T_1 values, it is impossible to obtain a PRFT spectrum in which both are nulled and the resonances from B(3,3′,5,5′) are clearly resolved. However, the B(3,3′,5,5′) doublet (Figure 3C) may be easily generated by digitally subtracting the PRFT spectrum containing only B(2,2′) and B(4,4′) (Figure 3B) from the normal spectrum containing all three resonances (Figure 3A). Computer simulation[14] of the low-field resonances generated from peaks of 90 Hz width shows that the doublet of intensity 4 must be the doublet at δ +10.7 ppm in order to reconstruct the normal spectrum, thus confirming our assignment.

The strength of the partially relaxed Fourier transform technique rests in the fact that it obtains increased spectral resolution *not* from chemical shift differences or high magnetic field strengths but from the inherent relative differences in spin–lattice relaxation times of the various types of nuclei in the molecule itself.

Acknowledgments. The authors gratefully note the support of the National Science Foundation (Grant No. GP-24266x). Professor Adam Allerhand, Mr. A. O. Clouse, and Mr. T. Roseberry are acknowledged for the design, building, and operation of the equipment necessary to observe PRFT spectra. Professor Allerhand is also thanked for many useful discussions.

---

[14] Software modified from NMRCAL, Nicolet Instrument Corp., Madison, Wis.

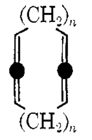
Diastereomeric Monocyclic Diallenes. Synthesis and Properties of the Diastereomeric 3,4,9,10-Cyclododecatetraene-1,7-diones and 3,4,10,11-Cyclotetradecatetraene-1,8-diones[1]

P. J. Garratt,* K. C. Nicolaou, and F. Sondheimer

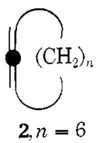
Contribution from the Department of Chemistry, University College London, London WC1H OAJ, England. *Received September 29, 1972*

Abstract: Reaction of 4,4,9,9-tetramethoxycyclododeca-1,6-diene (**3**) with bromoform and potassium *tert*-butoxide gave 6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (**4**), predominantly as the anti isomer. Treatment of **4** with methyllithium at −10° gave a mixture of the diastereomeric racemic (**5a**) and meso (**5b**) 5,5,11,11-tetramethoxy-1,2,7,8-cyclododecatetraenes, which on hydrolysis gave the corresponding racemic (**6a**) and meso (**6b**) 3,4,9,10-cyclododecatetraene-1,7-diones. A partial asymmetric synthesis of **5a**, **5b** using methyllithium in the presence of (−)-sparteine gave an optically active sample of **5a**, and allowed the identification of the racemic and meso isomers. The composition of the diketal mixture **5a**, **5b** was shown to be the same whether derived from the anti or syn tetrabromide (**4a** or **4b**) as a precursor. The diketal **5** rearranged with methyllithium at 35° to give 5,5,11,11-tetramethoxy-2,7-tricyclo[7.3.0.0^{2,7}]dodecadiene (**13**). Reaction of **5** with sodium in liquid ammonia gave a mixture of products, from which *cis,cis*-4,4,10,10-tetramethoxy-1,7-cyclododecadiene (**21**) was obtained. Reaction of **21** with bromoform and potassium *tert*-butoxide gave 7,7,14,14-tetrabromo-3,3,10,10-tetramethoxytricyclo[11.1.0.0^{6,8}]tetradecane (**24**), which, on treatment with methyllithium at −10°, gave a mixture of the diastereomeric racemic (**25a**) and meso (**25b**) 5,5,12,12-tetramethoxy-1,2,8,9-cyclotetradecatetraenes. Hydrolysis of **25a** and **25b** gave the corresponding racemic (**26a**) and meso (**26b**) 3,4,10,11-cyclotetradecatetraene-1,8-diones, these compounds again being identified through a partial asymmetric synthesis.

The preparation of cyclic allenes by treatment of the corresponding dibromocyclopropane derivatives with methyllithium has been studied by Skattebøl[2] and Moore and Ward.[3] Skattebøl[2] prepared two monocyclic diallenes, 1,2,6,7-cyclodecatetraene (**1**, n = 2) and 1,2,9,10-cyclohexadecatetraene (**1**, n = 5), by this route, as low melting, crystalline solids. Both of these diallenes possess two chiral centers and should exist in two diasteromeric forms, one diastereomer being racemic and the other a meso compound. However, no separation of the diastereomeric forms was reported. Moore and Ward[3] prepared 1,2-cyclononadiene (**2**, n = 6), 1,2-cyclodecadiene (**2**, n = 7), and 1,2-cycloundecadiene (**2**, n = 8) by the same type of reaction. The properties of 1,2-cyclononadiene have been extensively investigated, and both a partial reso-



1, n = 2
n = 5



2, n = 6
n = 7
n = 8

---

[1] For preliminary communications of part of this work, see P. J. Garratt, K. C, Nicolaou, and F. Sondheimer, *Chem. Commun.*, 1219 (1970); R. Baker, P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, *Tetrahedron Lett.*, 3425 (1972).

[2] L. Skattebøl, *Tetrahedron Lett.*, 1967 (1961); *Acta Chem. Scand.*, 17, 1683 (1963).

[3] W. R. Moore and H. R. Ward, *J. Org. Chem.*, 25, 2073 (1960); 27, 4179 (1962).