Direct Observation of ^{11}B–^{11}B Coupling in a Two Centre Boron–Boron Single Bond

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Summary Boron–boron coupling between boron atoms bonded by a two centre boron–boron single bond, in the compounds 1,2′-$(B_5H_8)_2$ and 1,5′-$(2,4\text{-}C_2B_5H_6)_2$ is reported.

WE recently reported[1] that the mercury sensitized photolysis of various small boranes and carbaboranes leads in certain cases to the formation of the corresponding boron–boron bonded coupled boranes or carbaboranes. Furthermore, we noted that when the two boron atoms which were involved in the cage linkage were chemically inequivalent the boron-11 n.m.r. resonances arising from these boron atoms were unusually broadened. We now report that the boron-11 n.m.r. spectra of these compounds recorded at high field indicate the source of this broadness is boron–boron coupling between the linked boron atoms. Although boron–boron coupling between boron atoms connected by three centre bonds has previously been observed in several boranes[2–4] and carbaboranes,[4,5] the results presented here are the first direct observations of boron–boron coupling between boron atoms bonded by a two centre, two electron boron–boron single bond.†

† Recently, ^{11}B—^{10}B coupling has also been measured from the longitudinal relaxation time data in tetrakis(dimethylamino)-diborane(4); F. Bachman, H. Nöth, H. Pommerening, B. Wrackmeyer, and T. Wirthlin, *J. Magnetic Resonance*, 1979, **34**, 237.

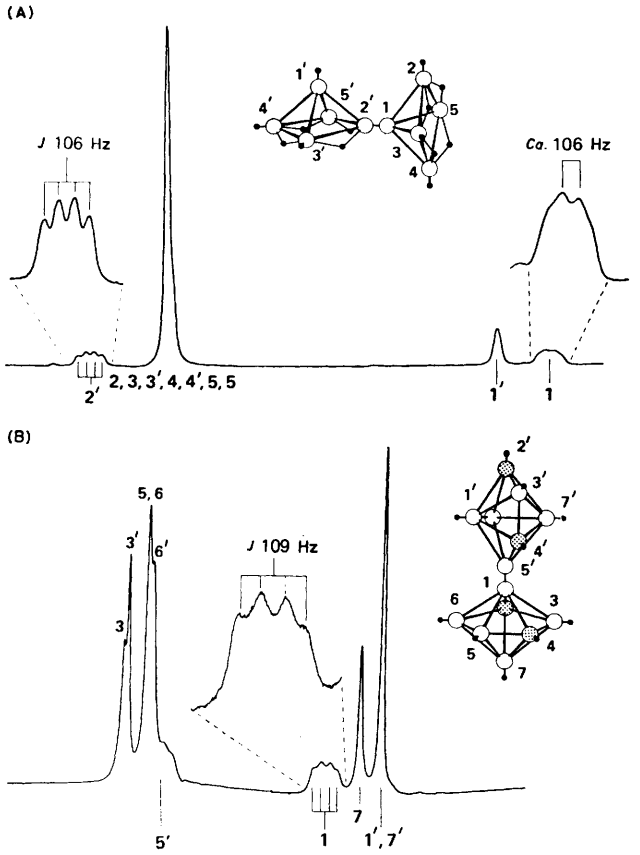

FIGURE. Proton spin decoupled 115·5 MHz boron-11 n.m.r. spectra (in C_6D_6) of 1,2′-$(B_5H_8)_2$ (A) and 1,5′-(2,4-$C_2B_5H_6)_2$ (B). The peak assignments and chemical shifts are consistent with those given previously (see reference 1 and D. Gaines, T. V. Iorns, and E. V. Clevenger, *Inorg. Chem.*, 1971, **10**, 1096).

The proton spin decoupled boron-11 n.m.r. spectra of 1,2′-$(B_5H_8)_2$ (Figure, A) and 1,5′-(2,4-$C_2B_5H_6)_2$ (Figure, B) were recorded at 115·5 MHz on a Bruker WH 360 spectrometer. For both compounds the resonances assigned to the boron atoms involved in the boron–boron linkage are broadened. Upon expansion, the resonance due to the 2′ boron position in 1,2′-$(B_5H_8)_2$ clearly shows the quartet structure which would be expected to arise from direct coupling to the 1 boron position. The middle two peaks of the expected 1 : 1 : 1 : 1 quartet (^{11}B, $I = 3/2$) are raised in intensity owing to the expected overlapping septet arising from ^{10}B–^{11}B coupling (^{10}B, $I = 3$). The observed ^{11}B–^{11}B coupling constant, 106 Hz, is larger than any previously reported boron–boron coupling and is consistent with theoretical calculations[6] for coupling in boron–boron single bonds. The upfield resonance due to the 1 boron position also shows a definite structure consistent with its coupling to the 2′ boron atom, but it is not as well defined. This is indeed expected, since previous work[2] has shown that the apex boron in pentaborane(9) is strongly coupled to the four basal boron atoms (J 19·4 Hz).

Similar effects are observed in the boron-11 n.m.r. spectrum of 1,5′-(2,4-$C_2B_5H_6)_2$. Thus, the resonance due to the 1 boron position appears again as a quartet with J 109 Hz indicating ^{11}B–^{11}B coupling with the 5′ boron. The resonance due to the 5′ boron is partially obscured, but does show a line width and structure consistent with this interpretation.

We thank the Army Research Office for support of this work, and the Mid-Atlantic Regional N.M.R. Facility for the high field n.m.r. spectra.

(*Received*, 13*th June* 1979; *Com.* 624.)

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