

An investigation of this is under way. A detailed report of the present study will be submitted when refinement is complete.

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DEPARTMENT OF CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE 39, MASSACHUSETTS

F. A. COTTON  
R. C. ELDER

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### *p*-Carborane [1,12-Dicarboclovododecaborane(12)]

Sir:

Two of the three possible geometrical isomers for the icosahedral carborane system,<sup>1</sup> carborane (*ortho*) and neocarborane (*meta*), have been reported<sup>2-5</sup> and variously studied. Assignment of structure has been made principally by comparison of the observed <sup>11</sup>B n.m.r. spectra of these two isomers and their decachloro derivatives to those theoretically deduced for them.<sup>6</sup> We now wish to report the synthesis and identification of the third possible isomer, *p*-carborane.

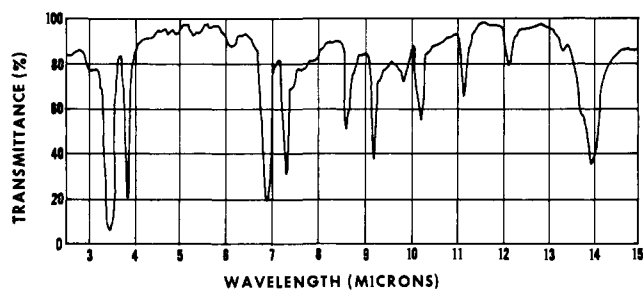


Fig. 1.—Infrared spectrum of *p*-carborane (Nujol mull).

While studying the thermal behavior of neocarborane which undergoes gross decomposition at 630°, it was observed that unfamiliar infrared absorptions appeared in samples which had been held at 500–620° for several hours.<sup>7</sup> To investigate further, 2.3 g. of neocarborane was placed in a nitrogen-flushed, 100-ml. stainless steel autoclave and heated at 615° for 17 hr. Sublimation of the residue (50° at 0.1 mm.) yielded 0.29 g. of sublimate. This sublimate was dissolved in 0.4 ml. of benzene and subjected to vapor phase chromatography at 150° using a 5 ft. column packed with 20% silicone SF-96 on firebrick. Two components were separated; the component first released was *p*-carborane followed rather closely by neocarborane. Carborane was found to pass through the column much more slowly and none was detected in the mixture above. *Anal.* Found for C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>: C, 17.1; H, 8.4.; B, 75.4. The *p*-carborane was recovered in 6.5% yield and melted at 259–261°.<sup>8</sup>

- (1) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).
- (2) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).
- (3) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).
- (4) L. I. Zakharkin, V. I. Stanko, V. A. Bratdsv, Y. A. Chapovskii, and Y. T. Dstruchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11**, 2069 (1963).
- (5) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).
- (6) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).
- (7) For infrared spectra of carborane and neocarborane, see H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963); and ref. 5.
- (8) Various melting points have been observed and reported for carborane and neocarborane. It has been our experience that their observed melting points are markedly influenced by the technique used, probably because of their extreme tendency to sublime. For purposes of comparison here we

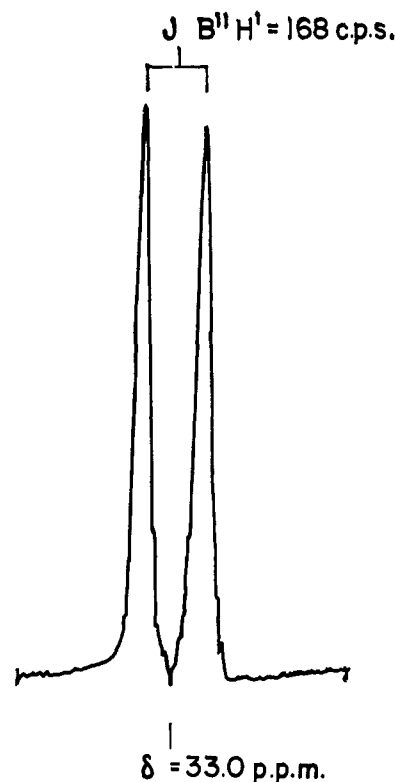


Fig. 2.—<sup>11</sup>B n.m.r. spectrum of *p*-carborane in deuteriochloroform; displacement from methyl borate (external).

The mass spectrum of *p*-carborane was typical of a carborane derivative with the expected cut-off peak appearing at 144 mass units. Although we have not attempted detailed assignments, the infrared spectrum (Fig. 1) is characteristically different from those of carborane and neocarborane in the 8.2–12.2 μ range. Conclusive proof of the *para* or 1-12 carbon orientation was obtained from the <sup>11</sup>B n.m.r. spectrum (Fig. 2) which consisted of only one doublet arising from the ten geometrically equivalent boron atoms. On decoupling this doublet collapsed to a singlet. This is in accord with the theoretical spectrum deduced by Schroeder and Vickers<sup>6</sup> for a *p*-carborane.

Additional investigations in this area are in progress and will be reported in detail subsequently.

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sealed off small sections of capillary tubes which were well filled with material and determined the melting points simultaneously using a Mel-Temp apparatus. Under these conditions we found for carborane 294–296°, neocarborane 272–273°, and *p*-carborane 259–261°. NOTE ADDED IN PROOF.—Dr. W. N. Lipscomb suggests that these variations in melting points could be associated with different amounts of partial ordering of the cubic structures of the carboranes in the solid state.

ORGANICS DIVISION  
OLIN MATHESON CHEMICAL CORPORATION  
NEW HAVEN, CONNECTICUT

STELVIO PAFETTI  
THEODORE L. HEYING

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### Computer Search for Active Site Configurations<sup>1</sup>

Sir:

The covalent bond structure of many large biological polymers such as the proteins insulin, ribonuclease,

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