Volume 5
Number 9
September 1, 1966

Inorganic Chemistry

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Molecular Structure of Carboranes. Molecular and Crystal Structure of o-$B_{10}Br_2H_8C_2H_2$

By JOSEPH A. POTENZA and WILLIAM N. LIPSCOMB

Received April 2, 1966

The reaction of Br_2 in the presence of $AlBr_3$ with o-carborane produces a dibromo substitution product, o-$B_{10}Br_2H_8C_2H_2$, in which the Br atoms are in the 9 and 12 positions, exactly opposite the two C atoms. Thus, the Br atoms are on adjacent B atoms, and the molecular symmetry is C_{2v}. Molecular orbital arguments suggest that electrophilic substitution has taken place. The crystal structure has the space group $Pbn2_1$, with four molecules in a unit cell having dimensions a = 7.42, b = 13.03, and c = 11.75 A.

This study is part of a series of investigations of probable electrophilic or nucleophilic substitution on polyhedral molecules. Recognition[1] that the carboranes are "superaromatic" systems led to a prediction of ground-state charge distributions, which, together with the free valence,[1] might form a basis for location of sites of electrophilic and nucleophilic substitution. Appropriate qualifications[1,2] are that the charge distribution of the ground state should also resemble that of the transition complex (probably more nearly applicable to polyhedral structures than to other structures) and that steric or neighbor effects as well as concerted mechanisms are not completely dominant. It has therefore seemed most appropriate to give initial attention to halogen attack or to N atom attack from bases for which steric problems are minimized in the initial tests of these reactivity predictions.

The near-icosahedral geometry, including multiple coordination and the relatively long C–C distance, of the $B_{10}C_2$ unit have been established.[2,3] In addition, the eight Cl atoms in $B_{10}Cl_8H_2C_2H_2$, which was prepared[4] by reaction of Cl_2 with o-carborane in the presence of ultraviolet light, have been shown[2] to substitute at all but the two most positively charged[1] B atoms of o-carborane. It was of special interest to study the earlier stages of halogenation under electrophilic conditions inasmuch as the molecular orbital results for total charge on B atoms yielded nearly equal probability for the 8, 9, 10, and 12 positions, which are furthest from the C atoms in o-carborane. We show here that dibromo-o-carborane, which had been prepared[5] by bromination of o-carborane in the presence of $AlBr_3$, is substituted at the 9 and 12 positions, opposite the two C atoms. The isolation[5] of this dibromo derivative thus produces a distinction between the 9 and 12 positions and the 8 and 10 positions. We also show that, although the charges on B atoms 8, 9, 10, and 12 are very nearly the same, the highest filled molecular orbitals show greater negative charge density at the 9 and 10 positions than at the 8 and 10 positions. Hence, an electrophilic interpretation of this reaction is plausible.

Structure Determination

A single crystal of o-$B_{10}Br_2H_8C_2H_2$ which was 0.7 mm in length and 0.06 mm square in cross section was mounted on the needle axis, designated as c. A second crystal, cut into a cube 0.05 mm on edge, was mounted on the a axis. Reciprocal lattice symmetry of D_{2h} and unit cell dimensions of $a = 7.42 \pm 0.02$, $b = 13.03 \pm 0.03$, and $c = 11.75 \pm 0.02$ A were established. Extinctions of $0kl$ where k is odd and of $h0l$ when $h + l$ is odd indicate either $Pbn2_1$ or Pbnm as probable space groups. Only upon unambiguous location of the Br atoms was the space group shown to be Pbn_21.

Diffraction data were collected on the Buerger automated X-ray diffractometer with the use of Cu Kα radiation and a Xe proportional counter. The time of scan, which is proportional to the angle of scan in degrees, was varied to maintain proportionality with the

---

[1] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

[2] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964); for an X-ray diffraction study of $B_{10}C_2Cl_{12}$ see W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 26.

[3] D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1679 (1964).

[4] H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

[5] H. D. Smith, T. A. Knowles, and H. Schroeder, *ibid.*, **4**, 107 (1965).

TABLE I[a,b]

LIST OF OBSERVED F_{hkl} VALUES

```
L= 0(K,H) ( 0)(0,8)7777/0,,4517/23,,2738/14,,854/4,,0*,( 1)(0,9),40/24,1356/
10,452/4,1416/7,165/11,1426/7,190/9,426/2,108/9,( 2)(0,9)U,493/2,3327/24,489/
4,1503/11,367/4,379/5,130/8,365/3,127/8,( 3)(0,8),260/6,2696/19,247/8,2563/
18,1216/9,1836/13,487/4,845/4,( 4)(0,8)477/2,297/2,241/7,444/4,815/6,233/5,0*,
354/5,231/4,( 5)(0,8),258/6,1512/11,1206/4,2110/15,682/5,1908/13,720/5,842/
4,( 6)(0,8)2965/21,1301/9,2424/17,688/5,1786/6,72/12,173/6,222/4,296/3,
( 7)(0,8),717/5,0*,337/6,267/7,318/5,98/10,286/9,148/7,( 8)(0,7)2309/16,2241/
8,1972/14,2064/15,998/7,693/5,386/5,132/8,( 9)(0,7),873/6,491/3,946/7,612/4,
684/2,537/4,242/8,(10)(0,7)1688/12,1127/8,1070/8,700/5,561/4,438/4,472/4,280/
4,(11)(0,6),330/5,508/4,939/7,478/4,780/6,544/4,(12)(0,5)553/4,75/13,42/23,
128/8,126/6,381/4,(13)(0,5),172/6,158/6,395/4,379/5,644/3,(14)(0,4)498/4,865/
6,158/12,416/4,0*,(15)(0,3),147/12,158/14,78/13
L= 1(K,H) ( 0)(0,7),U,,711/4,,374/3,,164/9,( 1)(0,9),2342/12,2526/18,297/5,
3110/22,536/4,2149/11,337/6,835/4,91/11,( 2)(0,8)4115/21,1750/9,3789/27,1331/
5,1675/12,502/4,408/2,126/14,202/5,( 3)(0,8),657/5,812/6,885/6,644/5,1016/7,
716/5,381/5,369/3,( 4)(0,8)5112/18,1807/13,4038/29,1320/9,2129/15,693/5,493/
4,168/18,177/6,( 5)(0,8),558/2,1073/8,789/6,1236/9,735/5,1029/4,306/6,325/3,
( 6)(0,8)2558/18,1291/9,2111/7,1205/9,1397/10,393/4,515/4,224/8,131/8,
( 7)(0,8),429/4,1417/10,1209/4,1532/5,1142/8,1259/4,744/5,528/3,( 8)(0,7)455/
3,898/6,357/6,514/4,214/9,349/5,294/6,332/5,( 9)(0,7),562/4,545/4,934/7,926/
7,854/6,722/5,486/4,(10)(0,7)1419/5,1533/5,986/7,925/7,554/4,265/6,0*,148/7,
(11)(0,6),387/4,446/5,0*,332/6,346/5,390/4,(12)(0,5)900/6,1286/9,733/5,944/
7,353/5,457/4,(13)(0,5),178/6,309/4,616/4,248/7,335/3,(14)(0,4)348/3,555/4,
207/5,481/3,171/12,(15)(0,2),168/6,339/6
L= 2(K,H) ( 0)(0,6)U,,4886/35,,2322/16,,450/4,( 1)(0,7),614/4,1265/9,1635/12,
1210/9,1262/9,722/5,652/5,( 2)(0,7)5153/36,2259/16,3942/28,1030/7,1630/12,745/
5,481/4,215/5,( 3)(0,7),91/12,1910/14,861/6,2898/10,549/4,1672/12,373/2,
( 4)(0,7)936/7,2227/16,550/4,1818/13,188/6,419/4,376/4,185/10,( 5)(0,7),542/
4,1155/8,783/3,1549/11,1285/5,1355/5,702/2,( 6)(0,7)2805/20,1819/13,2116/15,
1354/5,1048/7,480/4,415/5,113/9,( 7)(0,7),394/4,571/4,1056/7,579/4,626/4,480/
4,567/3,( 8)(0,7)2182/15,1810/6,2169/15,949/7,1173/8,495/3,296/6,243/6,
( 9)(0,7),239/7,385/4,544/4,758/5,670/2,523/4,438/3,(10)(0,6)868/3,1276/9,724/
3,953/7,512/4,588/4,0*,(11)(0,6),644/5,342/3,917/6,532/4,850/4,386/3,
(12)(0,5)713/5,336/5,450/3,106/10,535/4,323/4,(13)(0,4),188/11,250/4,187/6,
265/4,(14)(0,3)279/4,641/3,0*,379/3,(15)(0,2),0*,0*
L= 3(K,H) ( 0)(0,7),4574/23,,3016/15,,1330/7,,231/7,( 1)(0,8),610/4,2081/15,
1171/8,2100/15,978/3,1593/11,535/2,496/2,( 2)(0,7)4135/21,2734/19,2887/20,1345/
10,U,611/4,449/4,157/16,( 3)(0,7),1049/7,937/7,1483/5,1100/8,1670/6,533/4,935/
7,( 4)(0,7)U,1712/12,3150/22,808/6,1987/7,444/4,409/4,159/7,( 5)(0,7),884/6,
607/4,1485/11,1114/4,1198/8,685/5,764/5,( 6)(0,7)2148/15,2110/15,1952/14,1205/
9,729/5,525/4,501/4,316/6,( 7)(0,7),402/4,523/4,1005/7,1351/10,775/5,942/7,
486/3,( 8)(0,7)1265/9,1505/11,1275/9,904/6,767/5,471/4,69/16,206/7,
( 9)(0,6),659/5,883/6,687/5,800/6,874/3,556/4,(10)(0,6)934/7,924/7,723/5,648/
5,651/5,385/6,194/6,(11)(0,6),202/8,343/2,471/4,508/2,406/3,406/3,(12)(0,5)
562/4,1123/8,581/4,703/5,316/5,420/3,(13)(0,4),219/8,393/5,220/4,360/3,
(14)(0,3)417/4,487/2,570/3,347/3,(15)(0,2),237/4,274/4
L= 4(K,H) ( 0)(0,6)4127/21,,3091/22,,2117/15,,408/4,( 1)(0,7),909/5,639/5,1916/
14,830/6,2259/16,725/5,1160/8,( 2)(0,7)3361/17,3688/18,2068/15,2397/17,1110/
8,689/5,601/2,237/8,( 3)(0,7),1041/5,969/7,1114/8,1126/8,429/4,1148/8,435/5,
( 4)(0,7)852/3,3309/23,1389/10,1874/13,322/7,849/6,167/7,218/8,( 5)(0,7),585/
3,1163/8,1382/10,1223/9,785/3,837/6,646/2,( 6)(0,7)1803/13,1824/13,1113/8,1036/
7,1081/8,368/5,248/7,133/9,( 7)(0,7),1002/7,787/6,1027/7,912/6,1326/5,701/2,
785/4,( 8)(0,7)1531/11,1404/10,1143/8,1025/4,598/2,454/4,399/4,0*,( 9)(0,6),
192/6,137/8,844/3,621/4,677/5,522/4,(10)(0,6)1047/7,1068/4,1239/4,820/3,646/
5,401/4,45/27,(11)(0,5),213/5,303/4,460/4,330/5,503/3,(12)(0,5)878/6,661/5,
891/6,513/4,507/4,227/5,(13)(0,4),176/4,243/7,336/3,414/3,(14)(0,3)81/13,344/
3,321/3,319/4,(15)(0,1),0*
L= 5(K,H) ( 0)(0,7),4492/22,,3071/15,,952/5,,0*,( 1)(0,8),769/5,659/5,1208/
9,832/6,627/4,821/3,621/4,456/2,( 2)(0,7)1391/10,3307/23,1432/10,2052/15,1463/
10,643/5,347/5,0*,( 3)(0,7),1214/9,486/3,2186/15,633/4,2189/15,570/4,1261/9,
( 4)(0,7)2127/15,430/4,1256/9,376/5,535/2,247/3,544/2,334/6,( 5)(0,7),398/4,
720/5,1722/12,658/5,1351/10,710/5,747/5,( 6)(0,7)1988/14,2167/15,1246/9,1747/
12,789/6,509/4,224/4,290/6,( 7)(0,7),426/4,629/4,281/5,339/5,602/2,479/4,286/
5,( 8)(0,6)1431/10,1897/13,1263/9,1059/7,550/4,406/4,238/4,( 9)(0,6),247/4,
422/4,684/5,683/5,697/5,389/4,(10)(0,6)815/3,814/6,680/5,539/4,621/4,313/5,
226/6,(11)(0,5),285/5,488/4,549/4,786/6,421/3,(12)(0,4)439/4,508/4,334/5,595/
4,427/4,(13)(0,3),168/9,188/5,239/8,(14)(0,2)667/5,117/9,464/2
L= 6(K,H) ( 0)(0,8)861/4,,695/5,,590/2,,531/4,,0*,( 1)(0,8),1039/7,288/5,2429/
17,355/4,1873/13,0*,1205/9,184/6,( 2)(0,8)843/6,2598/18,984/7,2039/14,683/5,
516/4,313/6,227/4,120/8,( 3)(0,7),436/4,272/6,461/4,284/5,855/6,388/4,408/5,
( 4)(0,7)1712/12,3706/26,1408/10,2341/17,1006/4,754/3,76/13,167/12,
( 5)(0,7),377/2,677/5,884/6,625/4,1034/7,251/7,507/4,( 6)(0,7)934/7,1676/12,
408/4,1138/8,306/5,604/4,262/6,245/7,( 7)(0,7),144/7,707/5,1228/9,819/6,1129/
8,792/6,428/2,( 8)(0,6)670/5,385/4,313/6,284/7,288/5,239/6,392/5,( 9)(0,6),
490/3,420/4,530/4,698/5,643/5,643/5,(10)0,5) 1300/9,952/7,999/4,756/3,295/5,
176/7,(11)(0,5),253/4,28/30,132/8,217/9,285/4,(12)(0,4)1105/8,385/4,713/5,354/
4,599/4,(13)(0,3),136/7,454/4,323/5,(14)(0,1)383/4,309/2
L= 7(K,H) ( 0)(0,7),4330/22,,3377/17,,878/4,,0*,( 1)(0,7),211/9,631/4,1070/
8,237/7,905/3,219/5,548/4,( 2)(0,7)659/2,2199/15,419/4,1345/10,446/4,691/5,
221/9,115/9,( 3)(0,7),994/7,826/4,1675/12,609/5,1554/11,354/5,873/3,
( 4)(0,7)306/5,597/4,332/3,158/6,460/4,208/7,221/9,338/5,( 5)(0,7),484/4,363/
5,1205/9,547/4,1255/4,613/4,865/6,( 6)(0,6)1028/4,2030/14,866/6,877/6,436/3,
468/4,202/9,( 7)(0,6),218/5,194/5,196/10,294/3,265/7,317/5,( 8)(0,6)1577/11,
1300/9,1209/9,1000/7,587/4,419/4,273/5,( 9)(0,5),45/22,462/3,222/5,636/4,416/
4,(10)(0,5)644/5,696/5,500/4,628/4,382/4,228/4,(11)(0,4),407/4,437/4,434/4,
576/2,(12)(0,3)473/4,137/7,312/7,380/6,(13)(0,2),126/8,334/5
L= 8(K,H) ( 0)(0,6)1242/6,,280/6,,339/3,,442/4,( 1)(0,7),960/5,578/4,1452/10,
216/5,1447/10,330/2,935/7,( 2)(0,7)1062/5,2643/13,789/6,1184/8,251/7,639/5,
143/13,218/10,( 3)(0,7),356/5,785/6,497/4,785/3,558/4,444/4,368/5,( 4)(0,6)
648/5,2272/8,981/7,1746/12,434/4,748/5,210/8,( 5)(0,6),359/4,241/4,609/4,493/
3,479/4,529/4,( 6)(0,6)1041/7,1226/4,784/6,949/7,400/2,427/4,332/5,
( 7)(0,6),400/5,534/4,697/5,735/5,950/7,498/4,( 8)(0,5)524/4,283/4,491/3,144/
7,239/9,0*,( 9)(0,5),288/5,320/5,478/4,733/5,429/4,(10)(0,4)951/7,521/4,828/
6,0*,346/5,(11)(0,3),203/5,351/5,257/7,(12)(0,2)808/6,646/5,739/5,(13)(0,1),
40/24
L= 9(K,H) ( 0)(0,5),2532/13,,1407/7,,567/3,( 1)(0,6),513/4,590/4,239/8,1034/
7,524/4,486/4,( 2)(0,6)387/4,1821/9,882/6,1378/10,251/8,651/5,336/5,
( 3)(0,6),480/3,252/9,1133/4,356/5,1005/7,502/4,( 4)(0,6)1406/10,492/4,861/
6,364/5,222/5,176/10,147/8,( 5)(0,6),536/4,514/4,627/4,713/5,830/6,414/5,
( 6)(0,5)698/5,643/5,844/6,671/5,350/5,343/5,( 7)(0,5),0*,523/4,416/4,589/2,
383/5,( 8)(0,5)1024/7,1054/7,872/2,850/5,521/4,428/4,( 9)(0,4),85/14,261/7,
151/8,390/4,(10)(0,3)734/5,676/5,761/5,314/5,(11)(0,3),0*,411/4,0*,
(12)(0,1)112/16,0*
L=10(K,H) ( 0)(0,6)1461/7,,1262/6,,503/4,,262/3,( 1)(0,6),337/6,337/5,789/6,
440/4,792/6,374/5,( 2)(0,6)1071/5,843/6,849/6,810/6,393/4,221/5,203/11,
( 3)(0,6),259/8,623/4,336/5,905/6,247/7,627/3,( 4)(0,5)834/6,1424/10,419/4,
1040/7,390/4,471/4,( 5)(0,5),218/11,524/4,224/4,656/5,261/7,( 6)(0,5)970/7,
1000/4,801/6,742/5,378/6,351/6,( 7)(0,4),194/9,218/9,328/7,453/4,( 8)(0,4)624/
4,390/4,600/4,255/7,186/9,( 9)(0,3),144/5,479/3,499/4,(10)(0,2)519/4,96/12,
300/5,(11)(0,1),0*
L=11(K,H) ( 0)(0,5),998/5,,615/3,,444/3,( 1)(0,5),0*,773/4,305/4,749/4,211/
6,( 2)(0,5)1297/6,956/4,887/4,676/3,438/3,282/4,( 3)(0,5),278/4,0*,424/3,375/
3,70/17,( 4)(0,5)1107/6,268/4,900/4,128/9,377/3,0*,( 5)(0,4),0*,234/5,227/5,
392/3,( 6)(0,4)731/4,158/6,615/3,277/4,199/6,( 7)(0,3),275/4,404/3,477/2,
( 8)(0,3)481/2,456/2,357/3,375/3,( 9)(0,2),388/3,189/6,(10)(0,1)485/2,419/2
L=12(K,H) ( 0)(0,4)1295/6,,1102/6,,685/3,( 1)(0,4),218/5,0*,0*,283/4,
( 2)(0,4)874/4,174/6,742/4,163/7,0*,( 3)(0,4),0*,481/2,0*,649/3,( 4)(0,4)0*,
445/2,265/4,360/3,0*,( 5)(0,3),141/7,585/3,233/5,( 6)(0,3)656/3,566/3,587/3,
330/3,( 7)(0,2),0*,161/7,( 8)(0,1)445/2,323/3
L=13(K,H) ( 0)(0,3),0*,,507/3,( 1)(0,3),389/3,414/3,122/9,( 2)(0,3)676/3,151/
7,434/3,100/11,( 3)(0,3),0*,0*,178/6,( 4)(0,2)747/4,485/2,744/4,( 5)(0,2),270/
4,0*,( 6)(0,1)326/3,154/6
```

[a] F_{hkl} is listed followed by $\sigma_{F_{hkl}}$, as used in the least-squares refinement. The value of h and the range of k are given in parentheses. Unobserved reflections are indicated by a zero followed by an asterisk, experimentally unobserved reflections by a U, and space group extinctions by an extra comma. All reflections are on the same scale as F_{000}, which is given as a reference point. The summation for F_{000} is for the entire unit cell. All F_{hkl} values are included for which F_o as measured by the diffractometer was greater than zero. [b] Scattering factors for all atoms were used as obtained from the "International Tables of X-ray Crystallography," The Kynoch Press, Birmingham, England, Vol. III, 1962, p 202 ff. No corrections were made for the anomalous dispersion of Br.

Lorentz factor. Check reflections were inserted after every group of 15 reflections on each level, and a set of six zero-level reflections was measured after each level of the reciprocal lattice was completed. Equivalent reflections all agreed within $2\sigma_c$, where σ_c is the square root of the total number of counts. A total of 1080 independent diffraction maxima were measured on levels Hkl for $0 \leqslant H \leqslant 7$ and hkL for $0 \leqslant L \leqslant 10$. Backgrounds were subtracted, and the usual Lorentz and polarization corrections were made in order to obtain F_o^2 for each hkl (Table I). The data which were taken about the a and c axes were then correlated by use of a weighted least-squares procedure in which a separate scale factor was assigned to each level. In the first method of correlation the standard deviation σ_c of each F_o^2 was made proportional to the total number of counts of scan plus background (Table II). In the second method the standard deviation σ_p was taken as proportional to (actually 1% of) the number of net counts for $F_o^2 \geqslant \sigma_c$, and $\sigma_p = K$ for $F_o^2 \leqslant \sigma_c$, where K is 1% of F^2 at the value of $F_o^2 = 2\sigma_c$ where the change in σ_p was assigned. Scale factors for these two methods (Table II), as well as the values of

$$R_{\text{correlation}} = \sum w(F(1)^2 - F(2)^2)/\sum w(F(1)^2 + F(2)^2)$$

given in Table III show that the σ_p weights ($w^{-1/2} = \sigma_p$) yield more nearly consistent scale factors and better internal agreement than do the σ_c weights. The superiority of σ_p weights over σ_c weights was also clearly demonstrated in the last stages of refinement of the structure by least-squares procedures.

TABLE II

COMPARISON OF SCALE FACTORS FOR FRACTIONAL AND SQUARE-ROOT CORRELATION[a]

Level	Fractional weights scale factor	Square-root weights scale factor	Level	Fractional weights scale factor	Square-root weights scale factor
$hk0$	1.00	1.00	$hk9$	1.16	1.46
$hk1$	1.05	1.21	$hk10$	1.20	1.53
$hk2$	1.07	1.78	$0kl$	6.95	7.27
$hk3$	1.09	1.47	$1kl$	6.66	8.66
$hk4$	1.16	1.61	$2kl$	7.38	8.30
$hk5$	0.99	1.34	$3kl$	7.56	9.63
$hk6$	1.01	1.44	$4kl$	7.59	9.48
$hk7$	1.01	1.43	$5kl$	7.90	10.56
$hk8$	1.08	1.39	$6kl$	8.39	11.17
			$7kl$	10.13	13.49

[a] Deviations from constancy of the scale factors for each level are presumed to be due mostly to absorption errors for which no correction was made, but some errors in positioning of the crystal may also contribute.

TABLE III

COMPARISON OF $R_{\text{correlation}}$ FOR FRACTIONAL AND SQUARE-ROOT CORRELATION[a]

Lower intensity limit	No. of entries	$R_{\text{correlation}}$ Fractional	Square-root
200,000	1	0.011	0.060
100,000	8	0.148	0.048
50,000	18	0.060	0.071
20,000	73	0.060	0.093
10,000	93	0.047	0.081
5,000	138	0.063	0.095
2,000	192	0.093	0.112
1,000	118	0.188	0.197
500	71	0.255	0.267
200	43	0.417	0.403
100	15	0.643	0.643
50	5	0.629	0.636
0	3	0.769	0.772
Over-all	778	0.075	0.085

[a] $R_{\text{correlation}} = \Sigma w(F(1)^2 - F(2)^2)/\Sigma w(F(1)^2 + F(2)^2)$.

Solution of the structure by the heavy-atom method was accomplished in a straightforward way. Analysis of the symmetry plane and lines of the three-dimensional Patterson function yielded two nonenantiomorphic structures, which yielded values of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.44$ and 0.28 for Br positions only when the 770 largest of the 1080 reflections were included. It was shown at a later stage of the study that the structure which yielded $R_F = 0.44$ would not refine, and hence all further comments apply to the second set of Br positions. A three-dimensional electron density map phased by the Br atoms, which clearly indicated that the space group is $Pbn2_1$, yielded 36 peaks ranging in height between 20 and 60% of the expected height of a B atom. Unfortunately, the Br atoms are related by a pseudo-center of symmetry at a point not suitable for either of the space groups indicated by extinctions. Hence, the $B_{10}C_2$ polyhedron had to be chosen from its pseudo-enantiomorph, which occurred in the same region of the map. Numerical values were then computed for positions in Patterson space for all 36 peaks, from which 12 were selected as a basis for a model which indicated 5 B (or C) atoms in an icosahedral fragment. The remaining atoms of both the true structure and its pseudo-enantiomorph were then easily found, even though only 9 of the 12 B and C atoms were present among the original 36 peaks. Actually both the structure and its pseudo-enantiomorph were refined by least-squares procedures, but the pseudo-enantiomorph did not refine. The correct structure yielded a value of $R_F = 0.082$ for 913 of the 1080 observed reflections. Inclusion of H atoms at presumed positions in the model reduced R_F to 0.073 after two more cycles of least-squares refinement of these same reflections.

Until this point of the study, no distinction had been attempted between B and C atoms. We shall show that the structure is most probably completely ordered and that the pair of C atoms is opposite the pair of B–Br units in the icosahedron. It was first noted that the distances 2–9 and 1–12 of the icosahedron (Figure 1) were substantially shorter than the other four pairs of similarly related distances (Table IV). For comparison, values of these distances are also given in Table IV for an idealized icosahedral arrangement in which B–B = 1.76, B–C = 1.70, and C–C = 1.64 A. Secondly, we show in Table V comparisons of electron density, atom multipliers, distances, and thermal parameters. Columns I, IV, and V refer to the structure composed of 2 Br, 12 B, and 10 H atoms (R_F = 0.073), while column VI refers to the final structure. In column I we show the interpolated electron density remaining at the nuclei after subtraction of 2 Br, 12 B, and 10 H atoms. In column II the atom multipliers listed were obtained after two cycles of least-squares refinement of only these multipliers starting with the best structure for 2 Br, 12 B, and 10 H atoms. Similar results are shown in column III for a structure having initially 2 Br, 10 B, 2 C (at positions 1 and 2), and 10 H atoms. In column IV the average nearest neighbor bond lengths are shown, and in column V the average isotropic equivalents of the anisotropic thermal parameters are given. The final column shows the interpolated electron density in the final map. Thus, in varying degrees, these several criteria support the ordered structure. This final ordered structure yielded values of $R_F = 0.072$, $R_{F^2} = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2 = 0.120$, and $R_{wF^2} = |\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4|^{1/2} = 0.189$ after two further cycles of least-squares refinement of positions and anisotropic thermal parameters. The details

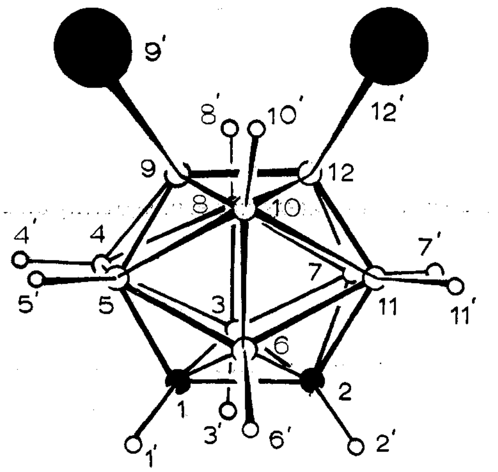

Figure 1.—The molecular structure and numbering scheme for $B_{10}Br_2H_8C_2H_2$. Atoms are designated as follows: H(1',2',3',4',5',6',7',8',10',11'); B(3,4,5,6,7,8,9,10,11,12); C(1,2); Br(9',12').

TABLE IV

para DISTANCES IN ICOSAHEDRON FROM 12 B REFINED STRUCTURE (R = 0.0733)

Atoms	Measd distance, A[a]	Idealized distance	Atoms	Measd distance, A[a]	Idealized distance
1–12	3.24 ± 0.027	3.23	4–11	3.37 ± 0.027	3.34
2–9	3.18 ± 0.027	3.23	5–7	3.32 ± 0.033	3.34
3–10	3.30 ± 0.032	3.34	6–8	3.44 ± 0.028	3.34

[a] These distances and standard deviations (obtained from the full variance–covariance matrix) clearly indicate that the ordered structure is correct.

TABLE V

EVIDENCE FOR 9,12 SUBSTITUTION[a]

Atom	I[b]	II[c]	III[d]	IV[e]	V[f]	VI[g]
1	111	1.11 ± 0.05	1.01 ± 0.04	1.69	3.52	508
2	105	1.04 ± 0.04	0.98 ± 0.04	1.70	2.71	550
3	82	0.96 ± 0.05	0.97 ± 0.05	1.72	6.01	415
4	−12	0.99 ± 0.05	0.99 ± 0.04	1.74	3.76	479
5	−37	0.97 ± 0.05	0.97 ± 0.05	1.72	3.84	451
6	53	0.99 ± 0.05	0.98 ± 0.05	1.73	5.22	426
7	68	1.01 ± 0.04	1.01 ± 0.04	1.75	3.41	426
8	3	1.00 ± 0.04	0.99 ± 0.04	1.79	3.14	495
9	66	0.97 ± 0.05	0.97 ± 0.04	1.75	3.90	454
10	21	0.96 ± 0.04	0.98 ± 0.04	1.74	3.13	423
11	−49	0.98 ± 0.05	0.99 ± 0.05	1.78	3.35	406
12	73	0.99 ± 0.04	0.99 ± 0.04	1.77	3.60	469

[a] All standard deviations were obtained from the inverse least-squares matrix. [b] Three-dimensional linearly interpolated electron density at B positions from three dimensional difference Fourier. Fourier was calculated on the basis of 12 B, 12 H, and 2 Br atoms with $R_F = 0.073$. One electron per cubic angstrom is 350 on this arbitrary scale. The highest nonresidual peak on the map was 206. [c] The atom multipliers of the "12 B" atoms after two cycles of least-squares refinement (from the $R_F = 0.073$ parameters). [d] The atom multipliers of the 10 B and 2 C atoms after two cycles of least-squares refinement (from $R_F = 0.071$, or final, parameters). [e] The average nearest neighbor bond distances as calculated from the "12 B" $R_F = 0.073$ parameters. [f] The average isotropic equivalents as calculated from the anisotropic temperature factors of the "12 B" $R_F = 0.073$ parameters. [g] Three-dimensional linearly interpolated electron density from the final Fourier ($R_F = 0.072$) on an arbitrary scale. The highest peak not that of a known atom was 61 on this scale.

of values of R for different classes of reflection and different ranges of scattering angle are shown in Table VI. We wish to emphasize the importance of local details, such as bond distances, electron densities, atom multipliers, and thermal parameters for producing such fine distinctions as identification of B and C atoms, especially when heavy atoms are also present in the structure. The insensitivity of values of the various R's is illustrated by least-squares refinement of a somewhat disordered structure arising from the assumption of equal probability of Br substitution at any adjacent pair of the set of B atoms numbered as 8, 9, 10, and 12. The crystal structure obtained by ordering of the Br atoms would then have 0.6 C and 0.4 B at both positions 1 and 2, and 0.4 C and 0.6 C at both positions 3 and 6. Refinement of this structure led to values of $R_F = 0.073$, $R_{F^2} = 0.122$, and $R_{wF^2} = 0.193$ for the same 909 ($F_o \geqslant 1.5\sigma_c$) of 1080 observed reflections tested for the final ordered structure. Even in the unlikely event that some disorder of this type is present, we feel that the detailed criteria indicate predominantly substitution of Br at positions 9 and 12.

TABLE VI

FINAL VALUES FOR $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for 909 OF 1080 REFLECTIONS (ORDERED STRUCTURE)

hkl	R_F	*hkl*	R_F
All ($h, k, l \neq 0$)	0.073	$k + l$ even	0.071
h even	0.074	$k + l$ odd	0.074
h odd	0.071	$h + l$ even	0.072
k even	0.063	$h + l$ odd	0.074
k odd	0.083	$h + k$ even	0.080
l even	0.067	$h + k$ odd	0.066
l odd	0.078	$h + k + l$ Even	0.078
		$h + k + l$ Odd	0.068

Range of sin θ	R_F	No. of reflections	Range of sin θ	R_F	No. of reflections
0.00–0.40	0.065	80	0.70–0.75	0.063	90
0.40–0.50	0.049	81	0.75–0.80	0.084	100
0.50–0.60	0.056	122	0.80–0.85	0.115	101
0.60–0.65	0.052	75	0.85–0.90	0.115	106
0.65–0.70	0.080	92	0.90–1.00	0.140	62

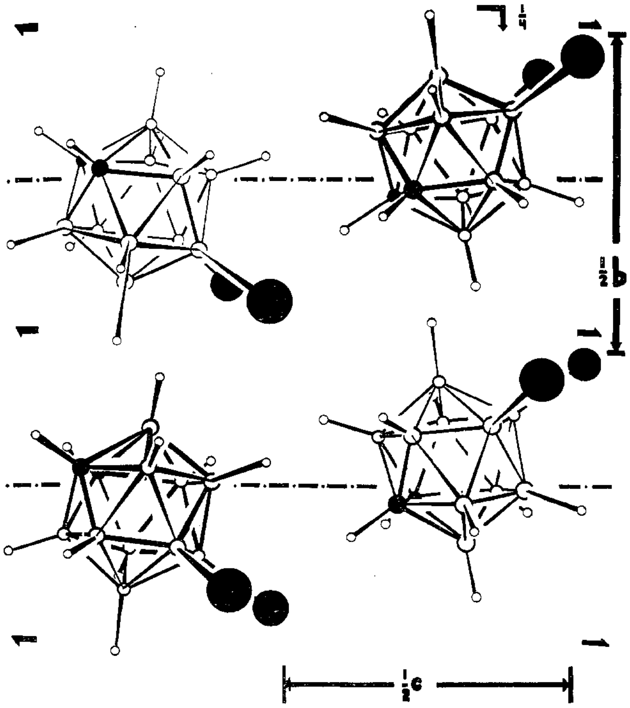

Figure 2.—The molecular packing as seen in the 0*kl* projection.

Results and Discussion

The crystal structure is shown in projection in Figure 2, atomic parameters are in Table VII, and bond distances are listed in Table VIII. No corrections of the bond distances for thermal motion have been made, because of the somewhat large standard deviations of the distances between light atoms. Comparison of this "icosahedral" structure, averaged to C_{2v} symmetry, with structures of o-$B_{10}H_{10}(CCH_2Br)_2$[3] and o-$B_{10}Cl_8$-$H_2C_2H_2$[2] shows a general trend toward longer bond distances as one moves further from the C atoms (Table IX). The somewhat short B-9–B-12 distance in o-$B_{10}Br_2H_8C_2H_2$ is an exception, which may be real. On the other hand, this exception may be associated with the proximity of these atoms to the Br atoms which can yield difficulties in the location of nearby atoms in crystal structure analysis. Comparison of these results with those of $B_{10}H_{12}(NCCH_3)_2$[6] is also included for contrast because it is a precursor of o-carborane, but, in the polyhedral fragments, bond distances around the periphery tend to be longer, on the average, than those in the interior of these fragments.

Molecular orbital calculations have been made on

---

(6) J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

TABLE VII

FINAL ATOMIC COORDINATES IN FRACTIONS OF CELL LENGTHS AND THERMAL PARAMETERS ($\times 10^4$)[a,b]

Type	Atom	x	σ_x	y	σ_y	z	σ_z
C	1	0.502	0.003	0.780	0.001	0.238	0.002
C	2	0.291	0.002	0.770	0.001	0.272	0.002
B	3	0.400	0.005	0.670	0.002	0.210	0.002
B	4	0.613	0.003	0.667	0.002	0.269	0.002
B	5	0.629	0.003	0.778	0.002	0.359	0.002
B	6	0.431	0.004	0.841	0.002	0.363	0.003
B	7	0.245	0.003	0.645	0.002	0.323	0.002
B	8	0.443	0.003	0.582	0.001	0.318	0.001
B	9	0.596	0.003	0.651	0.001	0.411	0.002
B	10	0.477	0.003	0.756	0.002	0.470	0.002
B	11	0.257	0.003	0.755	0.002	0.416	0.002
B	12	0.371	0.002	0.638	0.001	0.449	0.002
H	1′[c]	0.554		0.832		0.161	
H	2′	0.171		0.811		0.220	
H	3′	0.372		0.644		0.114	
H	4′	0.742		0.639		0.218	
H	5′	0.766		0.821		0.378	
H	6′	0.431		0.927		0.380	
H	7′	0.110		0.602		0.309	
H	8′	0.444		0.484		0.303	
Br	9′[d]	0.784	0.0002	0.579	0.0001	0.500	0.0000
H	10′	0.508		0.786		0.565	
H	11′	0.128		0.789		0.469	
Br	12′	0.287	0.0003	0.551	0.0002	0.573	0.0002

Type	Atom	β_{11}	$\sigma\beta_{11}$	β_{22}	$\sigma\beta_{22}$	β_{33}	$\sigma\beta_{33}$	β_{12}	$\sigma\beta_{12}$	β_{13}	$\sigma\beta_{13}$	β_{23}	$\sigma\beta_{23}$
C	1	266	47	51	11	64	15	−17	18	−16	23	10	11
C	2	173	33	54	9	51	12	−9	17	20	20	16	9
B	3	473	94	79	17	31	14	−53	33	−30	30	37	12
B	4	147	43	60	12	67	16	−8	17	79	22	9	12
B	5	138	40	65	13	75	17	−24	18	−65	22	−19	13
B	6	299	63	43	13	95	24	−50	23	−12	32	2	14
B	7	231	49	59	13	33	12	−9	18	−9	20	31	10
B	8	168	39	51	11	28	10	0	15	−6	17	8	9
B	9	242	47	35	10	63	14	19	17	−20	23	−28	11
B	10	175	40	52	12	40	13	22	16	−17	17	−6	9
B	11	151	37	51	12	69	15	47	15	27	21	26	11
B	12	88	33	41	10	107	18	25	14	−86	21	−10	11
H	1′[c]	210		55		60		−1		−16		5	
H	2′	210		55		60		−1		−16		5	
H	3′	210		55		60		−1		−16		5	
H	4′	210		55		60		−1		−16		5	
H	5′	210		55		60		−1		−16		5	
H	6′	210		55		60		−1		−16		5	
H	7′	210		55		60		−1		−16		5	
H	8′	210		55		60		−1		−16		5	
Br	9′	188	4	73	1	99	2	38	2	−41	3	−13	1
H	10′	210		55		60		−1		−16		+5	
H	11′	210		55		60		−1		−16		+5	
Br	12′	217	5	74	1	70	1	33	2	21	3	23	1

[a] The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The standard deviations (σ) were obtained from the full least-squares inverse matrix. [c] The ten hydrogen atoms were not unambiguously found on the final electron density map; their positions were calculated so as to place them 1.2 A from their respective B or C atoms and directed radially outward from the lines joining *para* atoms; the thermal parameters used for hydrogen were the average of the thermal parameters for the B and C atoms. [d] As $Pbn2_1$ is a polar space group, the z coordinate of atom 9′ was held constant and not refined.

$B_{10}C_2H_{12}$ by a nonempirical method[7] in which parameters for the potential energy matrix are taken from self-consistent field results on B_2H_6 and C_2H_6. There are therefore no variable parameters, such as those which exist in extended Hückel theories.[1,8] In general, the results (Table X) are similar to those obtained from the extended Hückel theory, in that they indicate that the most negative (or least positive) B atoms in the ground state of $B_{10}C_2H_{12}$ are B-10 (and B-8), followed very closely by B-9 (and B-12). Of the 72 molecular orbitals, orbital 36 is the highest filled MO, while orbital 72 is the most stable MO. The cumulative charge up to and including each orbital in order of decreasing stability is shown in columns 3–12 of Table X. On the basis of the net total charge, one might expect approximately equal probability for electrophilic substitution at positions 8, 9, 10, and 12, with, of course, the qualifications noted in the Introduction. It may

---

(7) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353, 2361, 2367 (1966); W. E. Palke and W. N. Lipscomb, *ibid.*, **88**, 2384 (1966).

(8) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 86 ff.

TABLE VIII

BOND DISTANCES[a,b]

Bond	Uncor length, A	σ	Bond	Uncor length, A	σ
	Br–Br			B–B	
9′–12′	3.80	0.010	3–4	1.73	0.041
	B–Br		3–7	1.79	0.032
9–9′	1.98	0.022	3–8	1.75	0.025
12–12′	1.95	0.020	4–5	1.80	0.030
	C–C		4–8	1.78	0.026
1–2	1.63	0.029	4–9	1.69	0.030
	C–B		5–6	1.68	0.032
1–3	1.66	0.035	5–9	1.79	0.026
1–4	1.73	0.028	5–10	1.74	0.028
1–5	1.70	0.032	6–10	1.71	0.030
1–6	1.74	0.034	6–11	1.82	0.034
2–3	1.70	0.032	7–8	1.69	0.030
2–6	1.75	0.034	7–11	1.80	0.032
2–7	1.76	0.026	7–12	1.75	0.030
2–11	1.72	0.027	8–9	1.81	0.030
			8–12	1.78	0.027
			9–10	1.77	0.028
			9–12	1.73	0.029
			10–11	1.75	0.030
			10–12	1.75	0.028
			11–12	1.79	0.024

[a] Standard deviations (A) for the various types of bonds are: C–B, 0.032; B–B, 0.037. The standard deviations were computed by averaging equivalent bond lengths based on a molecular symmetry of C_{2v} and applying the equation

$$\sigma = \left[\sum_{i=1}^{n} (X_i - \bar{X})^2/(N-1)\right]^{1/2}$$

where the final average is a weighted average over all nonsymmetry-related groups of atoms of the same type. [b] Individual standard deviations were obtained from the full variance–covariance matrix calculated during the final refinement of all position and anisotropic temperature factors.

TABLE IX

AVERAGE C_{2v} MOLECULAR BOND DISTANCES

Type of bond[a]	No. of equiv bonds[b]	o-$B_{10}H_{10}(CCH_2Br)_2$	o-$B_{10}Cl_8H_2C_2H_2$	o-$B_{10}Br_2H_8C_2H_2$	$B_{10}H_{12}(NCCH_3)_2$
1–2	1	1.64	1.67	1.63	
1–3	4	1.71	1.73	1.71	
1–4	4	1.73	1.70	1.73	
4–5	2	1.79	1.79	1.80	1.88
3–8	2	1.76	1.75	1.73	1.75
3–4	4	1.78	1.81	1.76	1.85
4–8	4	1.75	1.78	1.74	1.74
8–9	4	1.77	1.81	1.78	1.76
9–12	1	1.81	1.82	1.73	1.84
4–9	4	1.75	1.76	1.76	1.78

[a] Numbering corresponds to Figure 1. Atoms in $B_{10}H_{12}(NCCH_3)_2$ are numbered 3 through 12. [b] Equivalent bonds are based on C_{2v} framework molecular symmetry.

be of some significance, however, that the total charge in the five highest filled (and therefore most polarizable) molecular orbitals yield 0.79 electron on atom B-9 but only 0.60 electron on atom B-10. These five MO's lie very closely together in energy and are separated by a gap of about 1.3 ev from orbital 41, which has an energy corresponding to a simulated self-consistent field molecular Hartree–Fock eigenvalue of −0.45 au. Thus, this set of five highest filled molecular orbitals may be dominating the choice of site of electrophilic attack at positions B-9 and B-12.

Both the greater acidity[9] of the protons attached to C as opposed to protons attached to B and the final chlorination[2] of all B atoms of *o*-carborane before C is chlorinated suggest that the C atoms are least susceptible to electrophilic attack. This chemical result is consistent with the framework charges (Table X) which combine the charges of C and H or B and H, but there is some problem if only the net charges on C and B are considered. Our opinion is that this difficulty arises only because of the inappropriateness of the parameters from B_2H_6 and C_2H_6 for the carborane molecule. Thus, the complete self-consistent field results[7] yield a charge of −0.03 e$^-$ on terminal H and of 0.00 on bridge H in diborane, but these same parameters plus similarly appropriate parameters for C yield charges of −0.035 on H of CH and about −0.25 on H of BH. Very probably one can expect considerably more appropriate parameters for carboranes from SCF results for simpler molecules such as $C_2B_3H_5$ or $C_2B_4H_6$, but until such results become available the charges in Table X represent the best presently possible nonempirical molecular orbital calculations on the ground state of *o*-carborane. The uniformity of transfer of charge from the various types of B atoms to their attached H atoms leaves the relative charges on B atoms in the same order and, in particular, leaves B-3 as the boron atom probably least susceptible to electrophilic attack as has been noted earlier in the X-ray diffraction study[2] of *o*-$B_{10}Cl_8H_2C_2H_2$. One final observation on the cumulative orbital charges is that the highest filled orbitals on C-1 accumulate charge much more slowly than do any of the B atoms, including B-3. Hence, if electrophilic substitution is dominated by the charges in the highest filled orbitals of comparable energy, one would expect attack at B-3 before C-1, as has been found[4] in the chlorination reaction. It has also been noted, in general agreement with the charge distributions as indicated by extended Hückel theory,[1] that *o*-carborane can be tetrabrominated, whereas *m*-carborane can only be dibrominated.[5]

---

(9) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

TABLE X

CUMULATIVE ORBITAL CHARGES FOR $B_{10}C_2H_{12}$ FROM NONEMPIRICAL MOLECULAR ORBITAL CALCULATIONS[a,b]

Orbital[c]	Energy, au	C-1	B-3	B-4	B-10	B-9	H-1′	H-3′	H-4′	H-10′	H-9
36	−0.38	0.034	0.139	0.038	0.181	0.102	0.073	0.116	0.001	0.135	0.143
37	−0.39	0.116	0.163	0.099	0.198	0.395	0.201	0.116	0.001	0.135	0.477
38	−0.40	0.122	0.167	0.285	0.292	0.453	0.201	0.116	0.233	0.135	0.477
39	−0.40	0.129	0.198	0.423	0.330	0.673	0.218	0.163	0.381	0.168	0.515
40	−0.40	0.135	0.325	0.437	0.599	0.793	0.218	0.375	0.381	0.403	0.515
41	−0.45	0.151	0.498	0.742	0.776	0.811	0.218	0.375	0.382	0.403	0.520
42	−0.46	0.210	0.739	0.810	1.107	0.865	0.218	0.377	0.447	0.456	0.520
43	−0.47	0.215	0.795	0.902	1.185	0.869	0.218	0.477	0.651	0.616	0.520
44	−0.48	0.240	0.920	0.906	1.299	0.915	0.263	0.781	0.651	0.870	0.560
45	−0.49	0.431	1.058	1.066	1.453	1.056	0.263	0.781	0.678	0.870	0.560
46	−0.49	0.497	1.061	1.155	1.456	1.175	0.377	0.781	0.847	0.870	0.779
47	−0.50	0.698	1.067	1.276	1.528	1.477	0.380	0.783	0.874	0.925	0.843
48	−0.53	0.765	1.322	1.330	1.696	1.544	0.380	1.010	0.912	0.936	0.843
49	−0.54	0.980	1.322	1.516	1.696	1.597	0.563	1.010	0.974	0.936	0.904
50	−0.55	1.170	1.336	1.560	1.819	1.864	0.684	1.046	1.012	0.948	0.989
51	−0.67	1.202	1.584	1.666	2.030	1.951	0.700	1.149	1.013	1.004	1.023
52	−0.68	1.309	1.752	1.883	2.129	1.985	0.700	1.149	1.091	1.004	1.023
72	−11.28	5.673	4.484	4.774	5.043	4.999	1.035	1.258	1.241	1.233	1.245
Net Mulliken charge[d]		0.327	0.516	0.226	−0.043	0.001	−0.035	−0.258	−0.241	−0.233	−0.245
Framework charge[e]		0.292	0.258	−0.015	−0.276	−0.244					

[a] See ref 8. [b] Numbering scheme corresponds to Figure 1; only those atoms nonequivalent to C_{2v} symmetry are shown. [c] Orbital 36 is the highest filled molecular orbital of this system; the next highest orbital lies at an energy of −0.09 au. Orbital 72 is the lowest filled molecular orbital. [d] Net Mulliken charge is the total charge on the atom minus the atomic number of the atom. [e] Framework charge = net charge of B–H or C–H pair.

It seems to us of some importance that the qualifications which we have previously repeatedly stated and which are reiterated in this paper be kept in mind when electrophilic and nucleophilic reactions of polyhedral molecules are discussed. We do not imply that all reactions of carboranes or polyhedral boranes can be uniformly interpreted on a simple electrophilic or nucleophilic basis, especially under circumstances where steric effects and cooperative transition states may be important and, hence, have restricted this and earlier discussion to relatively simple atomic, ionic, or small molecule reactions with the polyhedral species. Moreover the relative charge transfer between a polyhedral molecule and a reactant may be different from that between an aromatic molecule and the same reactant, depending upon relative orbital energies, and hence the criteria of carbon chemistry may be a moderately good guide, but some exceptions to a parallelism between borane reactions and reactions of aromatic systems are to be expected.

Further structural studies in this general area of substituted polyhedral molecules are in progress.

Acknowledgment.—We wish to thank the Office of Naval Research, the Advanced Research Projects Agency, and the U. S. Army Research Office for support of this research. We are also indebted to Dr. H. Schroeder for the sample.