near invariance in bonding which occurs when the bridge H atoms (H_b) of B_2H_6 are moved into the B nuclei in order to convert them conceptually to C atoms. It is not yet known how general these orbital invariances are, but it must be noted that the corresponding B–B bond[5] of 1.596 ± 0.012 Å. in B_6H_{10} is by far the shortest known B–B distance in the boron hydrides, and our study of these dihydrocarboranes may well indicate that this B–B distance in B_6H_{10} involves some multiple bonding. Chemical studies which explore this idea may be worth the effort.

Finally, we strongly emphasize that short C–C bonds are not general in the carboranes.[8]

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Molecular Structure of Carboranes. A 1,2-Dicarbaclovododecaborane Derivative, $B_{10}Cl_8H_2C_2H_2$

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The near-icosahedral geometry of the $B_{10}C_2$ unit exists in $B_{10}Cl_8H_2C_2H_2$. The C–C bond distance of 1.67 ± 0.02 Å. can be predicted from proportional distribution of the thirteen electron pairs among the thirty icosahedral edges. Chlorine substitution has occurred at all B atoms except those two which are most positive and which are bonded to both C atoms. There are eight molecules in the unit cell which has dimensions $a = 17.11$, $b = 13.47$, and $c = 13.65$ Å.; the space group is Pbna.

o-Carborane[1,2] (1,2-dicarbaclovododecaborane, $B_{10}H_{10}C_2H_2$) is most frequently assumed[3,4] to have nearly regular icosahedral symmetry, differing from the $B_{12}H_{12}^{-2}$ ion[5] by the slight shortening of C–C and B–C bonds in accord with the decrease in covalent radius from 0.83 Å. for B to 0.77 Å. for C. This assumption has been based, in part, on the extraordinary thermal stability of *o*-$B_{10}H_{10}C_2H_2$, which transforms to neocarborane[6,7] (*m*-$B_{10}H_{10}C_2H_2$) without decomposition at 470°.

However, a model with a short C–C distance of 1.54 Å. has been suggested[7] for *o*-carborane, which is conjectured to transform to *m*-carborane by expansion of this short distance to one of about 1.77 Å. in the transition state, but the valence theory here is not clear, especially as to the nature of the barrier between these suggested structures. In even stronger disagreement with the usually accepted structure is the recent report of an X-ray diffraction study[8] which indicates an ethylenedecaborane type of structure for the $B_{10}C_2$ unit. We show below that both the proposal of the short C–C bond and the ethylenedecaborane unit are not correct for the $B_{10}C_2$ unit in $B_{10}Cl_8H_2C_2H_2$ and, furthermore, that the near-icosahedral structure is indeed correct. Thus the two bonded C atoms share in the electron deficiency of the boron polyhedral environment to an extent not hitherto proven.

The possibility[3] that polyhedral boranes form a superaromatic system raises questions of position and mechanism of electrophilic and nucleophilic substitution. The ground-state charge distribution should be reasonably indicative of the position of substitution under the conditions that the charge distribution in the transition state resembles that in the ground state, and that steric or neighbor effects are not dominant. Successive substitution changes the charge distribution for predictions of yet further substitution. Nevertheless, the very strongly positive character found[3] for the two B atoms bonded to *both* C atoms might be preserved in successive Cl substitution such that eight Cl atoms would appear on all B atoms except these two. We show that this result is indeed correct and, hence, that probably electrophilic substitution has taken place.

Structure Determination

A needle-like crystal, 0.8 mm. in length with a square base 0.11 mm. on edge, was mounted along the needle axis (*b*). The reciprocal lattice symmetry is D_{2h}, and unit cell dimensions are (λ 1.5418 Å.) $a = 17.11 \pm 0.02$, $b = 13.47 \pm 0.02$, and $c = 13.65 \pm 0.02$ Å. Extinctions of $0kl$ when k is odd, of $hk0$ when h is odd,

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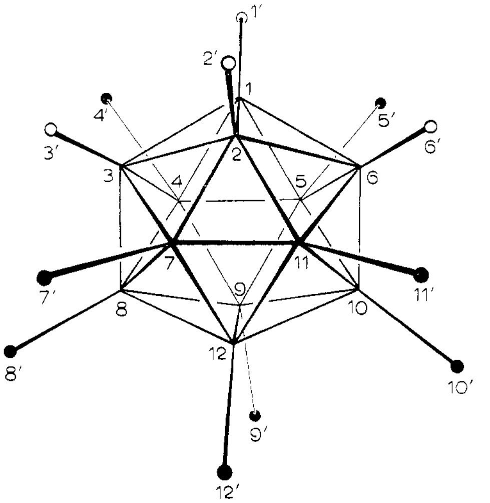

Fig. 1.—The molecular structure and numbering scheme for $B_{10}Cl_8H_2C_2H_2$. Atoms are designated as follows: H, (1′, 2′, 3′, 6′); C, (1, 2); B, (3, 4, 5, 6, 7, 8, 9, 10, 11, 12); Cl, (4′, 5′, 7′, 8′, 9′, 10′, 11′, 12′).

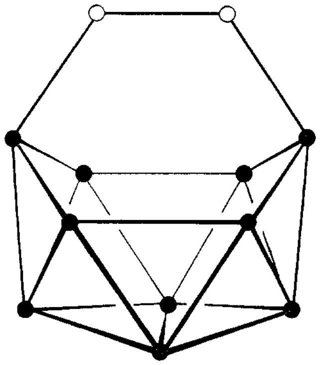

Fig. 2.—The earlier reported[8] $B_{10}C_2$ unit for $B_{10}H_{10}C_2(CH_2Br)_2$. Open circles indicate C, black circles B atoms.

and of $h0l$ when $h + l$ is odd indicate the space group Pbna. Relative intensities of 2600 independent diffraction maxima were measured for levels $k = 0$ to 11, inclusive, about the needle axis. Background radiation was subtracted and the usual Lorentz and polarization factors $(1/LP = (2 \cos^2 \mu \sin \Upsilon)/(1 + \cos^2 2\theta))$ were applied in order to obtain F_{hkl}^2.

Diffraction data were collected on the Buerger automated X-ray diffractometer which employed Weissenberg geometry. The Xe proportional counter terminals were set at 1658 volts, in order to include Cu Kα radiation, but to exclude the escape peak[9] which occured at a slightly smaller pulse amplitude than did the desired peak. A Ni filter was used to exclude Cu Kβ radiation. The base line of the pulse height analyzer, the window voltage, and the counter voltage were all maintained constant throughout the experiment. Measurement of a reflection included the following steps: (a) positioning the counter to the proper value of Υ, the vertical Weissenberg film coordinate; (b) rotating the crystal about the spindle axis until the angle ϕ (the horizontal film coordinate) was $\phi_r - \delta$, where ϕ_r is the value of ϕ for the particular reflection and δ is proportional to the Lorentz factor; (c) reading the background for a time t, also proportional to the Lorentz factor; (d) increasing ϕ in a time $2t$ at a rate of

TABLE I

LIST OF OBSERVED F_{hkl} VALUES[a]

```
 K=0 (H)(L) ( 0)(0,16)1616,,U,,129,,25,,153,,28,,33,,31,,44, ( 1)(1, 9)53,,*,,
130,,85,,137, ( 2)(2,16)66,,77,,*,,139,,*,,16,,45,,40, ( 3)(1,13)76,,76,,44,,
62,,56,,34,,48, ( 4)(0,16)69,,118,,196,,27,,30,,*,,30,,46,,*, ( 5)(1,13)69,,
30,,34,,92,,67,,36,,51, ( 6)(0,14)107,,120,,*,,74,,70,,*,,23,,*, ( 7)(1,15)
72,,37,,141,,51,,34,,40,,41,,40, ( 8)(0,12)38,,82,,247,,107,,31,,43,,47,
 ( 9)(1,15)117,,50,,33,,88,,*,,40,,*,,28, (10)(0,14)*,,39,,*,,23,,*,,*,,41,,
*, (11)(1,11)99,,32,,*,,*,,42,,37, (12)(0,10)140,,49,,31,,83,,82,,28,
 (13)(1,11)42,,102,,91,,54,,57,,33, (14)(0,10)*,,40,,27,,80,,*,,22,
 (15)(1, 1)43, (16)(0, 8)58,,*,,*,,*,,47, (17)(3, 3)60, (18)(0, 8)49,,49,,
26,,*,,*, (20)(0, 4)63,,*,,28
 K=1 (H)(L) ( 1)(3,14)24,*,138,41,35,*,42,34,34,*,32,23, ( 2)(1,15)U,*,75,
316,49,*,59,51,21,*,34,25,*,33,28, ( 3)(2,14)47,53,39,115,51,81,38,78,41,37,
57,*,39, ( 4)(0,16)44,76,72,229,26,*,35,57,45,*,25,*,40,24,*,*,37, ( 5)(1,14)
151,113,*,25,*,*,92,21,98,33,*,21,*,28, ( 6)(0,12)423,50,73,30,68,*,*,*,148,
*,23,70,40, ( 7)(1,14)37,39,74,67,108,35,78,38,47,*,36,*,*,27, ( 8)(1,11)76,
*,52,38,62,65,84,50,53,32,21, ( 9)(1,13)79,46,*,75,*,*,30,37,*,18,*,*,33,
 (10)(0,10)68,49,*,*,42,99,*,46,46,52,33, (11)(1,13)59,73,36,80,21,*,*,52,*,
22,19,*,28, (12)(0,13)56,82,80,30,20,19,*,24,*,38,28,26,21,27, (13)(1, 8)27,
*,28,24,91,48,34,14, (14)(1,10)37,21,30,78,*,*,*,20,*,33, (15)(1, 9)81,31,
36,*,*,21,26,*,29, (16)(1,10)26,*,*,*,33,*,33,*,*,27, (17)(2, 9)29,*,*,*,26,
*,*,34, (18)(3, 6)22,25,*,21, (19)(1, 5)20,*,37,*,30
 K=2 (H)(L) ( 0)(1,15)141,60,93,101,54,103,55,53,*,26,89,36,42,23,48,
 ( 1)(1,16)20,27,46,222,48,24,53,53,*,75,*,22,*,*,*,22, ( 2)(1,12)126,*,220,
26,229,*,98,*,48,45,55,44, ( 3)(2,14)102,113,153,95,*,82,36,*,*,16,36,*,21,
 ( 4)(0,15)88,63,188,67,116,37,81,22,28,99,*,40,*,*,*,34, ( 5)(2,16)122,76,
25,42,*,69,30,*,51,24,21,*,*,*,25, ( 6)(0,11)26,71,35,*,57,89,*,90,*,*,22,
49, ( 7)(1,13)55,70,24,77,58,68,27,39,*,33,38,*,29, ( 8)(0,15)62,31,50,33,
80,*,50,*,21,*,*,*,*,65,*,23, ( 9)(2,12)76,52,81,*,*,*,51,24,17,25,42,
 (10)(0,11)24,57,*,111,*,51,*,24,*,46,*,43, (11)(2,14)109,*,18,*,53,34,21,
33,39,*,*,*,22, (12)(0,13)47,25,52,*,26,*,44,39,*,23,*,51,30,33, (13)(1,11)
31,31,24,29,*,36,*,*,*,26,23, (14)(0,11)44,*,25,*,26,*,*,*,*,*,32,25,
 (15)(1, 8)15,73,41,*,*,*,*,29, (16)(0, 9)42,32,37,15,*,41,*,20,*,27,
 (17)(2, 8)61,21,37,*,29,25,27, (18)(1, 1)36, (19)(2, 6)35,*,36,*,38,
 (20)(1, 1)31
 K=3 (H)(L) ( 1)(1,14)25,*,79,*,*,*,109,*,41,*,28,*,*,23, ( 2)(1,16)29,288,
37,49,117,74,27,*,39,*,38,35,31,*,*,28, ( 3)(1,12)24,33,80,54,24,45,126,71,
66,*,26,80, ( 4)(0,15)40,238,84,325,*,159,55,98,*,42,52,40,*,25,*,20,
 ( 5)(1,15)102,94,74,30,21,46,*,71,*,24,30,45,*,*,38, ( 6)(0,15)107,37,91,
66,20,28,79,38,89,39,*,63,*,*,*,27, ( 7)(1,14)22,37,57,*,84,*,23,40,42,30,
57,*,*,25, ( 8)(0,11)104,96,26,*,50,93,*,29,46,36,*,27, ( 9)(1, 9)47,78,102,
*,68,84,57,*,39, (10)(0,13)74,*,110,83,*,35,58,43,60,45,24,*,45,21,
 (11)(1,13)33,35,115,*,50,54,41,28,22,*,24,*,27, (12)(0, 8)91,48,87,63,*,30,
*,50,32, (13)(2,12)46,31,33,24,35,*,*,*,34,*,21, (14)(1,10)32,37,*,*,*,45,*,
*,*,32, (15)(1,10)50,50,*,*,26,35,*,*,*,32, (16)(1,10)28,25,*,28,30,*,*,*,
37,27, (17)(2, 7)79,23,*,21,66,38, (18)(2, 7)37,30,*,22,22,22, (19)(3, 3)45,
 (20)(3, 3)24
 K=4 (H)(L) ( 0)(1,16)100,217,66,183,69,-0,92,47,67,23,*,*,29,*,23,38,
 ( 1)(1,15)32,65,104,36,*,57,29,103,56,39,89,36,*,*,20, ( 2)(0,14)75,249,33,
97,*,41,*,88,43,46,47,35,40,25,35, ( 3)(1,13)36,*,57,46,*,54,66,41,25,21,27,
33,38, ( 4)(0,12)41,23,160,108,77,21,29,78,21,62,*,*,33, ( 5)(1,14)31,*,28,
41,*,26,101,41,21,31,43,30,*,22, ( 6)(0, 9)42,*,117,71,37,*,28,*,74,22,
 ( 7)(1,15)25,37,59,29,47,*,*,*,43,38,*,*,*,34,28, ( 8)(0,13)176,41,64,39,
85,33,124,*,29,42,27,*,33,21, ( 9)(1, 7)68,58,*,22,*,73,70, (10)(0,14)28,99,
*,54,36,79,*,42,17,30,*,*,26,25,21, (11)(1,13)37,75,49,23,38,57,*,*,*,*,*,*,
22, (12)(2, 8)30,51,30,*,54,25,62, (13)(3,10)71,*,38,21,*,*,25,31, (14)(1,10)
23,34,*,*,22,61,*,23,*,25, (15)(2, 7)22,*,28,*,37,40, (16)(1, 8)25,56,30,33,
*,*,19,24, (17)(1, 6)*,*,28,27,21,25, (18)(1, 3)32,*,22, (19)(1, 5)12,50,*,
31,*, (20)(0, 2)21,42,22
 K=5 (H)(L) ( 1)(1,14)49,*,*,31,*,*,88,*,60,38,25,*,*,26, ( 2)(0,12)240,113,
53,*,124,96,44,28,122,37,32,*,23, ( 3)(1,14)42,94,56,49,20,*,119,18,50,33,*,
19,*,27, ( 4)(0,12)48,76,*,99,*,28,*,58,*,*,30,36,67, ( 5)(1,15)47,59,62,*,
126,64,21,-0,27,*,44,24,*,*,27, ( 6)(0,15)88,31,70,41,199,*,*,44,84,25,*,36,
26,*,30,33, ( 7)(1,12)82,33,113,30,44,*,*,*,41,30,38,27, ( 8)(0,14)41,71,31,
*,35,*,59,43,*,*,74,26,*,*,33, ( 9)(1,13)55,*,37,49,*,23,32,*,30,*,*,*,30,
 (10)(0,13)24,22,*,24,35,48,*,*,*,*,28,33,25,31, (11)(1,11)57,*,48,66,*,*,
24,*,27,*,35, (12)(0,10)73,47,41,*,*,*,*,*,27,45,56, (13)(1, 9)57,29,56,34,*,
*,24,*,63, (14)(0, 8)92,36,49,30,25,*,*,*,34, (15)(1, 7)60,18,23,*,82,45,51,
 (16)(1, 6)26,*,*,*,*,26, (17)(4, 4)25, (18)(0, 6)29,*,27,*,*,25,30,
 (19)(1, 1)24
 K=6 (H)(L) ( 0)(2, 8)97,42,42,383,78,95,*,135, ( 1)(1,11)44,49,90,74,162,
42,54,55,*,*,38, ( 2)(0,12)73,158,*,*,*,83,*,*,39,*,*,*,43, ( 3)(1, 9)42,*,
70,*,*,87,*,38,35, ( 4)(0, 8)171,72,*,37,43,51,*,39,89, ( 5)(3, 9)71,61,*,*,
*,*,43, ( 6)(0,10)36,*,39,*,*,50,65,45,*,*,44, ( 7)(1, 9)125,51,*,*,*,63,41,
*,59, ( 8)(0,10)276,36,*,78,69,44,46,*,61,*,34, ( 9)(2,11)45,68,*,57,*,46,*,
*,*,19, (10)(1, 5)39,*,69,46,51, (11)(2,12)71,*,*,67,*,*,*,*,*,*,16,
 (12)(0,12)24,*,*,*,84,*,*,*,*,*,*,*,19, (13)(1, 9)107,*,46,*,*,*,*,*,34,
 (14)(0,10)43,*,*,*,*,*,*,*,*,*,30, (16)(4, 4)31, (19)(2, 3)37,32
 K=7 (H)(L) ( 1)(1, 9)58,*,*,*,*,35,*,33,58, ( 2)(2, 9)54,*,*,87,*,*,35,13,
 ( 3)(2,12)39,*,*,68,48,*,72,49,*,33,21, ( 4)(1, 8)198,56,166,54,88,62,80,
56, ( 5)(2,13)50,50,*,106,*,38,47,*,35,*,29,24, ( 6)(4,12)227,39,*,44,*,*,*,
41,23, ( 7)(1, 8)72,*,*,*,*,*,30,39, ( 8)(1,10)153,55,51,65,40,*,*,*,*,46,
 ( 9)(1, 9)55,40,*,*,61,93,*,29,35, (10)(1,10)39,60,83,73,*,-0,*,50,*,27,
 (11)(1, 9)54,*,*,50,38,40,*,*,34, (12)(3, 8)59,*,*,16,40,36, (13)(1, 9)38,
35,*,*,*,*,*,*,43, (14)(8, 8)28, (15)(3, 6)36,30,46,32, (16)(1, 5)49,*,47,*,
23, (17)(2, 2)64
 K=8 (H)(L) ( 0)(2,13)19,41,71,*,86,120,*,34,52,44,*,38, ( 1)(1,12)51,*,35,
45,U,*,*,28,30,*,*,65, ( 2)(1,11)109,79,135,82,42,*,81,38,45,*,44, ( 3)(3, 8)
47,32,94,50,62,71, ( 4)(0,11)83,87,36,101,71,*,33,*,*,*,*,34, ( 5)(3,12)67,
31,59,41,*,*,41,*,*,33, ( 6)(1, 8)78,*,65,*,*,*,32,26, ( 7)(1, 8)30,*,*,*,*,
*,*,46, ( 8)(3,11)36,68,*,35,*,38,29,*,32, ( 9)(2,12)35,*,*,*,41,*,64,*,*,*,
39, (10)(0, 7)43,64,17,63,*,57,*,53, (11)(2,10)77,33,*,*,39,33,*,*,26,
 (12)(5, 7)41,*,30, (13)(10,10)32, (14)(3, 8)45,50,*,*,*,43, (15)(3, 6)32,
34,36,21, (16)(0, 3)55,36,*,37, (17)(2, 2)36
 K=9 (H)(L) ( 1)(2,12)23,74,*,*,*,*,*,*,*,54,40, ( 2)(1, 9)44,110,52,104,34,
62,*,47,20, ( 3)(2,11)65,77,78,44,*,*,62,*,*,54, ( 4)(1,12)71,*,44,*,81,*,
89,*,30,*,45,33, ( 5)(4,10)75,30,*,46,*,*,46, ( 6)(1,13)100,53,*,90,25,*,24,
31,*,*,*,*,30, ( 7)(1,12)60,*,46,34,*,36,56,*,*,*,*,25, ( 8)(3,10)63,28,27,*,
*,28,35,41, ( 9)(2,10)52,49,*,*,*,49,*,*,29, (10)(2,11)46,*,*,*,45,*,*,26,*,
60, (11)(2, 7)65,55,26,*,*,24, (12)(1,10)69,*,*,*,*,*,32,47,40,26, (13)(1, 8)
17,*,25,29,32,47,*,46, (14)(1, 8)36,25,*,*,*,*,28,31, (15)(3, 5)31,*,53,
 (16)(1, 1)27, (17)(2, 2)51
 K=10(H)(L) ( 0)(1,12)16,96,57,191,55,45,*,77,29,*,36,60, ( 1)(5, 8)25,74,
120,41, ( 2)(1,12)38,51,62,35,*,*,41,40,41,*,*,43, ( 3)(3,11)47,*,*,*,*,*,*,
34,43, ( 4)(1,10)65,101,*,*,*,58,*,30, ( 5)(3,12)34,*,35,*,37,32,*,*,42,36,
 ( 6)(0,12)30,37,*,32,*,*,39,*,*,30,*,*,34, ( 7)(1,11)60,*,*,54,38,*,*,32,*,
*,46, ( 8)(0,10)83,67,65,*,79,22,46,*,66,40,45, ( 9)(3,10)65,*,*,*,*,39,*,
45, (10)(3, 5)30,*,21, (11)(2, 9)44,50,*,*,*,*,37,52, (12)(0, 7)76,57,60,*,
50,30,*,30, (13)(1, 7)81,31,*,32,*,*,37, (14)(1, 6)29,29,*,*,*,51
 K=11(H)(L) ( 1)(6,11)44,*,*,*,*,41, ( 2)(2,11)61,36,66,41,*,*,*,*,*,34,
 ( 3)(2,11)34,*,*,*,*,*,*,*,*,44, ( 4)(1, 8)42,*,*,*,*,*,*,60, ( 5)(3, 9)39,
*,*,46,40,*,78, ( 6)(1,10)35,45,*,76,*,47,*,45,*,29, ( 7)(1, 7)37,*,*,*,46,
30,66, ( 8)(2, 6)44,*,*,*,45, ( 9)(5, 5)31, (10)(3, 9)29,31,50,42,*,*,42,
 (12)(2, 7)46,29,*,*,40,50, (13)(4, 5)30,37, (14)(1, 4)29,43,*,57, (15)(1, 1)
31
```

[a] The value of h and the range of l are given in parentheses. Unobserved reflections are indicated by an asterisk, experimentally unobservable reflections by U, and space group extinctions by an extra comma. All reflections are on the same scale with 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 either F_o or F_c is greater than 20.

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(9) International Tables for X-ray Crystallography, Vol. III, 152.

TABLE II

FINAL VALUES FOR $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|)$

hkl	*R*	Range of sin θ	*R*
All	0.108	0.00 to 0.40	0.074
h even	0.110	0.40 to 0.50	0.076
h odd	0.105	0.50 to 0.60	0.092
k even	0.110	0.60 to 0.65	0.118
k odd	0.107	0.65 to 0.70	0.117
l even	0.111	0.70 to 0.75	0.139
l odd	0.105	0.75 to 0.80	0.193
$k + l$ even	0.108	0.80 to 0.85	0.152
$k + l$ odd	0.108	0.85 to 0.90	0.180
$h + l$ even	0.105	0.90 to 1.00	0.160
$h + l$ odd	0.111		
$h + k$ even	0.107		
$h + k$ odd	0.109		
$h + k + l$ even	0.113		
$h + k + l$ odd	0.103		

TABLE III

FINAL ATOMIC COORDINATES IN FRACTIONS OF CELL LENGTHS AND THERMAL PARAMETERS[a]

Atom	*x*	*y*	*z*	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
1	0.2406	0.5135	0.2536	155	137	331	25	26	−8
2	0.3106	0.5995	0.2457	188	105	338	13	4	−21
3	0.3066	0.5315	0.3515	259	215	271	−7	10	43
4	0.2761	0.4064	0.3104	203	162	286	−3	18	38
5	0.2641	0.4132	0.1821	155	116	291	3	−11	−4
6	0.2815	0.5435	0.1400	177	133	295	17	−21	36
7	0.3946	0.5634	0.2957	202	191	370	−27	−57	−24
8	0.3769	0.4431	0.3374	228	226	329	4	−79	46
9	0.3516	0.3663	0.2329	172	113	361	34	−9	21
10	0.3525	0.4472	0.1263	182	152	287	14	34	−16
11	0.3803	0.5691	0.1646	172	143	348	−12	21	25
12	0.4240	0.4649	0.2216	141	186	436	20	−11	14
1′[b]	0.1771	0.5235	0.2619	. . .	. . .	. . .	. . .	. . .	. . .
2′[b]	0.2868	0.6753	0.2498	. . .	. . .	. . .	. . .	. . .	. . .
3′[b]	0.2833	0.5536	0.4234	. . .	. . .	. . .	. . .	. . .	. . .
4′	0.2135	0.3386	0.3832	338	328	434	−62	110	114
5′	0.1870	0.3466	0.1255	227	241	490	−61	−81	−36
6′[b]	0.2448	0.5713	0.0798	. . .	. . .	. . .	. . .	. . .	. . .
7′	0.4575	0.6481	0.3552	340	374	630	−123	−164	−94
8′	0.4231	0.3852	0.4390	434	502	510	−8	−242	178
9′	0.3715	0.2378	0.2226	282	125	675	77	1	26
10′	0.3800	0.4005	0.0093	382	368	371	−4	141	−105
11′	0.4325	0.6557	0.0969	284	271	565	−83	92	103
12′	0.5239	0.4304	0.2033	146	402	919	56	17	27

[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 four hydrogen atoms were not unambiguously found on the final electron density map; their positions were calculated so as to place them 1.1 Å. from their respective B or C atoms and directed radially outward from the average center of the icosahedron.

2°/min. until it became $\phi_r + \delta$; (e) counting the background again for a time t; and (f) computing $LPF_{hkl}{}^2$ as the scan count minus the sum of the background counts. The measurement of each of six reflections 25 times provided an initial check on the diffractometer readings. All intensities before correction for background and *LP* factors were within 2.5σ, where σ is the square root of the number of counts. The needle-like shape of the crystal, which we unsuccessfully tried to cut into a favorable shape for photographs about a different axis, led us to treat scale factors as follows. In the complete solution of the structure, the various levels *k* were assumed to be correlated by the diffractometer, but in the final refinement stages, nine scale factors for the levels $0 \leqslant k \leqslant 11$ were found empirically as 0.50, 0.50, 0.50, 0.49, 0.49, 0.45, 0.28, 0.30, 0.32, 0.40, 0.35, 0.35 for these successive levels. The same scale factor was applied to the following pairs of levels: *h*1*l* and *h*2*l*, *h*3*l* and *h*4*l*, *h*10*l* and *h*11*l*. Internal correlation within a given level was constant in time, as was shown by measurement of a given check reflection on each level at intervals of 15 reflections.

The structure was solved from a three-dimensional Patterson function, from which all but a double Cl· · ·Cl interaction had been subtracted at the origin. This function was sharpened so that the average intensities were independent of sin θ. Analysis of the Harker sections for Cl· · ·Cl interactions led to three most likely Cl positions, each of which formed the basis of a three-dimensional superposition function. The six highest peaks in each of these superposition functions led to the same structure for this part of the Cl arrangement in the molecule. A three-dimensional electron density map computed from the 934 largest F_{hkl} and signs obtained from these six Cl atoms yielded the remaining two Cl atoms unambiguously and reduced $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ from 0.46 to 0.37. A three-dimensional difference map then yielded all B atoms and C atoms as an essentially icosahedral arrangement, with no other assumptions than the signs of F_{hkl} as determined by the eight Cl atoms of the molecule. In the next three-dimensional difference map the signs were determined by eight Cl atoms and the eight B atoms, omitting the two C atoms and the two B atoms attached to the C atoms. Again, these four omitted atoms were found as the only peaks of

Table IV

Bond Distances[a]

Bond	Uncorrected length, Å.	Bond	Uncorrected length, Å.
B–Cl		B–B	
4–4′	1.723	4–8	1.830
5–5′	1.771	4–9	1.754
7–7′	1.765	5–6	1.869
8–8′	1.776	5–9	1.765
9–9′	1.768	5–10	1.753
10–10′	1.778	6–10	1.786
11–11′	1.736	6–11	1.756
12–12′	1.788	7–8	1.743
Cl–Cl		7–11	1.807
4′–5′	3.547	7–12	1.742
4′–8′	3.718	8–9	1.815
4′–9′	3.734	8–12	1.799
5′–9′	3.722	9–10	1.817
5′–10′	3.732	9–12	1.821
7′–8′	3.766	10–11	1.787
7′–11′	3.554	10–12	1.801
7′–12′	3.766	11–12	1.769
8′–9′	3.666	C–B	
8′–12′	3.701	1–3	1.766
9′–10′	3.646	1–4	1.745
9′–12′	3.685	1–5	1.713
10′–11′	3.747	1–6	1.748
10′–12′	3.638	2–3	1.711
11′–12′	3.710	2–6	1.701
B–B		2–7	1.664
3–4	1.850	2–11	1.677
3–7	1.742	C–C	
3–8	1.703	1–2	1.668
4–5	1.766		

[a] Standard deviations (Å.) for the various types of bonds are: B–C, $\sigma = 0.0335$; B–B, $\sigma = 0.0337$; B–Cl, $\sigma = 0.0154$; Cl–Cl, $\sigma = 0.0205$. The standard deviations were computed by averaging equivalent bond lengths based on a molecular symmetry of C_{2v} and applying the equation

$$\sigma = \left(\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1} \right)^{1/2}$$

where the final average is a weighted average over all non-symmetry-related groups of atoms of the same type. It is probable that $\sigma_{\mathrm{Cl-Cl}}$ represents true molecular distortion due to packing, since it is larger than $\sigma_{\mathrm{B-Cl}}$. Corrections for thermal vibrations were computed using the least-squares rotation tensor and were found to be small compared to the standard deviation in bond lengths. For B–B, B–Cl, and Cl–Cl bonds, the largest corrections were 0.0019, 0.0002, and 0.0017 Å., respectively.

any significance (which were not residuals of known atoms) and, furthermore, the greater electron density of C as compared with B was clearly apparent. These four peaks completed the icosahedral arrangement of the $B_{10}C_2$ unit.

Refinement of the structure was carried out by a procedure[10] which incorporates molecular rigidity. For the 1326 largest F_{hkl} only 12 min. of time on the IBM 7094 was required for two cycles of three-dimensional least-squares refinement, which brought all parameters within 50% of their standard deviations. The parameters which were refined were: 60 atomic positions of $Cl_8B_{10}C_2$, nine scale factors, six mean-square translational tensor components, six mean-square rotational tensor components, and the three coordinates of the center of rotation of the molecule. Thus only 15 thermal parameters were refined, rather than the 120 which would have had to be refined if each atom was assumed to have six independent anisotropic thermal parameters. A comparison at this point with a full anisotropic refinement showed no significant difference in values of R_F, and hence all further refinements were of the rigid body type.

The three final refinement procedures are summarized below. A total of 2169 independent reflections which were greater than zero gave $R_F = 0.15$ after all but twelve of the changes in the 84 parameters had decreased to less than one standard deviation. In the second final refinement, all reflections for which $F_o < 17$ on a scale on which the average standard deviation was 15 and the largest reflection was 425 were omitted; values of

$$R_F = 0.13,\ R_{F^2} = \Sigma \left| F_o^2 - F_c^2 \right| / \Sigma F_o^2 = 0.15$$

and

$$R_{wF^2} = \left| \Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4 \right|^{1/2} = 0.25$$

were obtained. In the third final refinement, we included the 1293 diffraction maxima (Table I) for which $F_o > 20$ and, in addition, those observed reflections for which F_c was >20 in the previous refinements. Two cycles of refinement yielded $R_F = 0.11$, $R_{F^2} = 0.14$, and $R_{wF^2} = 0.28$ (Table II). All parameter shifts were finally less than 0.7σ and all but one were less than 0.25σ, where σ is the standard deviation. The weighting scheme in these final refinements was $w = 1$ for $F_o \leqslant 34$ and $w = 34/F_o$ for $F_o \geqslant 34$, where w is the weighting factor in the observational equations of the least-squares treatment. A near-linear plot of $\left| F_o^2 - F_c^2 \right| / \sigma$ *vs.* log F_o^2 indicated that this weighting scheme was reasonable, but perhaps that it somewhat underemphasized the smaller reflections. The final parameters are shown in Table III.

A final three-dimensional electron density map computed from the 2169 reflections for which $F_o > 0$ showed eight Cl atoms varying in peak heights from 1050 to 1200, ten B atoms varying from 250 to 350, and the two C atoms at 340 and 360. Subtraction of all of these atoms yielded a map in which the highest peak, on the same arbitrary scale, was 66 and was, moreover, in a chemically unreasonable position. Peaks in the range 30–60 around the Cl atoms indicated incomplete correction for anisotropy of thermal vibrations, and, most interestingly, peaks ranging from 34 to 40 were found at reasonable positions for H atoms (Table III).

Results and Discussion

The numbering scheme is shown in Fig. 1, the incorrect ethylenedecaborane $B_{10}C_2$ unit[8] sketched in Fig. 2, and a line drawing of the projection of the molecular packing is given in Fig. 3. Only a sufficient number of symmetry elements to generate the space group are included for simplicity. Bond distances, before and after correction for thermal motion, in Table IV have

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[10] G. S. Pawley, *Acta Cryst.*, **17**, 457 (1964).

TABLE V

MODEL DRILLING ANGLES

Center atom	Coordinating atom	ϕ,[a] deg.	ρ,[a] deg.
1	2	90.0	0.0
	3	0.0	59.7
	4	320.4	110.6
	5	254.5	109.9
	6	211.0	59.7
	13	108.9	129.0
2	1	90.0	0.0
	3	0.0	63.0
	6	149.0	62.5
	7	38.1	113.0
	11	111.0	112.6
	14	251.1	112.0
3	1	90.0	0.0
	2	0.0	57.3
	4	221.8	57.7
	7	325.8	104.8
	8	262.6	105.6
	15	119.5	118.8
4	1	90.0	0.0
	3	0.0	58.8
	5	219.9	58.4
	8	323.3	101.2
	9	260.9	104.0
	16	108.2	118.5
5	1	90.0	0.0
	4	0.0	60.2
	6	216.1	58.2
	9	319.1	104.9
	10	254.6	104.2
	17	109.7	118.2
6	1	90.0	0.0
	2	0.0	57.8
	5	134.7	56.4
	10	97.4	101.4
	11	35.1	105.1
	18	238.8	120.8
7	2	90.0	0.0
	3	0.0	60.3
	8	39.4	104.8
	11	143.8	57.6
	12	103.7	103.5
	19	252.4	121.7
8	3	90.0	0.0
	4	0.0	63.0
	7	137.2	60.7
	9	36.2	108.6
	12	100.2	107.5
	20	253.3	122.2
9	4	90.0	0.0
	5	0.0	60.2
	8	135.3	61.7
	10	35.5	107.8
	12	98.4	109.1
	21	251.6	119.4
10	5	90.0	0.0
	6	0.0	63.7
	9	137.8	59.2
	11	37.6	110.0
	12	100.4	107.8
	22	247.0	121.7
11	2	90.0	0.0
	6	0.0	59.3
	7	215.1	56.9
	10	316.6	103.2
	12	254.1	101.8
	23	109.7	123.6
12	7	90.0	0.0
	8	0.0	59.0
	9	36.3	108.0
	10	100.1	108.9
	11	138.8	62.0
	24	251.9	123.6

[a] See ref. 4, p. 228, for definitions of ϕ and ρ.

been computed from the final parameters in Table III. Bond angles are listed in Table V in a form suitable for construction of a model; ϕ is the azimuthal angle in the x, y plane and ρ is measured from the z axis of the usual spherical coordinate system.[4] The average bond angles (Table VI) indicate that the B_{10} unit and Cl_8 arrangement are very closely icosahedral, but that some distortion of bond angles around the C atoms occurs because the C–C and B–C bonds are shorter than the B–B bonds.

TABLE VI

AVERAGE BOND ANGLES (DEG.)

No. of measurements	Bond type	Average angle	Largest angle	Smallest angle	Std. dev.
36	B–B–B	59.999	63.01	55.13	1.610
24	Cl–Cl–Cl	59.999	61.77	56.76	1.395
11	B–B–C	58.454	60.29	56.87	1.102
6	B–C–B	63.422	65.49	59.65	1.707
4	B–C–C	61.211	62.63	59.65	1.785
2	C–B–C	57.570	57.83	57.32	0.366

The C–C distance of 1.67 ± 0.02 Å. is strongly indicative that the C atoms share the electron deficiency on a near-equal basis with the B atoms. Hence, the geometrical and valence structures[7] having a very short C–C distance can be discarded in favor of a nearly icosahedral model. This C–C distance of 1.67 Å., the average B–C distance of 1.71 Å., and the average B–B distance of 1.79 Å. can be predicted reasonably well if it is assumed that the available electrons of each atom in the $B_{10}C_2$ unit contribute equally to the bonding of all nearest neighbors and not at all to any of the other atoms. We define bond order as the number of electron pairs per contact (icosahedron edge) and examine C–C, B–C, and B–B bond orders individually. Thus, for the C–C bond we have 1 contact which utilizes 0.6 electron pair (three framework electrons per C atom divided equally among the five neighbors) and gives a bond order of 0.6. Bond orders of 0.5 and 0.4 for B–C and B–B bonds, respectively, are found similarly (B–C: 4.0 electron pairs, 8 contacts; B–B: 8.4 electron pairs, 21 contacts). A single-bonded B radius[11] can be calculated from the average B···B distance of 1.77 Å. in the $B_{12}H_{12}^{-2}$ ion[5] and the equation for bond

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[11] W. N. Lipscomb and R. Lewin, "Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 312.

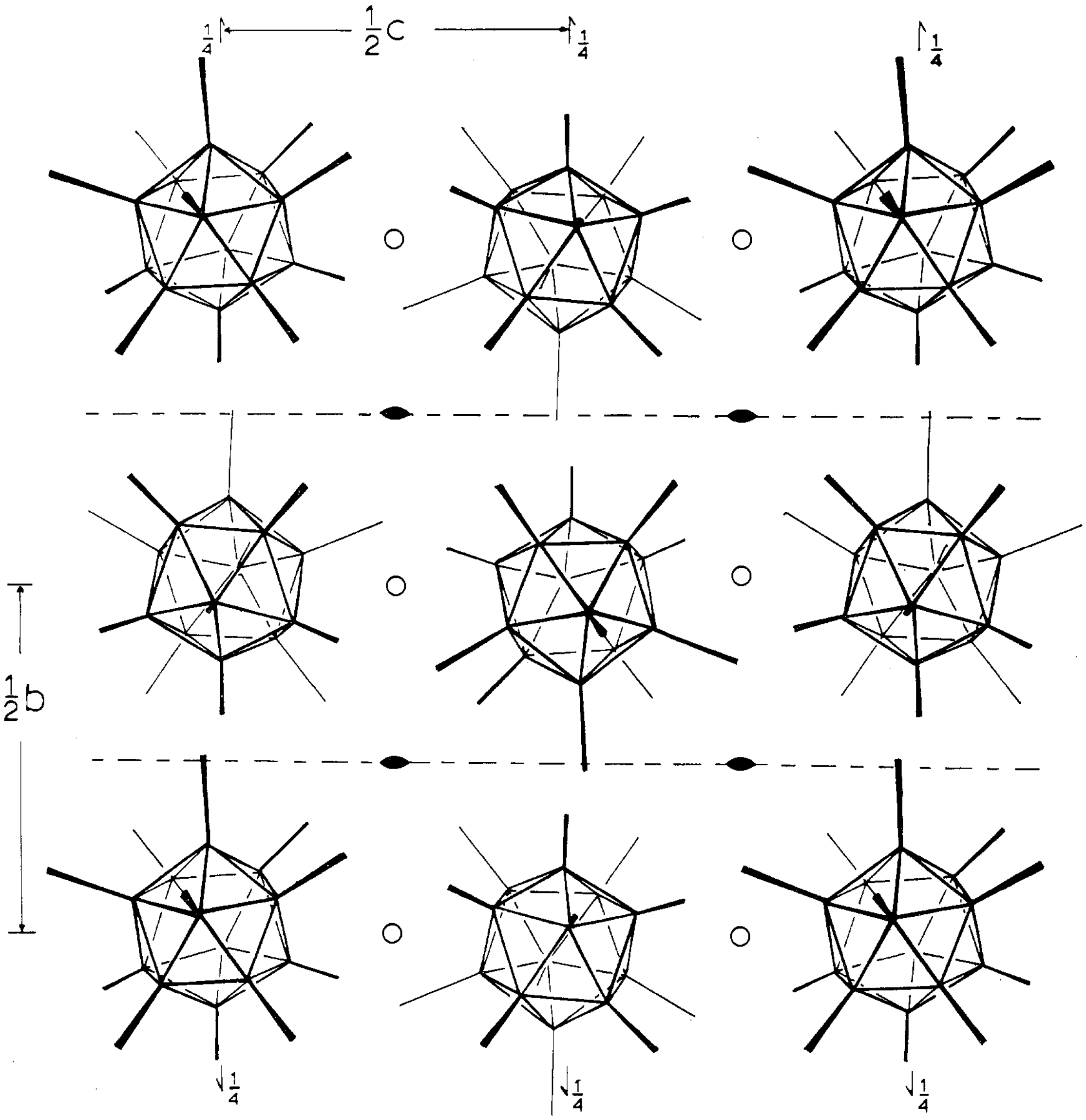

Fig. 3.—The molecular packing as seen in the 0*kl* projection. Only those symmetry elements necessary to generate the space group are shown. Molecules related by the *n* glide planes are omitted for clarity.

length *vs.* bond order.[12] Thus, the single-bonded B radius $r_b = {}^1/_2\,[1.77 + 0.6 \log (8.4/21)] = 0.765$, where 8.4 is the number of electron pairs distributed by the above assumption among the 21 B–B contacts.

If a single-bonded C radius is assumed to be 0.77 Å., single-bonded B–B, B–C, and C–C distances of 1.53, 1.54, and 1.54 Å., respectively, are increased by the various bond orders above to predicted values of 1.77, 1.72, and 1.67 Å., respectively, in reasonable agreement with the observed values. (The predicted B–C distance, if corrected for electronegativity by the Schomaker–Stevenson relationship, becomes 1.68 Å.; however, we feel that this correction, since it is based on isolated bonds, may overestimate the contraction. The most reasonable value is perhaps somewhere between 1.68 and 1.72 Å.) We therefore feel that there is some evidence for C–C and B–C bond orders which are higher than those of B–B in the $B_{10}C_2$ framework. We have not been able to formulate a discussion as internally consistent as this one on other assumptions, such as equal distribution of bonding electrons among all atoms of the $B_{10}C_2$ framework.

On the other hand, the very short C–C distances of 1.42 Å. in the $B_4C_2H_8$ molecule[13] and of 1.43 Å. in the $B_4H_6C_2(CH_3)_2$ molecule[14] are very probably indicative of multiple C–C bonding. The electronic structures of these two compounds are related to the B_6H_{10} structure in somewhat the same way that $B_{10}H_{10}C_2H_2$ is related to $B_{12}H_{12}^{-2}$. The short B–B distance[15] of 1.596 Å. in B_6H_{10} is evidence that this probable multiple bonding also exists in B_6H_{10}. We therefore feel that the valence structures of the icosahedral C_2B_{10} unit and the B_4C_2 unit are not as related to one another as they are to their corresponding isoelectronic boron–hydrogen analogs.

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[12] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 413.

[13] F. P. Boer, W. E. Streib, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1666 (1964).

[14] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2231 (1963).

[15] F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).

As further chemical and molecular structural studies of substituted carboranes become available, the nature of electronic and steric effects may become clearer in substitution reactions on the carboranes. In particular, models for activated complexes may be guessed, and the relevance of ground-state electronic structure gauged. This study indicates clearly that Cl substitution did not occur on the two most positively charged B atoms which were identified in both the molecular orbital and resonance studies.[3,4] Further studies are in progress.

Acknowledgment.—The Fourier maps were calculated using Sly, Shoemaker, and Van den Hende's ERFR2 program, the least-squares refinements using G. S. Pawley's rigid body least-squares program, which is a special case of a more general treatment of rigid body motion in a crystal developed independently by V. Schomaker. We acknowledge support of this research by the Office of Naval Research, the National Science Foundation, and the U. S. Army Research Office (Durham). We wish to thank Dr. H. Schroeder for providing us with the sample.

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Molecular Structure of Carboranes. A 1,2-Dicarbaclovododecaborane Derivative, $B_{10}H_{10}(CCH_2Br)_2$

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A three-dimensional X-ray diffraction study of single crystals of 1,2-bis(bromomethyl)carborane has proved the icosahedral structure of the $B_{10}C_2$ unit. The covalently linked ethylenedecaborane $B_{10}C_2$ unit is not correct, and the C–C distance of 1.64 Å. within the $B_{10}C_2$ icosahedron is not abnormally short. The space group is $P2_12_12_1$, and there are four molecules in a unit cell having dimensions of $a = 9.46$, $b = 10.12$, and $c = 13.78$ Å.

The carboranes,[1,2] $B_{10}C_2H_{12}$, their isomers,[3-5] and their derivatives form an unusually thermally stable group of compounds. The probable isoelectronic relation to the regular icosahedral $B_{12}H_{12}^{-2}$ ion[6] led to the detailed prediction[7-9] of a near-icosahedral geometrical and valence structure, in which the C atoms of the $B_{10}C_2$ unit participate in the electron deficiency of the assumed near-icosahedral framework. A detailed X-ray diffraction study became desirable when a distorted icosahedral structure was proposed[3] in which a short C–C bond about 1.54 Å. in length was assumed to distinguish one isomer, carborane, from a regular icosahedral isomer, neocarborane. Then, a detailed study became urgent when Zakharkin, *et al.*,[10] published the results of an X-ray diffraction study which indicated that the $B_{10}C_2$ unit of $B_{10}H_{10}(CCH_2Br)_2$ had not a near-icosahedral structure, but an ethylenedecaborane covalent unit in which the two C atoms are joined to the outermost 6, 9 B atoms of the B_{10} cage.

We show in the present study that the $B_{10}C_2$ unit in $B_{10}H_{10}(CCH_2Br)_2$ has a near-icosahedral structure in which the C–C distance of 1.64 Å. indicates not a single bond, but an electron-deficient type of bonding similar to that of the B atoms.

Structure Determination

1,2-Bis(bromomethyl)carborane was prepared by the method of Heying, *et al.*,[1] and then purified by vacuum sublimation at 100°. The melting point of 65–66.5° is comparable with published values of[2] 68–69.5° and of[10] 66°. Also the infrared absorption spectrum of our sample was identical with that of a sample of the same material kindly supplied to us by Dr. H. Schroeder.

Single crystals were grown by sublimation at 60° onto a glass surface at room temperature. Two nearly spherical crystals, each about 0.2 mm. in diameter, were sealed into capillaries and aligned by X-ray diffraction methods along the *a* and *c* axes, respectively. These methods also established the reciprocal lattice symmetry as D_{2h}, the space group of $P2_12_12_1$, and the unit cell dimensions of $a = 9.46 \pm 0.02$, $b = 10.12 \pm 0.02$, and $c = 13.78 \pm 0.05$ Å.: systematic extinctions of $h00$ when h is odd, of $0k0$ when k is odd, and of $00l$ when l is odd were noted on the zero level Weissenberg photographs, which were calibrated with an Al powder diffraction pattern. The reasonable assumption of four molecules per unit cell leads to the calculated density of 1.64 g. cm.$^{-3}$, in essential agreement with a very rough value of 1.5 g. cm.$^{-3}$ found by flotation methods.

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