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Crystal and Molecular Structure of Tetramethylammonium *C,C'*-Diphenylundecahydrodicarba-*nido*-dodecaborate(1−)

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The anion of the salt $(Me_4N^+)(PhCHB_{10}H_{10}CPh^-)$, tetramethylammonium *C,C'*-diphenylundecahydrodicarba-*nido*-dodecaborate(1−), is an opened icosahedron. Except for the orientation of phenyl rings, this ion has C_s symmetry. One carbon is in the $B_{10}C$ icosahedral fragment, while the second carbon bridges two boron atoms in the open face of this fragment. This second carbon is also bonded to H and to a phenyl group. The unit cell contains four formula weights in the orthorhombic space group $P2_12_12_1$. Unit cell dimensions are $a = 15.983$ (10) Å, $b = 11.158$ (5) Å, and $c = 12.941$ (3) Å. The final value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.093 for 1544 observed X-ray diffraction maxima.

Either *o*- or *m*-carborane can be reduced by 2 equiv of alkali metal to the corresponding 2− formulas and then oxidized back to this same *o*-carborane.[1-4] Reduced carborane can be monoprotonated to give a stable salt.[4,5] Polarographic reduction of icosahedral carboranes is said to be an irreversible two-electron process leading to dodecahydrodicarba-*nido*-dodecaborate(2−), which can be protonated to yield a stable tridecahydrodicarba-*nido*-dodecaborate(1−) ion,[6,7] $B_{10}C_2H_{13}^-$.

The basic problems of structural chemistry here are concerned with opening of the polyhedral cage. Molecular orbital studies[8] of two-electron addition to icosahedral *o*- and *m*-carborane are consistent with retention of the cage structure for the 2− ions. On the other hand, as negative charges and then electrophiles (*e.g.*, H^+) are added to polyhedral boranes or carboranes, these structures are expected to open.[9] Indeed, a reasonably general polyhedral opening reaction of the polyhedral carboranes has been found[10] and employed for subsequent reaction to incorporate a metal atom into the cage. A recent structural study of one of these compounds, $(\pi\text{-}C_5H_5)Co(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$, shows that the $B_{10}C_2$ polyhedron is opened and that the Co is bonded to an open face of four borons and two carbons.[11] However, this model is unlikely to be correct for opening to a protonated species, such as $B_{10}C_2H_{13}^-$, because localization of the proton to a terminal or bridge position may influence the structure of the $B_{10}C_2$ framework. This influence is present in a structure suggested for this ion,[12] although the proposed positions of carbon in the structure are to be revised on the basis of our study below of the analogous diphenyl derivative, $PhCHB_{10}H_{10}CPh^-$. Also, this study is a continuation of our studies of isomerization mechanisms in these borane and carborane cages.[13-15]

Experimental Section

The compound $(Me_4N^+)(PhCHB_{10}H_{10}CPh^-)$ was prepared by reduction of *o*-diphenylcarborane under argon in tetrahydrofuran,[4] followed by precipitation with Me_4N^+ in water free of dissolved oxygen. Chemical analysis and infrared spectra were used to confirm the identity of the product.[5] Crystals for X-ray diffraction study were grown by recrystallization from acetone–water and were sealed under argon in glass capillaries.

Precession photographs indicated Laue symmetry D_{2h}-*mmm* and the absence of *h*000, 0*k*0, and 00*l* reflections when *h, k,* or *l* is odd. Thus the probable space group is $P2_12_12_1$. From a least-squares fit of 20 Bragg reflection angles measured on a Picker diffractometer, we determined the unit cell dimensions of $a = 15.983$ (10) Å, $b = 11.158$ (5) Å, and $c = 12.941$ (3) Å. Assumption of four formula weights per unit cell gave a calculated density of 1.069 g/cm³, comparable with the approximate value of 1.060 g/cm³ determined by floatation in a bromobenzene–xylene mixture.

Two asymmetric units of three-dimensional X-ray diffraction data were taken on a Picker automatic diffractometer using Cu Kα (1.542 Å) radiation filtered through Ni foil. The shape of the crystal was complex, of approximate dimensions 1 mm × 0.5 mm × 0.67 mm. More precise measurements gave a crystal volume of 0.155 mm³. The crystal was mounted on the *b* (1.0 mm) axis, and reflections for which $2\theta < 115°$ were scanned at 1°/min over an ω-scan interval of 2.2°. Stationary-background counts were taken before and after each scan. No appreciable decline of intensities (less than 5%) was noted from check reflections during the time of X-ray exposure. Collimator diameter was 1.5 mm for both the incident and diffracted beams.

The X-ray data were reduced after applying an absorption correction using a gaussian quadrature numerical integration procedure:[16] transmission coefficients varied only from 0.84 to 0.88, and the linear absorption coefficient μ was 3.95 cm⁻¹. After correction for Lorentz and polarization factors and after a separate scale[17] was applied to the 20 largest reflections which had been attenuated by Al foil, the two asymmetric sets correlated to a value of $\Sigma_{H,i}|I_{H,i} - \bar{I}_H|/\Sigma_{H,i}\bar{I}_H$ of 0.03, where *H* is *hkl*, $I_{H,i}$ is the intensity of reflection *H* in asymmetric data set *i*, and $\bar{I}_H$ is the average value of symmetry-related reflections. This correlation value is somewhat misleading because 101 of the weak reflections, which correlated poorly, were given zero weight. The final data set consisted of 1544 independent reflections for which $I > 3\sigma$, where $\sigma(I)$ is $[C + (T_c/2T_b)^2(B_1 + B_2)]^{1/2}$. Here, *C* is the total count for the scan, B_1 and B_2 are the background counts, T_c is the scan time, and T_b is the time for counting a single background.[18]

Structure Determination and Refinement

The structure was solved by direct phasing with the use of the tangent formula.[19-21] Reflections were approximately scaled[22] and cor-

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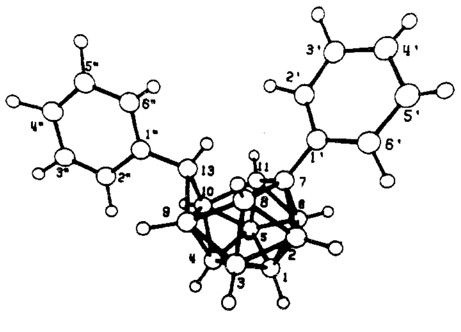

Figure 1. Stereoview of $PhCHB_{10}H_{10}CPh^-$.

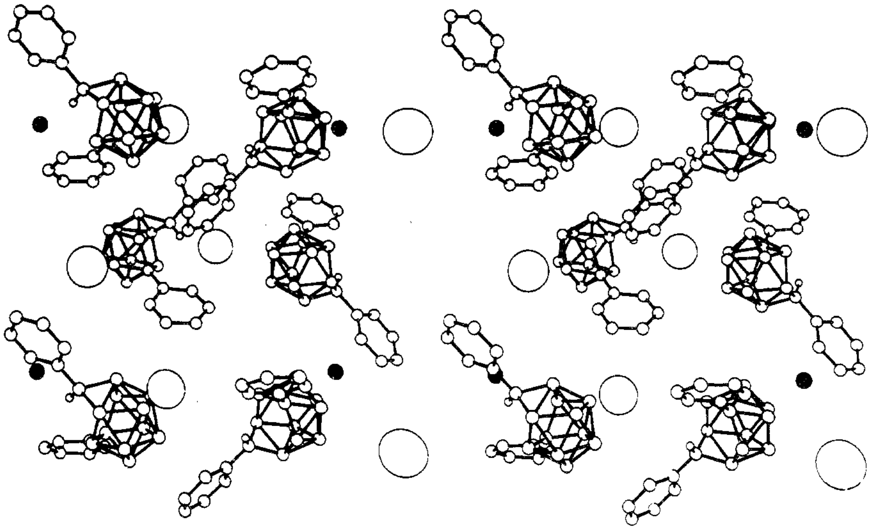

Figure 2. Stereoview of the unit cell looking down the *y* axis. Cations are represented by spheres of radii equal to two-fifths of the actual N–C bond length. The *x* axis is horizontal and the *z* axis is vertical with the origin (blackened sphere) in the upper left-hand corner.

rected to normalized structure factors[23]

$$E_{hkl} = |F(hkl)|\epsilon^{-1}e^{B(\sin^2\theta)/\lambda^2}\left[\sum_{i=1}^{N} f_i^{\,2}(hkl)\right]^{-1/2}$$

Here, $\epsilon = \sqrt{2}$ for $h00$, $0k0$, and $00l$ reflections, $\epsilon = 1$ for all other reflections,[24] B is determined from the Wilson plot,[22] $f_i(hkl)$ are the atomic scattering factors, and N is the number (248) of atoms in the unit cell.

Phasing was performed using the 349 E_{hkl} values greater than 1.1. Three of these values were used to assign the origin: one was used to specify the enantiomorph and two were used to obtain the appropriate multiple relationships. Using the criterion of Germain, *et al.*,[21] we found one best solution, from which an E map, simulating electron density, was computed. Of the 24 peaks of the anion 22 were clearly seen in chemically reasonable positions. A structure factor calculation yielded a value of 0.41 for $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and led to a three-dimensional electron density map which showed the two additional first-row atoms of the anion and the nitrogen of the cation.

The disorder in the tetramethylammonium group produced some minor difficulties in the refinement. At first we assigned four small diffuse peaks, appropriately distant from the nitrogen peak, to these four carbon atoms of the cation. Least-squares refinements were made minimizing the function $\Sigma w[k^2|F_o|^2 - |F_c|^2]^2$, where k is the scale factor, w is $1/F_o^2$ for $|F_o| > 22.5$, and $w = 1/22.5F_o$ for $|F_o| < 22.5$.[25] This assignment of carbon of the CH_3 group allowed refinement of positional and isotropic thermal parameters to reach an R value of 0.24. No improvement was obtained upon refinement using anisotropic thermal parameters. At this stage we began using our final data set, obtained upon removal of the 147 weak reflections for which $I < 3\sigma(I)$. Three cycles of positional and anisotropic thermal least-squares refinement led to a value of 0.15 for R. However, the tetramethylammonium group was not tetrahedral. A difference

Table I. Disagreement Factors[a]

$\sin\theta$	No. of refl	R_F	Class	No. of refl	R_F
			All	1544	0.09
			$0kl$	118	0.09
0.0–0.02	41	0.05	$h0l$	159	0.08
0.02–0.04	64	0.08	$hk0$	121	0.11
0.04–0.06	79	0.07	h(even)	811	0.09
0.06–0.08	88	0.09	h(odd)	733	0.09
0.08–0.10	96	0.11	k(even)	800	0.09
0.10–0.12	101	0.09	k(odd)	744	0.09
0.12–0.14	117	0.09	l(even)	788	0.09
0.14–0.16	118	0.08	l(odd)	756	0.09
0.16–0.18	129	0.08	$h + k$(even)	779	0.09
0.18–0.20	121	0.11	$h + k$(odd)	765	0.09
0.20–0.22	127	0.12	$k + l$(even)	780	0.09
0.22–0.24	119	0.12	$k + l$(odd)	764	0.09
0.24–0.26	115	0.16	$h + l$(even)	769	0.09
0.26–0.28	124	0.15	$h + l$(odd)	775	0.10
0.28–0.30	105	0.18	$h + k + l$(even)	777	0.09
			$h + k + l$(odd)	767	0.09

[a] Values listed here are $R_F = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.093$. We add that $R_w = [\Sigma w|F_o^2 - F_c^2|^2 / \Sigma w F_o^4]^{1/2} = 0.018$ for all reflections.

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Table II. Atomic Coordinates in Fractions of Cell Lengths[a]

Anion

Type	Atom	x	y	z
B	1	0.2046 (7)	0.0968 (11)	0.5245 (9)
B	2	0.2272 (7)	0.2502 (11)	0.5347 (9)
B	3	0.2165 (7)	0.1853 (10)	0.4084 (9)
B	4	0.2554 (7)	0.0318 (11)	0.4146 (9)
B	5	0.3036 (8)	0.0199 (10)	0.5443 (8)
B	6	0.2782 (8)	0.1493 (11)	0.6161 (8)
C	7	0.3328 (5)	0.2602 (8)	0.5540 (6)
B	8	0.3013 (6)	0.2850 (10)	0.4318 (8)
B	9	0.3132 (8)	0.1508 (12)	0.3640 (7)
B	10	0.3686 (7)	0.0414 (11)	0.4306 (8)
B	11	0.3801 (7)	0.1298 (11)	0.5538 (8)
C	13	0.4148 (6)	0.1595 (8)	0.3781 (6)
C	1′	0.3697 (6)	0.3638 (9)	0.6088 (6)
C	2′	0.4576 (7)	0.3786 (9)	0.6166 (7)
C	3′	0.4936 (6)	0.4758 (10)	0.6634 (8)
C	4′	0.4435 (8)	0.5619 (10)	0.7062 (8)
C	5′	0.3562 (8)	0.5502 (9)	0.7066 (8)
C	6′	0.3192 (7)	0.4535 (9)	0.6560 (7)
C	1″	0.4752 (5)	0.1377 (8)	0.2946 (7)
C	2″	0.4632 (6)	0.0436 (9)	0.2191 (8)
C	3″	0.5209 (6)	0.0274 (6)	0.1408 (7)
C	4″	0.5896 (6)	0.1033 (10)	0.1315 (7)
C	5″	0.6027 (6)	0.1923 (9)	0.2025 (7)
C	6″	0.5469 (5)	0.2081 (8)	0.2827 (7)
H	1	0.1363 (33)	0.0617 (48)	0.5377 (39)
H	2	0.1830 (32)	0.3259 (49)	0.5668 (37)
H	3	0.1575 (31)	0.2063 (46)	0.3618 (38)
H	4	0.2223 (32)	−0.0600 (47)	0.3784 (40)
H	5	0.3091 (32)	−0.0812 (47)	0.5758 (39)
H	6	0.2762 (32)	0.1662 (50)	0.6999 (40)
H	8	0.3067 (31)	0.3685 (47)	0.3946 (38)
H	9	0.3168 (33)	0.1532 (50)	0.2525 (37)
H	10	0.4050 (34)	−0.0529 (50)	0.4136 (40)
H	11	0.4487 (32)	0.1138 (48)	0.5880 (39)
H	13	0.4371 (29)	0.2255 (44)	0.4154 (36)
H	2′	0.5005 (31)	0.3418 (49)	0.5649 (38)
H	3′	0.5633 (32)	0.4996 (47)	0.6472 (39)
H	4′	0.4622 (42)	0.6112 (62)	0.7389 (51)
H	5′	0.3287 (38)	0.6120 (57)	0.7243 (48)
H	6′	0.2573 (38)	0.4294 (54)	0.6757 (45)
H	2″	0.4056 (34)	−0.0149 (47)	0.2200 (40)
H	3″	0.5142 (34)	−0.0302 (52)	0.0814 (42)
H	4″	0.6221 (32)	0.0955 (47)	0.0568 (38)
H	5″	0.6568 (33)	0.2558 (50)	0.2045 (43)
H	6″	0.5493 (30)	0.2646 (45)	0.3274 (37)

Cation[b]

Type	Atom	x	y	z	Fractional population
N	1	0.1150 (8)	0.6581 (11)	0.4940 (8)	1.0
C	2	0.1002 (13)	0.6441 (23)	0.6033 (15)	0.67
C	3	0.036 (19)	0.6951 (30)	0.4368 (21)	0.55
C	4	0.1531 (29)	0.5600 (28)	0.4491 (27)	0.40
C	5	0.2044 (16)	0.6733 (39)	0.4667 (27)	0.45
C	6	0.0844 (32)	0.7740 (25)	0.4722 (41)	0.45
C	7	0.0925 (57)	0.5578 (67)	0.4819 (79)	0.33
C	8	0.1421 (31)	0.7464 (36)	0.5777 (32)	0.33
Spherical function[c]	9	0.1150 (8)	0.6581 (11)	0.4940 (8)	0.41

[a] Standard deviations in parentheses are from full-matrix least squares. [b] Statistical representation of the disordered tetramethylammonium ion. [c] Disordered tetracarbon spherical function with nitrogen coordinates.

electron density map from which all first-row atoms had been subtracted showed 17 of the 21 hydrogen atoms of the anion and also showed some seven peaks of various size near the tetramethylammonium cation. Sixteen of these hydrogens were then introduced into the refinement, omitting at these stages the hydrogen bonded to the bridging carbon external to the $B_{10}C$ polyhedral fragment (Figure 1). After a few unsuccessful attempts at further refinement, a spherically disordered cation, which had the nitrogen positional parameters, was introduced using the scattering factor[26]

$$f = 4f_c(\sin Kx)/Kx$$

where f_c is the scattering factor for carbon, x is the radius of the disorder, and K is $4\pi(\sin\theta)/\lambda$. The improvement in agreement was only slight. Finally, a partially static description of the cation was approximated by using fractional populations of the seven peaks about the nitrogen atom and then assigning most of the residual population of the cation to the spherical scattering function. Least-squares refinement of positional, thermal (first isotropic and then anisotropic), and population parameters reduced R to 0.12. A difference electron density map at this stage revealed the four remaining terminal hydrogen atoms and also showed again the hydrogen bonded to bridging carbon. These four terminal hydrogens were introduced, and three cycles of block-matrix and two cycles of full-matrix least-squares refinement were made of positional and anisotropic thermal parameters of the first-row atoms of the anion. At this stage ($R = 0.10$ and parameter shifts were less than their standard deviations) a difference map revealed for the third time the last hydrogen of the anion, singly bonded to the carbon external to the $B_{10}C$ icosahedral fragment. Block-matrix refinement of coordinates of hydrogen gave the final R value of 0.093.

In Table I we show R values for classes of reflections and for ranges of $\sin\theta$. A final difference electron density map from which all atoms except hydrogens of methyl had been subtracted showed no peaks higher than 0.20 electron/Å^3 within 2 Å of the anion. In these calculations we used scattering factors for B, C, and N^+ from ref 27a and a scattering factor for H which had been especially prepared for covalent hydrogen for use in the CRYRM computing system.[27b]

Results and Discussion

Coordinates are given in Table II, thermal parameters are in Table III, bond distances are in Table IV, and bond angles are in Table V. The observed and calculated structure factors are available.[28]

A stereoview of the crystal structure (Figure 2) along the b axis shows the tetramethylammonium group as spheres about two-fifths of the N-C bond length.[29,30] The closest contact of the cation and anion is close to the sum of van der Waals radii[29] of a methyl group of the cation and a hydrogen of the anion. The closest approach between cations is greater than 5 Å. Closest intermolecular contacts between carbons of phenyl groups is 4.91 Å, rather greater than the van der Waals distance between aromatic molecules. However, there are hydrogen-hydrogen contacts between rings, the shortest of which is 2.66 Å, close to the sum (2.4 Å) of van der Waals radii.

The anion (Figure 1) shows how the icosahedron has become opened upon reduction and protonation of the original substituted carborane. The extra hydrogen, in addition to a phenyl, is singly bonded to C(13). The cage itself has essentially C_s symmetry, having a mirror plane through B(1), B(4), C(7), C(13), H(13), C(1′), and C(1″) (Table VI). Also, the atoms C(7), B(8), B(9), B(10), and B(11) in the open face are approximately coplanar. The average of the C(13)-B(9) and C(13)-B(10) distances is 1.67 (1) Å and that of C(7)-B(8) and C(7)-B(11) is 1.66 (2) Å, while the average of C(7)-B(2) and C(7)-B(6) is somewhat longer, at 1.71 Å. This last distance is not in the open face or external to the cage, so that the coordination is somewhat higher to B(2) and B(6) as compared with that of other atoms in these C-B bonds.

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Table III. Thermal Parameters[a]–Anisotropic[b] and Isotropic[c]

Anion

Type	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B	1	0.056 (6)	0.127 (15)	0.084 (8)	−0.006 (18)	0.040 (14)	0.044 (20)
B	2	0.052 (6)	0.100 (11)	0.083 (9)	−0.017 (32)	0.057 (12)	0.030 (20)
B	3	0.045 (5)	0.105 (12)	0.085 (9)	0.011 (15)	0.010 (14)	0.046 (18)
B	4	0.054 (6)	0.099 (13)	0.075 (9)	−0.009 (17)	−0.013 (14)	0.007 (19)
B	5	0.076 (7)	0.077 (11)	0.066 (8)	−0.024 (17)	0.019 (15)	0.031 (17)
B	6	0.083 (8)	0.107 (13)	0.051 (6)	0.027 (18)	0.025 (14)	0.012 (18)
C	7	0.048 (9)	0.083 (9)	0.060 (6)	0.022 (12)	0.016 (10)	−0.018 (15)
B	8	0.037 (5)	0.112 (12)	0.056 (7)	0.005 (15)	0.012 (12)	0.034 (18)
B	9	0.045 (5)	0.141 (13)	0.048 (7)	0.003 (19)	0.013 (12)	0.029 (21)
B	10	0.058 (6)	0.105 (12)	0.059 (7)	0.041 (18)	0.011 (13)	−0.025 (18)
B	11	0.066 (6)	0.100 (11)	0.054 (7)	0.049 (17)	−0.008 (12)	0.069 (16)
C	13	0.047 (4)	0.069 (8)	0.051 (5)	0.009 (11)	−0.015 (10)	−0.001 (13)
C	1′	0.065 (5)	0.111 (9)	0.039 (5)	0.033 (15)	0.002 (11)	0.028 (15)
C	2′	0.061 (5)	0.112 (10)	0.054 (5)	−0.008 (15)	0.020 (11)	−0.003 (18)
C	3′	0.066 (6)	0.132 (12)	0.082 (7)	0.004 (16)	0.013 (12)	0.048 (19)
C	4′	0.099 (7)	0.127 (12)	0.070 (7)	−0.031 (17)	−0.048 (15)	−0.021 (17)
C	5′	0.108 (8)	0.108 (10)	0.082 (7)	0.007 (18)	−0.020 (16)	−0.080 (18)
C	6′	0.076 (6)	0.124 (11)	0.068 (6)	0.071 (15)	0.014 (13)	0.015 (16)
C	1″	0.040 (4)	0.084 (8)	0.062 (6)	0.030 (11)	−0.005 (11)	0.001 (14)
C	2″	0.053 (5)	0.103 (9)	0.071 (6)	−0.032 (14)	0.014 (11)	−0.048 (16)
C	3″	0.061 (5)	0.112 (10)	0.072 (7)	−0.008 (15)	0.019 (11)	−0.072 (16)
C	4″	0.050 (4)	0.122 (11)	0.083 (7)	0.024 (15)	0.025 (11)	−0.035 (17)
C	5″	0.035 (4)	0.120 (10)	0.097 (8)	0.010 (13)	0.002 (12)	0.005 (18)
C	6″	0.036 (4)	0.092 (8)	0.072 (6)	0.014 (12)	−0.025 (10)	−0.046 (15)

Type	Atom	B, Å^2	Type	Atom	B, Å^2	Type	Atom	B, Å^2
H	1	3.57	H	9	3.66	H	5′	6.79
H	2	3.58	H	10	4.44	H	6′	5.78
H	3	3.31	H	11	3.68	H	2″	3.98
H	4	3.67	H	13	2.78	H	3″	4.48
H	5	3.56	H	2′	3.32	H	4″	3.51
H	6	3.77	H	3′	4.13	H	5″	4.55
H	8	3.29	H	4′	8.42	H	6″	3.26

Cation

Type	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equiv B, Å^2
N	1	0.004 (1)	0.011 (1)	0.007 (1)	0.002 (2)	0.004 (2)	0.003 (2)	3.3
C	2	0.007 (2)	0.031 (4)	0.012 (3)	0.010 (5)	−0.006 (4)	0.007 (7)	8.6
C	3	0.021 (3)	0.015 (5)	0.018 (3)	0.015 (7)	0.000 (6)	−0.017 (7)	10.4
C	4	0.009 (3)	0.071 (10)	0.021 (4)	−0.003 (11)	0.020 (6)	0.047 (14)	8.1
C	5	0.024 (5)	−0.022 (11)	0.028 (5)	0.033 (14)	0.002 (10)	0.047 (15)	17.6
C	6	0.004 (8)	0.099 (18)	0.019 (10)	−0.029 (22)	0.028 (17)	0.033 (27)	13.2
C	7	0.030 (8)	0.036 (18)	0.054 (12)	−0.056 (25)	0.001 (20)	0.080 (28)	20.2
C	8	0.012 (3)	−0.015 (12)	0.013 (6)	−0.021 (12)	−0.001 (9)	−0.060 (17)	8.3
Spherical function	9	$B = 27.6$ (4) Å^2						

[a] Standard deviations in parentheses are from full-matrix least squares. [b] Anisotropic temperature factors are calculated by the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [c] Isotropic temperature factors are given by $\exp[-B(\sin^2\theta)/\lambda^2]$. Hydrogen isotropic values were set equal to the heavy-atom isotropic values and were not refined.

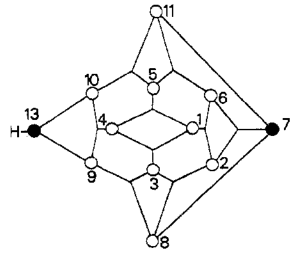

Figure 3. Proposed preferred 0,10,4,0 valence structure of $HCHB_{10}H_{10}CH^-$. Framework single bonds are C_{13}–B_{10}, C_{13}–B_9, C_7–B_8, and C_7–B_{11}. The distortion of bond lengths, made in order to represent the ion in the plane of the drawing, is artificial.

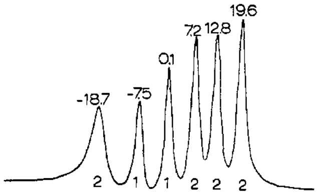

Figure 4. Hydrogen-decoupled 32.1-MHz ^{11}B nmr of (Me_4N^+)-$(PhCHB_{10}H_{10}CPh^-)$ measured in perdeuterioacetone. Chemical shifts in ppm relative to $BF_3 \cdot OEt_2$ are indicated above peaks. Relative areas are given below peaks. Also, a singlet of area appropriate to one H atom was found at τ 5.23 in the 60-MHz ^1H nmr spectrum and is assigned to the unique face H atom at C(13).

In Figure 3, we show the one probably preferred three-center valence structure, of the very large number of possible valence arrangements. This structure has the full C_s molecular symmetry and places as many single bonds as possible to carbon, in order to keep the charge distribution as nearly neutral as this type of representation can. The *styx* bond representation is 0,10,4,0.[31] The single C–B bonds of this structure also correlate with the relatively short distances found in this experimental study.

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(31) Reference 9, Chapter 2.

Table IV. Bond Distances of the Anion with Standard Deviations in Parentheses[a]

Bond	Length, Å	Bond	Length, Å
B(1)–B(2)	1.78 (2)	B(10)–B(11)	1.88 (2)
–B(3)	1.82 (2)	–C(13)	1.66 (2)
–B(4)	1.85 (2)	–H(10)	1.21 (6)
–B(5)	1.81 (2)	B(11)–H(11)	1.20 (5)
–B(6)	1.78 (2)	C(13)–C(1″)	1.47 (1)
–H(1)	1.17 (5)	–H(13)	0.95 (5)
B(2)–B(3)	1.80 (2)	C(1′)–C(2′)	1.42 (1)
–B(6)	1.74 (2)	–C(6′)	1.42 (1)
–C(7)	1.71 (1)	C(2′)–C(3′)	1.37 (1)
–B(8)	1.82 (2)	–H(2′)	1.04 (5)
–H(2)	1.18 (5)	C(3′)–C(4′)	1.37 (2)
B(3)–B(4)	1.82 (2)	–H(3′)	1.16 (5)
–B(8)	1.78 (2)	C(4′)–C(5′)	1.40 (2)
–B(9)	1.79 (2)	–H(4′)	0.76 (7)
–H(3)	1.14 (5)	C(5′)–C(6′)	1.39 (1)
B(4)–B(5)	1.85 (2)	–H(5′)	0.85 (6)
–B(9)	1.85 (2)	C(6′)–H(6′)	1.06 (6)
–B(10)	1.82 (2)	C(1″)–C(2′)	1.45 (1)
–H(4)	1.24 (5)	–C(6′)	1.40 (1)
B(5)–B(6)	1.76 (2)	C(2″)–C(3″)	1.38 (1)
–B(10)	1.82 (2)	–H(2″)	1.13 (5)
–B(11)	1.74 (2)	C(3″)–C(4″)	1.39 (1)
–H(5)	1.20 (5)	–H(3″)	1.01 (6)
B(6)–C(7)	1.71 (2)	C(4″)–C(5″)	1.37 (1)
–B(11)	1.83 (2)	–H(4″)	1.10 (5)
–H(6)	1.10 (5)	C(5″)–C(6″)	1.38 (1)
B(7)–B(8)	1.68 (1)	–H(5″)	1.12 (5)
–B(11)	1.64 (1)	C(6″)–H(6″)	0.86 (5)
–C(1′)	1.48 (1)		
B(8)–B(9)	1.87 (2)		
–H(8)	1.05 (5)		
B(9)–B(10)	1.86 (2)		
–C(13)	1.68 (1)		
–H(9)	1.21 (5)		
	Bond Summary for Cage[b,c]		
B(1)–B(2)	1.78 (0)	B(3)–B(8)	1.76 (2)
B(1)–B(3)	1.82 (1)	B(3)–B(9)	1.81 (2)
B(1)–B(4)	1.85 (2)	B(4)–B(9)	1.84 (2)
B(2)–B(3)	1.78 (2)	C(7)–B(8)	1.66 (2)
B(2)–B(6)	1.74 (2)	B(8)–B(9)	1.88 (1)
B(2)–C(7)	1.71 (0)	B(9)–B(10)	1.86 (2)
B(2)–B(8)	1.83 (1)	B(9)–C(13)	1.67 (1)
B(3)–B(4)	1.84 (2)	C(13)–H(13)	0.95 (5)

[a] See ref 23, p 417 formula 18.3–uncorrelated). [b] C_s symmetry. [c] Average deviation of symmetry-related bonds.

The ^{11}B nmr spectrum (Figure 4) shows six different boron environments and is similar to that for the $\mathrm{MeCHB_{10}H_{10}CMe^-}$ ion.[32] The hydrogen singly bonded to C(13) shows a ^{1}H singlet at τ 5.23 relative to TMS.

The phenyl ring bonded to C(13) lies in the mirror plane of the cage, while the C(13)–C(1″) distance of 1.47 Å is nearly the same as that [1.51 (0.03) Å] for $\mathrm{CH_3}$-C bonds in *C,C′*-dimethylcarborane.[33] The other phenyl group is slightly twisted out of the mirror plane of the cage and bonded at a distance of 1.48 Å for C(7)–C(1′). Thus rather little evidence exists either for conjugative shortening of these bonds or for preferred orientations of the phenyl groups. Perhaps some inductive effects may be present, as suggested in ^{19}F nmr studies of related compounds.[5,7]

We find that opening of the icosahedral $\mathrm{B_{10}C_2}$ cage upon reduction and protonation gives a considerably more localized bond situation in the opened face than is present in the somewhat related Co compound.[11] An interesting question re-

Table V. Anion Bond Angle Summary[a,b]

Angle	Value, deg	Angle	Value, deg
B(2)–B(1)–B(3)	59.9 (10)	B(2)–C(7)–B(6)	61.2 (10)
B(2)–B(1)–B(4)	110.6 (12)	B(2)–C(7)–B(8)	65.0 (10)
B(2)–B(1)–B(5)	105.3 (12)	B(2)–C(7)–B(11)	113.3 (11)
B(2)–B(1)–B(6)	58.7 (10)	B(2)–C(7)–C(1′)	121.0 (11)
B(3)–B(1)–B(4)	60.8 (10)	B(6)–C(7)–B(8)	114.0 (11)
B(3)–B(1)–B(5)	106.4 (12)	B(6)–C(7)–B(11)	66.0 (10)
B(3)–B(1)–B(6)	106.9 (12)	B(6)–C(7)–C(1′)	122.9 (11)
B(4)–B(1)–B(5)	62.1 (10)	B(8)–C(7)–B(11)	106.3 (11)
B(4)–B(1)–B(6)	111.5 (13)	B(8)–C(7)–C(1′)	116.2 (11)
B(5)–B(1)–B(6)	59.0 (10)	B(11)–C(7)–C(1′)	120.7 (11)
B(1)–B(2)–B(3)	61.3 (10)	B(2)–B(8)–B(3)	59.8 (9)
B(1)–B(2)–B(6)	60.6 (10)	B(2)–B(8)–C(7)	58.2 (9)
B(1)–B(2)–C(7)	106.0 (12)	B(2)–B(8)–B(9)	109.1 (11)
B(1)–B(2)–B(8)	106.6 (12)	B(3)–B(8)–C(7)	106.6 (11)
B(3)–B(2)–B(6)	109.3 (12)	B(3)–B(8)–B(9)	58.4 (9)
B(3)–B(2)–C(7)	104.8 (12)	B(7)–B(8)–B(9)	113.3 (11)
B(3)–B(2)–B(8)	58.9 (9)	B(3)–B(9)–B(4)	60.3 (10)
B(6)–B(2)–C(7)	59.5 (9)	B(3)–B(9)–B(8)	58.2 (10)
B(6)–B(2)–B(8)	106.0 (12)	B(3)–B(9)–B(10)	106.7 (12)
C(7)–B(2)–B(8)	56.8 (9)	B(3)–B(9)–C(13)	135.5 (13)
B(1)–B(3)–B(2)	58.8 (10)	B(4)–B(9)–B(8)	103.9 (11)
B(1)–B(3)–B(4)	58.5 (10)	B(4)–B(9)–B(10)	58.9 (10)
B(1)–B(3)–B(8)	106.6 (12)	B(4)–B(9)–C(13)	114.0 (12)
B(1)–B(3)–B(9)	110.0 (12)	B(8)–B(9)–B(10)	102.9 (11)
B(2)–B(3)–B(4)	107.8 (12)	B(8)–B(9)–C(13)	84.5 (10)
B(2)–B(3)–B(8)	61.3 (10)	B(10)–B(9)–C(13)	55.5 (9)
B(2)–B(3)–B(9)	114.5 (12)	B(4)–B(10)–B(5)	61.1 (10)
B(4)–B(3)–B(8)	108.6 (12)	B(4)–B(10)–B(9)	60.0 (10)
B(4)–B(3)–B(9)	61.5 (10)	B(4)–B(10)–B(11)	102.9 (11)
B(8)–B(3)–B(9)	63.4 (10)	B(4)–B(10)–C(13)	116.3 (12)
B(1)–B(4)–B(3)	60.6 (10)	B(5)–B(10)–B(9)	106.9 (12)
B(1)–B(4)–B(5)	59.6 (10)	B(5)–B(10)–B(11)	55.9 (9)
B(1)–B(4)–B(9)	109.2 (12)	B(5)–B(10)–C(13)	133.8 (12)
B(1)–B(4)–B(10)	109.7 (12)	B(9)–B(10)–C(13)	56.6 (8)
B(3)–B(4)–B(5)	104.4 (12)	B(11)–B(10)–C(13)	83.5 (10)
B(3)–B(4)–B(9)	58.3 (10)	B(5)–B(11)–B(6)	59.2 (10)
B(3)–B(4)–B(10)	106.7 (12)	B(5)–B(11)–C(7)	107.6 (12)
B(5)–B(4)–B(9)	106.2 (12)	B(5)–B(11)–B(10)	60.1 (10)
B(5)–B(4)–B(10)	59.3 (10)	B(6)–B(11)–C(7)	58.9 (10)
B(9)–B(4)–B(10)	61.0 (10)	B(6)–B(11)–B(10)	110.4 (11)
B(1)–B(5)–B(4)	58.3 (10)	C(7)–B(11)–B(10)	114.9 (12)
B(1)–B(5)–B(6)	59.7 (10)	C(9)–C(13)–C(10)	67.9 (10)
B(1)–B(5)–B(10)	108.9 (12)	C(9)–C(13)–C(1″)	116.3 (11)
B(1)–B(5)–B(11)	107.5 (12)	C(9)–C(13)–H(13)	122.3 (5)
B(4)–B(5)–B(6)	108.8 (12)	C(10)–C(13)–C(1″)	117.6 (11)
B(4)–B(5)–B(10)	59.6 (10)	C(10)–C(13)–H(13)	125.1 (5)
B(4)–B(5)–B(11)	107.8 (12)	C(1″)–C(13)–H(13)	104.9 (5)
B(6)–B(5)–B(10)	116.7 (12)	C(1′)–C(2′)–C(3′)	122.7 (14)
B(6)–B(5)–B(11)	63.0 (10)	C(2′)–C(3′)–C(4′)	119.4 (15)
B(10)–B(5)–B(11)	64.0 (10)	C(3′)–C(4′)–C(5′)	121.3 (15)
B(1)–B(6)–B(2)	60.6 (10)	C(4′)–C(5′)–C(6′)	119.5 (15)
B(1)–B(6)–B(5)	61.3 (10)	C(5′)–C(6′)–C(1′)	120.4 (14)
B(1)–B(6)–B(7)	105.8 (12)	C(6′)–C(1′)–C(2′)	116.7 (13)
B(1)–B(6)–B(11)	104.7 (12)	C(1″)–C(2″)–C(3″)	120.1 (13)
B(2)–B(6)–B(5)	108.5 (12)	C(2″)–C(3″)–C(4″)	120.7 (13)
B(2)–B(6)–B(7)	59.3 (9)	C(3″)–C(4″)–C(5″)	120.3 (13)
B(2)–B(6)–B(11)	103.1 (12)	C(4″)–C(5″)–C(6″)	119.9 (13)
B(5)–B(6)–B(7)	103.2 (12)	C(5″)–C(6″)–C(1″)	122.7 (12)
B(5)–B(6)–B(11)	57.7 (10)	C(6″)–C(1″)–C(2″)	116.3 (12)
B(7)–B(6)–B(11)	55.0 (9)		

[a] See ref 23, p 419 (formula 18.11–uncorrelated). [b] Only the unique face hydrogen is included.

Table VI. Least-Squares Planes

Plane 1: $0.4770X - 0.6450Y + 0.5970Z - 4.929 = 0$
Plane 2: $0.8802X + 0.3753Y - 0.2904Z - 3.757 = 0$

Plane 1		Plane 2	
Atom	Dev, Å	Atom	Dev, Å
B(1)	0.002	C(7)	−0.068
B(4)	−0.008	B(8)	0.053
C(7)	0.016	B(9)	−0.020
C(13)	0.006	B(10)	−0.017
H(13)	0.031	B(11)	0.052
C(1′)	−0.025		
C(1″)	−0.022		

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mains as to whether or not the cage is opened in the intermediate $B_{10}C_2H_{12}^{2-}$ ion and its derivatives.

In the $PhCHB_{10}H_{10}CPh^-$ ion C(13) bridges in a way known previously for some nitrogen derivatives of boranes.[34] This result suggests that monocarbon carboranes may exist with either a bridging carbon atom or a skeletal type carbon atom. At least one of these two types of structures is known in the $B_{10}H_{12}CH^-$ ion.[35]

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Registry No. $(Me_4N)^+(PhCHB_{10}H_{10}CPh)^-$, 39322-84-4.

Supplementary Marterial Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2257.

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Crystal and Molecular Structure of Triphenylmethylphosphonium 1,1,1-Tricarbonyl-4,6-dicarba-1-mangana-*closo*-nonaborate(1−)[1]

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Crystals of $[(C_6H_5)_3PCH_3]^+[(B_6C_2H_8)Mn(CO)_3]^-$ are triclinic, space group $P\bar{1}$, with $a = 11.216$ (5) Å, $b = 11.285$ (4) Å, $c = 11.464$ (5) Å, $\alpha = 105.79$ (1)°, $\beta = 104.46$ (1)°, $\gamma = 98.04$ (1)°, $d_o = 1.25$ g/cm^3, and $d_c = 1.29$ g/cm^3 for $Z = 2$. X-Ray diffraction intensities were collected by stationary-crystal, stationary-counter technique using Mo Kα radiation. The structure was refined to $R = 0.042$ for 2862 independent reflections. The predicted structure of the anion is confirmed; manganese is bonded to two carbon atoms (at 2.04 Å) and three boron atoms (two at 2.35 Å and one at 2.23 Å) of the eight-atom carborane cage. The anion has almost exact mirror symmetry, and the manganese–carborane cage can be described as a tricapped trigonal prism with one boron and two carbon atoms as the capping atoms.

Introduction

The $(B_6C_2H_8)Mn(CO)_3^-$ ion was synthesized by Hawthorne and Pitts,[2] and a tentative structure was assigned to it on the basis of ir and nmr spectroscopic data.[3] This study of the triphenylmethylphosphonium (TPMP) salt, undertaken to verify the structure by X-ray crystallographic means, confirms that it is triphenylmethylphosphonium 1,1,1-tricarbonyl-4,6-dicarba-1-mangana-*closo*-nonaborate(1−).[4]

Experimental Procedure

Clear, orange-red, needlelike crystals of the compound were supplied to us by M. Frederick Hawthorne as prepared by A. Denise Pitts. Optical extinction between crossed polarizers was very sharp. Precession photographs indicated that the unit cell was triclinic, and preliminary cell dimensions were obtained from *hk*0 and *h*0*l* photographs. A crystal of approximate dimensions 0.18 mm × 0.14 mm × 0.19 mm was attached to a glass fiber and mounted on a General Electric XRD-5 single-crystal diffractometer equipped with a manual quarter-circle Eulerian cradle goniostat. A strong reflection, $(\bar{1}\bar{2}1)$, was set at $\chi = 90°$ to facilitate checking of the orientation of the crystal. Twenty-seven high-angle reflections were then accurately centered in χ, ϕ, and 2θ using molybdenum radiation ($\lambda(K\alpha_1)$ 0.709261 Å, $\lambda(K\alpha_2)$ 0.713543 Å, $\lambda(K\beta)$ 0.632253 Å), and a least-squares analysis yielded accurate cell dimensions and the crystal orientation matrix. The derived cell dimensions (and standard deviations) are $a = 11.216$ (5) Å, $b = 11.285$ (4) Å, $c = 11.464$ (5) Å, $\alpha = 105.79$ (1)°, $\beta = 104.46$ (1)°, and $\gamma = 98.04$ (1)°. The density measured by flotation in a mixture of *n*-hexane and carbon tetrachloride was 1.25 g/cm^3 compared to 1.29 g/cm^3 calculated for two formula units in a unit cell volume of 1318 Å^3. The measured density is low due to difficulties in getting the solution to wet the crystals.

Intensity data were collected on the same crystal using filtered Mo Kα radiation (0.003 in. of Zr in the diffracted beam) with the distances from the source and receiving apertures to the crystal 14.5 and 17.8 cm, respectively. All reflections lying in a hemisphere in reciprocal space $\chi = 0$–90°, $\phi = 0$–360° from $2\theta = 0°$ to $2\theta = 45°$ ($(\sin\theta)/\lambda = 0.5385$) were counted for 10 sec each with both crystal and counter stationary at an X-ray tube takeoff angle of 4°. Background counts were taken from a plot of background *vs.* 2θ averaged over several values of χ and ϕ. The background was measured individually for each reflection which was seriously affected by streaking. Periodic checks of three standard reflections showed only small (±1%) random fluctuations in intensity. The data included 3445 reflections, of which 583 had $I < \sigma(I)$.

Inspection of the intensity of $(\bar{1}\bar{2}1)$ as a function of ϕ at $\chi = 90°$ showed no significant variation, the values of μ and μR are 5.9 cm^{-1} and 0.11, and the transmission factors are estimated to vary by less than 5%; no absorption correction was made to the intensities. The intensities were corrected for Lorentz and polarization factors.

Atomic scattering factors of Cromer and Waber[5] for the nonhydrogen atoms and those of Stewart, Davidson, and Simpson[6] for spherical hydrogen atoms were used. Real and imaginary dispersion corrections of Cromer[7] were used for manganese and phosphorus.

The function minimized by least-squares was $\Sigma w(\Delta F)^2/\Sigma w F_o^2$. The weighting scheme used throughout the refinement was $w = 0.0$ for $F^2 < \sigma(F^2)$ and $w = 1/\sigma^2(F)$ otherwise; $\sigma(F^2)$ was calculated as previously described[8] with the ignorance factor $p = 0.04$. The programs used in this study are listed in the same paper.[8]

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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