Comparison of the observed S–S bond length (2.109 (4) Å) and sulfur bond angle (100.5 (1)°) with those of other related compounds reveals no unusual bonding in $(dtp)_2$. According to Pauling's convention of summing covalent radii, the length of an S–S single bond is 2.08 Å.[28] From an extensive survey of sulfur-containing compounds, Abrahams found that the S–S bond varies in length from 1.89 to 2.39 Å.[29] By comparison, the length of the S–S bond in S_8, in which a small amount of double-bond character is believed to exist, is 2.037 (5) Å.[30] Therefore, it appears that the S–S bond in $(dtp)_2$ is essentially an unperturbed single bond. A survey of sulfur valency angles by Abrahams reveals a range of from 66 to 119°.[29] Of these, S–S–S bond angles are found to vary only from 103 to 108° with a mean value of 106°. The observed bond angle in S_8, for example, is 107.8°.[30] P–S–P angles in the phosphorus sulfides also fall into this range (102–109°).[29] Consequently, our observed S–S–P angle, though slightly smaller than the sulfur valency angle found in most sulfur-containing compounds, does not reveal any unusual bonding.

The two phosphorus–sulfur bonds are unequal in length. According to Pauling's scheme, the lengths of P–S single and double bonds are 2.14 and 1.94 Å, respectively.[28] By comparison, our observed (corrected) bond lengths were 2.081 (2) and 1.923 (3) Å, indicating the presence of multiple bonding in both cases.

The phosphorus–oxygen bond lengths in $(dtp)_2$ are similar to those found in previously determined metal phosphorodithioates.[1–6,8] If 1.76 and 1.44 Å are accepted as the single and double P–O bond lengths, respectively,[31] the average measured value 1.569 (5) Å (cor) in $(dtp)_2$ indicates the presence of some double-bond character in these bonds as well. This presence would be consistent with the vast majority of other compounds containing P–O– bonds. The bond order estimated from the Robinson equation[31]

$$n_{P-O} = 23.8/r_{P-O}^{8} + 0.74$$

is 1.4. Such a value would not seem unreasonable if some π bonding due to delocalization of lone-pair electrons on oxygen into vacant $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of phosphorus occurs.[31–38]

The C–H···S and C–H···O interactions are unexceptional. No distances less than 3.1 and 2.6 Å, respectively, were found, based on coordinates for the hydrogen atoms adjusted to give C–H bond lengths of 1.1 Å.

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The Crystal and Molecular Structure of 1,2′:1′,2-Di-μ-carbonyl-bis[1,2-dicarba-*closo*-dodecaborane(12)]

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The dimeric carborane 1,2′:1′,2-di-μ-carbonyl-bis[1,2-dicarba-*closo*-dodecaborane(12)], $[o\text{-}B_{10}C_2H_{10}\cdot CO]_2$, crystallizes in the monoclinic space group $P2_1/n$, with two molecules per cell of dimensions a_0 = 9.528 (4) Å, b_0 = 13.704 (8) Å, c_0 = 7.078 (2) Å, and β = 95.64 (2)°, with Z = 2, ρ_{calcd} = 1.228 (2), and ρ_{obsd} = 1.23 ± 0.01 g/cm³. The phases were determined by the symbolic addition method. Least-squares refinement with 1059 X-ray data resulted in a final unweighted residual of 7.1%. The molecules are located on crystallographic centers of symmetry which fall at the centers of the planar, six carbon atom ring. The carbonyl bond length is 1.217 (4) Å for the riding model. No corrections for thermal motion were found necessary among the skeletal bond lengths where the average bond distances are C–B = 1.730 (7) Å, B–B = 1.778 (8) Å, C–C = 1.645 (4) Å [polyhedral], and C–C = 1.517 (4) Å [exopolyhedral]. The average B–H length is 1.09 (5) Å.

Introduction

There is a pronounced tendency of the substituents attached to the carbon atoms in the *o*-carborane moiety to form exopolyhedral rings. No structural data have yet appeared for such species or for the related doubly connected bis *o*-carboranes. We wish to report the structure for one such carborane, $[o\text{-}B_{10}H_{10}C_2\cdot CO]_2$, 1,2′:1′,2-di-$\mu$-carbonyl-bis[1,2-dicarba-*closo*-dodecabo-

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rane(12)]. The latter was originally prepared by Reiner, Alexander, and Schroeder,[2] who proposed that the individual *o*-carborane moieties were connected by a planar cyclohexane-like skeleton. The present single-crystal X-ray diffraction study of $[o\text{-}B_{10}H_{10}C_2 \cdot CO]_2$ confirms the proposed structure.

Experimental Section

The $[B_{10}H_{10}C_2 \cdot CO]_2$ studied in this X-ray investigation was prepared as previously described.[2] Crystals recovered from CCl_4 invariably proved to be twinned; however, suitable crystals were grown from CH_2Cl_2. The crystal used for the photographic analysis was an approximately rectangular parallelepiped elongated on c_0 with dimensions of 0.30 × 0.23 × 0.20 mm. Precession (Mo Kα) photographs of the *h*0*l*, *hll*, 0*kl*, and 1*kl* reciprocal lattice nets displayed the systematic absences 0*k*0 for *k* odd and *h*0*l* for $(h + l)$ odd, which uniquely determined the space group $C_{2h}{}^5$-$P2_1/n$. Accurate lattice parameters [a_0 = 9.528 (4) Å, b_0 = 13.704 (8) Å, c_0 = 7.078 (2) Å, and β = 95.64 (2)°] were measured on a Picker FACS-1 automated diffractometer using 12 reflections in a least-squares adjustment routine supplied with that system (λ 1.5418 Å). A measured density of 1.23 ± 0.01 g/cm^3 obtained by the sink–float method in KI solution agrees favorably with the value of 1.228 (2) g/cm^3 calculated on the basis of two molecules per unit cell. Therefore, since the general positions for $P2_1/n$ are fourfold, the molecular centers (center of six carbon atom ring) must reside at a pair of special positions. In the space group $P2_1/n$ the special positions are symmetry centers.

One set of data was collected for *hkL* (*L* = 0–4) using multiple-film Weissenberg techniques; intensities were estimated visually by comparison with a standard scale of reflections obtained from the same crystal. For a satisfactory refinement it was necessary to gather another set of data (*vide infra*). These intensity data were gathered using a General Electric XRD-5 single-crystal orienter equipped with a scintillation counter and a pulse-height analyzer. Nickel-filtered copper Kα radiation was used for taking the intensity record. The tube takeoff angle was set at 4° and the θ–2θ scan technique was used with an open counter (scan rate 2° in 2θ/min; range ±1°). The crystal used for the intensity record was an approximately rectangular parallelepiped elongated on a_0 with dimensions 0.36 × 0.23 × 0.14 mm. The long axis of the crystal was mounted approximately parallel to the instrument axis ϕ. Because of the low absorption coefficient (μ = 4.4 cm^{-1}; I/I_0 = 0.94 and 0.87 for minimum and maximum path lengths, respectively) no absorption corrections were deemed necessary. Zonal data (*h*0*l*, 0*kl*, and *hk*0 data) were collected out to 2θ = 140°. General *hkl* data were collected to 2θ = 100° yielding 1059 reflections of which 125 were considered to be zero; *i.e.*, background equaled or exceeded the peak measurement.

TABLE I

STATISTICAL DATA FOR THE DISTRIBUTION OF NORMALIZED STRUCTURE FACTORS

Obsd	Theoret	
	Centrosymmetric	Noncentrosymmetric
Av $\|E\|^2$ = 1.04	1.00	1.00
Av $\|E^2 - 1\|$ = 1.03	0.968	0.736
Av $\|E\|$ = 0.776	0.798	0.886

TABLE II

STARTING SET OF REFLECTIONS FOR THE SYMBOLIC ADDITION PHASE DETERMINATION

hkl	*E*	S	*hkl*	*E*	S
$\bar{3}\ 1\ 7$	3.16	+	$5\ 7\ \bar{4}$	2.76	B
$\bar{2}\ 7\ 6$	3.12	+	$6\ 2\ \bar{6}$	2.69	C
1 6 2	2.78	+	$11\ 6\ \overline{11}$	3.03	D
$\bar{8}\ 4\ 9$	2.78	A			

Solution and Refinement.—The 1093 visually estimated photographic data were corrected for Lorentz and polarization effects and then converted to normalized structure factors[3] so that the symbolic addition method of Karle and Karle[4] could be applied to determine phase relationships. The statistical data derived from the distribution of *E*'s and presented in Table I confirm the centrosymmetric space group. The starting set of origin-setting reflections and those for which symbolic signs were used are listed in Table II. The "sigma two" method[4] was applied to the data by initially accepting only relationships wherein the probability of a correct sign determination was 99% or better. As more signs were determined, the probability level was cautiously lowered and more contributing pairs were required for an acceptable sign indication. The probability level was lowered eventually to 98% when the total of 206 signs had been determined. The tendency of A to be negative and of both B and C to be positive was now evident, while the symbol D was rejected since it was contained in less than 3% of the knowns. Accordingly a three-dimensional Fourier was computed with the symbolic signs noted. From the initial Fourier the 14 heavy atoms which comprise the asymmetric unit of the molecule were easily recognized. The atom positions were entered directly into a least-squares refinement[5] using data from all levels and varying atom positions. Two cycles of refinement showed good agreement between F_c and F_o, for levels *hk*0, *hk*1, and *hk*2, but *hk*3 and *hk*4 showed major discrepancies and the conventional R_1 for nonzero data[5] was 49%. This difficulty suggested inadequacies in the photographic data. Accordingly, the best refinement obtained converged at R_1 = 24% for data from levels *hk*0, *hk*1, and *hk*2 with variable individual isotropic thermal parameters, atom positions, and one overall scale factor.

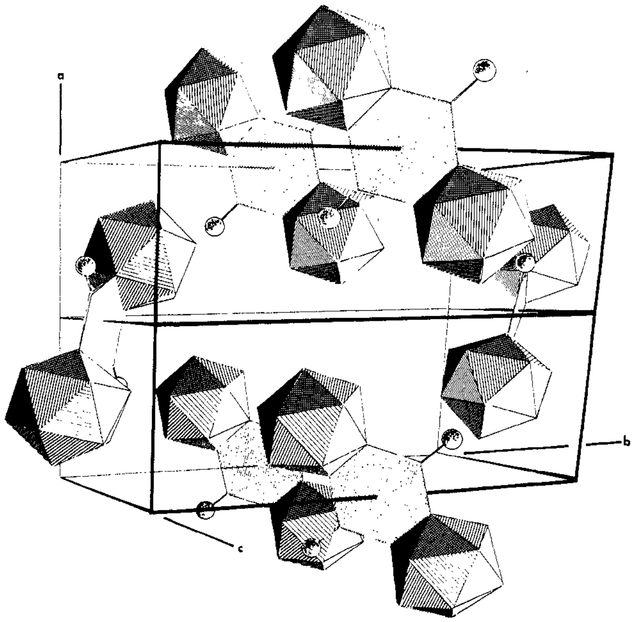

Figure 1.—Perspective view of the packing arrangement in the crystal. Molecular centers of inversion are located at (0, $^1/_2$, 0), ($^1/_2$, 0, $^1/_2$), ($^1/_2$, 1, $^1/_2$), (1, $^1/_2$, 0), (0, $^1/_2$, 1), and (1, $^1/_2$, 1). The (200) plane is outlined for clarity.

At this point it was apparent that better data were essential. Using the set of diffractometer data (*vide supra*), a satisfactory

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TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

K	L	FOB	FCA
***** H -11 *****			
0	1	0	27
0	3	11	20
***** H -10 *****			
0	2	39	42
0	4	0	13
***** H -9 *****			
0	1	51	54
0	3	0	25
0	5	0	20
1	1	27	34
1	2	52	53
2	1	31	35
2	2	0	21
3	1	35	37
3	2	4	20
4	1	24	24
***** H -8 *****			
0	2	80	84
0	4	30	34
0	6	0	3
1	1	54	55
1	2	23	35
1	3	53	54
1	4	55	61
2	1	57	58
2	2	109	105
2	3	11	29
2	4	23	28
3	1	8	10
3	2	65	66
3	3	50	57
4	1	222	229
4	2	10	8
4	3	49	45
4	4	56	54
5	1	16	6
5	2	26	29
5	3	0	5
6	1	46	40
6	2	54	56
7	1	0	8
***** H -7 *****			
0	1	24	31
0	3	372	376
0	5	26	28
0	7	0	10
1	1	0	2
1	2	200	197
1	3	54	61
1	4	74	75
1	5	0	5
2	1	225	222
2	2	219	212
2	3	148	144
2	4	149	151
2	5	13	21
3	1	123	112
3	2	65	63
3	3	36	46
3	4	11	12
4	1	155	150
4	2	91	94
4	3	119	127
4	4	108	109
5	1	105	115
5	2	16	17
5	3	25	24
5	4	0	8
6	1	88	89
6	2	22	33
6	3	74	72
6	4	85	86
7	1	51	67
7	2	0	16
7	3	58	60
8	1	72	69
8	2	80	82
9	1	0	3
***** H -6 *****			
0	2	183	177
0	4	121	124
0	6	88	90
1	0	106	104
1	1	0	7
1	2	18	18
1	3	132	124
1	4	38	38
1	5	63	57
2	0	323	323
2	1	6	11
2	2	34	42
2	3	204	203
2	4	67	65
2	5	141	145
3	1	118	118
3	2	20	21
3	3	60	56
3	4	115	115
3	5	9	28
4	1	80	80
4	2	65	65
4	3	55	60
4	4	60	55
4	5	84	91
5	1	50	56
5	2	127	128
5	3	43	49
5	4	13	14
5	5	0	1
6	1	133	135
6	2	64	77
6	3	39	43
6	4	0	21
6	6	59	72
7	1	113	111
7	2	7	18
7	3	101	107
7	4	46	39
8	1	45	56
8	2	87	99
8	3	86	91
9	1	28	22
9	2	117	117
9	3	51	50
10	1	26	21
10	2	41	49
***** H -5 *****			
0	1	29	27
0	3	111	114
0	5	0	20
0	7	0	4
1	1	87	77
1	2	98	97
1	3	0	13
1	4	153	151
1	5	173	177
1	6	111	121
2	1	142	133
2	2	218	215
2	3	17	23
2	4	0	2
2	5	10	5
2	6	88	90
3	1	46	52
3	2	19	24
3	3	0	6
3	4	81	72
3	5	164	168
3	6	0	13
4	1	20	27
4	2	105	107
4	3	292	282
4	4	75	69
4	5	23	29
5	1	84	89
5	2	20	25
5	3	37	35
5	4	94	94
5	5	86	85
6	1	208	213
6	2	57	48
6	3	118	114
6	4	111	119
6	5	27	26
7	1	34	26
7	2	185	192
7	3	23	15
7	4	56	52
7	5	28	30
8	1	162	158
8	2	41	33
8	3	32	32
8	4	48	48
9	1	112	117
9	2	0	3
9	3	14	23
9	4	0	4
10	1	28	28
10	2	34	35
10	3	0	6
10	5	46	45
11	1	16	22
11	2	0	13
***** H -4 *****			
0	2	60	59
0	4	227	213
0	6	60	68
0	8	115	130
1	1	90	84
1	2	72	75
1	3	24	29
1	4	116	113
1	5	176	194
1	6	52	61
2	1	202	176
2	2	18	13
2	3	71	67
2	4	0	16
2	5	19	22
2	6	15	10
3	1	115	100
3	2	121	115
3	3	45	52
3	4	82	72
3	5	52	52
3	6	0	16
4	1	32	32
4	2	8	6
4	3	74	77
4	4	31	31
4	5	22	9
4	6	0	7
4	8	12	19
5	1	274	268
5	2	140	139
5	3	182	177
5	4	0	3
5	5	98	103
5	6	39	41
6	1	186	173
6	2	55	57
6	3	68	72
6	4	38	34
6	5	9	7
7	1	302	293
7	2	84	78
7	3	37	31
7	4	118	121
7	5	39	42
8	1	31	36
8	2	52	54
8	3	54	58
8	4	0	5
8	5	107	108
9	1	78	85
9	2	99	85
9	3	23	12
9	4	11	15
10	1	9	17
10	2	165	172
10	3	6	10
11	1	131	124
11	2	0	2
11	3	0	3
***** H -3 *****			
0	1	56	56
0	3	429	395
0	5	88	97
0	7	58	56
1	1	70	66
1	2	165	155
1	3	265	251
1	4	416	389
1	5	215	212
1	6	163	161
2	1	22	25
2	2	90	80
2	3	68	57
2	4	50	44
2	5	15	3
2	6	107	117
3	1	108	104
3	2	101	95
3	3	111	102
3	4	0	1
3	5	127	124
3	6	30	7
4	1	369	337
4	2	2	10
4	3	135	129
4	4	16	15
4	5	32	26
4	6	44	44
5	1	133	128
5	2	173	161
5	3	27	25
5	4	164	161
5	5	98	92
5	6	21	24
6	1	183	166
6	2	97	87
6	3	114	106
6	4	138	130
6	5	11	4
6	6	18	11
7	1	17	17
7	2	141	148
7	3	32	41
7	4	70	69
7	5	45	45
8	1	87	86
8	2	109	109
8	3	18	34
8	4	109	110
8	5	59	58
9	1	87	88
9	2	61	60
9	3	228	229
9	4	0	0
9	5	61	72
10	1	162	169
10	2	35	43
10	3	66	66
10	4	54	49
11	1	57	68
11	2	197	198
11	3	24	27
12	1	69	65
12	2	38	41
***** H -2 *****			
0	2	319	304
0	4	67	59
0	6	115	122
0	8	0	8
1	1	235	229
1	2	0	2
1	3	287	257
1	4	134	120
1	5	22	23
1	6	0	37
2	1	147	137
2	2	26	31
2	3	105	91
2	4	38	36
2	5	53	50
2	6	62	62
3	1	95	95
3	2	122	119
3	3	24	23
3	4	134	142
3	5	78	75
3	6	118	111
4	1	88	79
4	2	36	25
4	3	49	46
4	4	12	15
4	5	65	61
4	6	97	103
5	1	107	104
5	2	24	22
5	3	219	210
5	4	96	88
5	5	275	273
5	6	107	101
6	1	218	205
6	2	51	63
6	3	49	56
6	4	57	64
6	5	156	156
6	6	33	42
7	1	55	58
7	2	34	25
7	3	43	44
7	4	286	281
7	5	52	47
7	6	14	22
8	1	64	49
8	2	132	122
8	3	227	222
8	4	93	91
8	5	25	25
9	1	0	2
9	2	216	219
9	3	87	84
9	4	90	86
9	5	12	26
10	1	24	27
10	2	74	79
10	3	201	198
10	4	35	22
11	1	117	127
11	2	18	22
11	3	15	9
11	4	0	13
12	1	28	41
12	2	101	102
12	3	0	9
13	1	0	11
***** H -1 *****			
0	1	874	894
0	3	134	124
0	5	92	98
0	7	0	38
1	1	37	35
1	2	255	238
1	3	233	210
1	4	62	62
1	5	72	70
1	6	0	10
2	1	42	38
2	2	170	164
2	3	24	26
2	4	40	45
2	5	35	36
2	6	148	151
3	1	221	230
3	2	26	31
3	3	92	85
3	4	59	63
3	5	166	159
3	6	0	15
4	1	327	333
4	2	67	63
4	3	0	8
4	4	43	36
4	5	211	217
4	6	102	98
5	1	308	292
5	2	257	243
5	3	26	32
5	4	182	172
5	5	28	22
5	6	0	10
6	1	245	221
6	2	216	203
6	3	6	14
6	4	57	42
6	5	102	98
6	6	19	21
7	1	66	65
7	2	239	238
7	3	23	28
7	4	0	15
7	5	0	24
7	6	76	83
8	1	57	57
8	2	60	70
8	3	90	87
8	4	68	60
8	5	35	29
9	1	259	255
9	2	43	34
9	3	21	50
9	4	6	34
9	5	41	48
10	1	26	17
10	2	126	131
10	3	20	31
10	4	17	6
11	1	82	74
11	2	116	123
11	3	0	14
11	4	26	36
12	1	24	14
12	2	29	31
12	3	0	7
13	1	9	18
***** H 0 *****			
-16	0	21	24
-14	0	67	57
-12	0	0	10
-10	0	123	118
-8	0	92	89
-2	0	570	626
0	2	285	263
0	4	27	21
0	6	128	128
0	8	94	94
1	1	641	664
1	2	109	101
1	3	83	88
1	4	130	128
1	5	120	122
1	6	25	34
1	7	32	33
1	8	68	69
2	1	821	889
2	2	70	66
2	3	75	71
2	4	0	0
2	5	231	222
2	6	0	10
2	7	39	44
2	8	167	175
3	1	70	50
3	2	30	34
3	3	32	26
3	4	196	197
3	5	72	81
3	6	17	6
3	7	127	134
3	8	0	5
4	0	92	90
4	1	231	237
4	2	51	51
4	3	102	95
4	4	23	17
4	5	66	65
4	6	67	76
4	7	70	66
4	8	21	41
5	1	99	98
5	2	239	229
5	3	8	33
5	4	72	71
5	5	106	109
5	6	0	1
5	7	41	42
5	8	57	61
6	0	172	177
6	1	243	234
6	2	81	77
6	3	173	169
6	4	101	100
6	5	0	27
6	6	0	14
6	7	48	50
6	8	4	19
7	1	64	64
7	2	102	98
7	3	83	76
7	4	80	84
7	5	37	47
7	6	41	45
7	7	0	34
8	1	150	165
8	2	100	106
8	3	38	42
8	4	107	102
8	5	0	24
8	6	61	48
13	5	0	7
14	1	30	37
14	2	62	60
14	3	18	31
14	4	0	8
15	1	19	26
15	2	30	58
15	3	37	44
16	1	48	42
16	2	76	78
8	7	0	10
9	1	0	9
9	2	21	31
9	3	11	21
9	4	8	1
9	5	0	17
9	6	44	55
9	7	53	50
10	1	68	73
10	2	131	133
10	3	64	78
10	4	32	35
10	5	10	14
10	6	0	18
11	1	82	92
11	2	21	16
11	3	0	2
11	4	21	38
11	5	27	34
11	6	41	39
12	1	16	14
12	2	77	81
12	3	5	5
12	4	18	29
12	5	9	3
12	6	26	24
13	1	16	23
13	2	27	34
13	3	36	38
13	4	0	5
***** H 1 *****			
0	1	242	221
0	3	231	224
0	5	237	232
0	7	46	44
1	0	576	613
1	1	418	403
1	2	135	134
1	3	171	155
1	4	12	4
1	5	20	23
1	6	0	18
2	0	643	663
2	1	179	183
2	2	362	350
2	3	0	3
2	4	178	171
2	5	10	5
2	6	96	97
3	0	6	18
3	1	144	137
3	2	158	156
3	3	301	264
3	4	0	7
3	5	13	25
3	6	14	33
4	0	242	245
4	1	155	151
4	2	535	525
4	3	38	31
4	4	59	65
4	5	161	164
4	6	17	23
5	0	46	52
5	1	186	189
5	2	231	202
5	3	127	124
5	4	69	66
5	5	9	20
5	6	32	36
6	0	70	63
6	1	217	210
6	2	222	216
6	3	350	351
6	4	63	56
6	5	40	57
6	6	0	30
7	0	170	150
7	1	6	29
7	2	71	70
7	3	0	12
7	4	205	206
7	5	50	47
8	0	18	5
8	1	123	146
8	2	62	70
8	3	236	225
8	4	168	177
8	5	40	55
9	0	25	19
9	1	37	36
9	2	103	96
9	3	10	3
9	4	0	6
9	5	75	74
10	0	139	138
10	1	196	194
10	2	41	30
10	3	40	60
10	4	121	123
11	0	24	35
11	1	88	92
11	2	59	56
11	3	41	52
11	4	5	10
12	0	62	62
12	1	0	9
12	2	0	17
12	3	27	38
13	0	0	12
13	1	0	6
14	0	0	5
15	0	9	6
16	0	43	41
***** H 2 *****			
0	0	675	674
0	2	227	217
0	4	144	135
0	6	0	11
0	8	31	38
1	0	33	24
1	1	129	137
1	2	283	268
1	3	164	143
1	4	123	122
1	5	121	116
1	6	9	15
2	0	123	122
2	1	114	111
2	2	305	289
2	3	238	214
2	4	207	209
2	5	38	29
2	6	33	36
3	0	279	283
3	1	27	30
3	2	470	438
3	3	175	164
3	4	47	41
3	5	219	216
3	6	28	33
4	0	166	156
4	1	46	43
4	2	116	117
4	3	224	207
4	4	46	47
4	5	45	52
4	6	61	75
5	0	193	189
5	1	150	131
5	2	81	75
5	3	229	220
5	4	11	7
5	5	0	20
5	6	0	3
6	0	14	35
6	1	28	36
6	2	86	82
6	3	127	121
6	4	78	82
6	5	82	93
6	6	56	62
7	0	14	7
7	1	67	73
7	2	35	34
7	3	189	181
7	4	117	121
7	5	71	77
8	0	31	35
8	1	128	128
8	2	61	63
8	3	119	126
8	4	88	99
8	5	81	91
9	0	0	4
9	1	266	266
9	2	0	12
9	3	5	23
9	4	166	181
10	0	132	132
10	1	0	7
10	2	33	34
10	3	64	71
10	4	9	15
11	0	56	51
11	1	70	70
11	2	73	69
11	3	48	60
12	0	15	17
12	1	51	53
12	2	28	15
13	0	13	20
13	1	41	38
14	0	9	4
15	0	37	39
16	0	0	4
***** H 3 *****			
0	1	181	172
0	3	0	11
0	5	86	75
0	7	0	7
1	0	184	182
1	1	15	22
1	2	55	56
1	3	146	137
1	4	166	155
1	5	104	104
1	6	14	28
2	0	199	192
2	1	103	102
2	2	107	108
2	3	167	156
2	4	64	66
2	5	109	108
2	6	0	17
3	0	119	116
3	1	134	133
3	2	140	130
3	3	55	60
3	4	301	293
3	5	92	96
3	6	26	32
4	0	21	28
4	1	85	82
4	2	70	71
4	3	0	8
4	4	11	31
4	5	40	50
4	6	48	48
5	0	62	58
5	1	122	114
5	2	55	60
5	3	41	40
5	4	0	11
5	5	78	77
6	0	221	215
6	1	48	54
6	2	74	75
6	3	91	82
6	4	121	126
6	5	20	30
7	0	23	24
7	1	134	137
7	2	25	17
7	3	29	37
7	4	84	93
7	5	34	40
8	0	16	5
8	1	28	14
8	2	118	120
8	3	147	151
8	4	47	58
8	5	41	53
9	0	48	42
9	1	59	54
9	2	68	71
9	3	73	79
9	4	7	21
10	0	58	49
10	1	23	29
10	2	21	22
10	3	32	29
10	4	39	46
11	0	0	0
11	1	99	97
11	2	13	3
11	3	92	93
12	0	17	5
12	1	0	6
13	0	17	12
14	0	45	44
15	0	34	33
16	0	71	71
***** H 4 *****			
0	0	307	292
0	2	0	5
0	4	122	129
0	6	0	19
1	0	370	364
1	1	342	319
1	2	119	111
1	3	39	39
1	4	157	158
1	5	86	93
1	6	0	7
2	0	367	352
2	1	0	8
2	2	71	66
2	3	62	62
2	4	54	59
2	5	96	99
2	6	34	36
3	0	343	328
3	1	0	8
3	2	143	132
3	3	152	146
3	4	65	66
3	5	167	167
4	0	57	56
4	1	111	103
4	2	43	43
4	3	159	160
4	4	52	58
4	5	0	2
5	0	74	73
5	1	0	9
5	2	160	163
5	3	19	17
5	4	98	101
8	2	9	24
8	3	0	7
8	4	15	28
9	0	192	197
9	1	163	161
9	2	0	24
9	3	35	40
9	4	22	40
10	0	81	92
10	1	78	83
10	2	35	24
10	3	30	39
11	0	35	32
11	1	13	18
11	2	25	27
12	0	29	37
12	1	0	10
13	0	27	26
14	0	11	18
15	0	62	62
5	5	0	7
6	0	109	110
6	1	47	45
6	2	37	53
6	3	54	53
6	4	106	109
6	5	4	27
7	0	93	92
7	1	127	129
7	2	206	200
7	3	121	136
7	4	0	2
7	5	11	37
8	0	63	63
8	1	118	116
***** H 5 *****			
0	1	123	117
0	3	87	94
0	5	44	44
0	7	16	33
1	0	155	140
1	1	48	50
1	2	201	194
1	3	45	41
1	4	232	231
1	5	36	35
2	0	109	111
2	1	100	101
2	2	33	39
2	3	62	67
2	4	0	3
2	5	102	107
3	0	84	79
3	1	77	86
3	2	45	45
3	3	272	271
3	4	211	212
3	5	107	117
4	0	37	36
4	1	45	40
4	2	62	65
4	3	138	134
4	4	36	38
4	5	40	45
5	0	40	48
5	1	54	50
5	2	273	273
5	3	201	198
5	4	83	84
5	5	38	41
6	0	74	73
6	1	62	60
6	2	256	256
6	3	40	37
6	4	29	36
7	0	37	37
7	1	272	266
7	2	73	66
7	3	19	31
7	4	62	59
8	0	174	182
8	1	145	148
8	2	113	114
8	3	58	52
8	4	0	14
9	0	53	43
9	1	86	84
9	2	53	56
9	3	38	30
10	0	98	98
10	1	0	2
10	2	0	9
10	5	9	2
11	0	26	20
11	1	74	71
12	0	29	31
13	0	68	64
14	0	23	19
15	0	9	9
***** H 6 *****			
0	0	69	66
0	2	313	326
0	4	105	108
0	6	28	30
1	1	41	48
1	2	77	71
1	3	0	0
1	4	44	37
2	1	19	23
2	2	111	116
2	3	211	212
2	4	85	92
3	0	75	74
3	1	93	91
3	2	60	57
3	3	75	82
3	4	0	7
4	0	81	84
4	1	195	185
4	2	144	151
4	3	120	119
4	4	56	55
5	0	30	34
5	1	57	58
5	2	0	8
5	3	13	10
5	4	33	39
6	0	0	11
6	1	43	37
6	2	136	144
6	3	22	24
6	4	0	4
6	6	86	83
7	0	39	50
7	1	3	16
7	2	28	34
7	3	24	14
8	0	98	102
8	1	16	17
8	2	22	31
8	3	57	56
9	0	40	49
9	1	37	42
9	2	20	25
10	0	19	21
10	1	76	70
11	0	67	69
12	0	107	105
13	0	42	42
14	0	15	16
***** H 7 *****			
0	1	11	9
0	3	103	106
0	5	57	62
1	0	77	83
1	1	65	63
1	2	12	34
1	3	0	14
1	4	0	11
2	0	93	92
2	1	137	145
2	2	71	80
2	3	0	5
2	4	41	43
3	0	52	50
3	1	59	63
3	2	96	99
3	3	0	9
4	0	215	226
5	0	11	20
6	0	102	108
7	0	44	40
8	0	89	92
9	0	39	46
10	0	20	25
11	0	14	23
12	0	6	2
13	0	52	48
***** H 8 *****			
0	0	34	32
0	2	77	80
0	4	61	64
1	0	46	38
1	1	90	106
1	2	0	3
1	3	15	28
2	0	167	186
2	1	0	24
2	2	15	6
2	3	36	42
3	0	119	134
3	1	73	83
3	2	0	5
4	0	39	55
4	1	18	26
4	2	20	26
5	2	71	68
6	0	72	70
6	1	0	4
7	0	0	12
8	0	19	21
9	0	51	10
10	0	49	57
11	0	14	14
12	0	106	107
***** H 9 *****			
0	1	81	88
0	3	37	41
1	0	67	71
1	1	19	19
2	0	64	70
2	1	12	19
3	0	0	4
4	0	0	6
5	0	37	39
6	0	0	2
7	0	0	0
8	0	18	23
9	0	35	40
10	0	12	10
***** H 10 *****			
0	0	32	34
0	2	0	5
1	0	15	7
2	0	16	12
3	0	44	44
4	0	60	59
5	0	38	37
6	0	25	25
7	0	38	36
8	0	0	11
***** H 11 *****			
0	1	58	60
1	0	5	9
2	0	9	25
3	0	49	48
4	0	9	17
5	0	0	32

refinement of the structure was accomplished by introducing the atom parameters derived from the photographic data into the least-squares refinement programs ORFLS.[5] Throughout the refinement the data were weighted according to a scheme suggested by Stout and Jensen[6] of the form

$$\sigma(F_o) = \frac{1}{2\sqrt{Lp}}\sqrt{\frac{NT + N_{\overline{BKG}} + (0.01N_{pk})^2}{NT - N_{\overline{BKG}}}}$$

where $\sigma(F_o)$ is the estimated standard error of F_o, Lp is the Lorentz–polarization correction term, NT is the total counts accumulated during the intensity scan, and $N_{\overline{BKG}}$ is the mean of two 10-sec background counts taken on both sides of the peak at $N_{pk} = NT - N_{\overline{BKG}}$.

Because of core size limitations in our IBM 7040 computer, all variables could not be treated as variables on any single pass. Accordingly, the latter stages of refinement were carried out using blocks of variables, one block per pass, with at least a four-atom "overlap" in each block. Hydrogen atom positions were varied simultaneously with the positional and thermal parameters of their bonded boron atoms. The thermal parameters of the H atoms were not refined, but assigned the values of the isotropic thermal parameters of their attached B atoms. Scattering factors for oxygen, carbon, and boron were taken from ref 7 and the scattering factors for hydrogen were taken from the work of Stewart, Davidson, and Simpson.[8]

Two cycles of least squares varying individual isotropic thermal parameters, positional parameters, and a scale factor brought the residual[5] for nonzero observed data to 15.6%. Two additional cycles of least squares allowing anisotropic thermal motion reduced the residual for nonzero observed data to 13.5%. A difference Fourier was calculated at this point using the program FORDAP.[9] All the hydrogen atoms were found from the Fourier map and all had peak intensities at least 1.5 times as large as the tallest nonhydrogen background peak in the Fourier. Two

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(6) G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457.

(7) K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(9) A. Zalkin, "FORDAP," Lawrence Radiation Laboratory, University of California, Berkeley, Calif., 1964.

TABLE IV

FINAL POSITIONAL[a] AND THERMAL PARAMETERS[b] FOR $[B_{10}H_{10}C_2 \cdot CO]_2$

Atom designation	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0.1859 (3)	0.5844 (2)	−0.2289 (3)	0.0074 (4)	0.0071 (2)	0.0182 (7)	0.0000 (2)	0.0045 (4)	−0.0054 (3)
C(μ)	0.1065 (4)	0.5483 (3)	−0.1299 (5)	0.0068 (5)	0.0033 (2)	0.0120 (9)	−0.0002 (3)	−0.0004 (5)	0.0004 (4)
C-1	0.0479 (3)	0.4211 (2)	0.1499 (4)	0.0061 (4)	0.0033 (2)	0.0085 (8)	−0.0001 (3)	0.0010 (5)	0.0003 (4)
C-2	0.1590 (3)	0.4721 (2)	0.0159 (5)	0.0058 (4)	0.0035 (2)	0.0105 (8)	0.0000 (3)	0.0018 (5)	0.0011 (4)
B-3	0.1688 (4)	0.5053 (3)	0.2539 (6)	0.0074 (6)	0.0046 (3)	0.0100 (10)	−0.0010 (4)	−0.0005 (6)	−0.0003 (5)
B-4	0.1291 (5)	0.3937 (3)	0.3706 (6)	0.0075 (3)	0.0054 (3)	0.0111 (10)	0.0005 (4)	−0.0011 (6)	0.0018 (5)
B-5	0.0922 (5)	0.3007 (3)	0.1976 (6)	0.0105 (7)	0.0037 (3)	0.0159 (11)	0.0005 (4)	0.0006 (7)	0.0024 (5)
B-6	0.1088 (5)	0.3516 (3)	−0.0334 (6)	0.0100 (6)	0.0035 (3)	0.0126 (10)	0.0008 (4)	0.0018 (7)	−0.0004 (5)
B-7	0.3234 (4)	0.4841 (4)	0.1347 (6)	0.0047 (5)	0.0065 (4)	0.0169 (12)	−0.0008 (4)	0.0001 (6)	0.0022 (6)
B-8	0.3056 (5)	0.4316 (4)	0.3624 (7)	0.0073 (6)	0.0071 (4)	0.0151 (11)	0.0002 (4)	−0.0019 (7)	0.0015 (6)
B-9	0.2593 (5)	0.3074 (4)	0.3273 (7)	0.0097 (7)	0.0051 (3)	0.0153 (11)	0.0015 (4)	−0.0006 (7)	0.0038 (5)
B-10	0.2471 (5)	0.2814 (4)	0.0784 (7)	0.0132 (8)	0.0046 (3)	0.0169 (12)	0.0037 (4)	0.0030 (8)	0.0011 (6)
B-11	0.2864 (5)	0.3920 (4)	−0.0369 (7)	0.0081 (6)	0.0063 (4)	0.0170 (12)	0.0029 (4)	0.0034 (7)	0.0022 (6)
B-12	0.3807 (5)	0.3627 (4)	0.1837 (7)	0.0085 (6)	0.0075 (4)	0.0174 (12)	0.0027 (4)	0.0018 (7)	0.0029 (6)
				B^c					
H-3	0.3678 (30)	0.0779 (21)	0.2097 (40)	2.7					
H-4	0.0620 (29)	0.3919 (19)	0.4945 (41)	2.6					
H-5	0.0091 (31)	0.2462 (23)	0.2044 (44)	3.5					
H-6	0.0393 (29)	0.3389 (20)	−0.1705 (41)	2.4					
H-7	0.3824 (31)	0.5520 (21)	−0.1114 (41)	2.7					
H-8	0.3665 (30)	0.4528 (21)	0.4799 (44)	2.8					
H-9	0.2841 (32)	0.2597 (23)	0.4267 (45)	3.4					
H-10	0.2723 (30)	0.2111 (22)	0.0224 (42)	3.1					
H-11	0.3226 (30)	0.3977 (21)	−0.1859 (44)	3.5					
H-12	0.4941 (32)	0.3371 (21)	0.1941 (41)	3.4					

[a] Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digits. [b] Thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Isotropic thermal parameters assigned to the H atoms and of form $\exp(-B(\sin^2\theta)/\lambda^2)$.

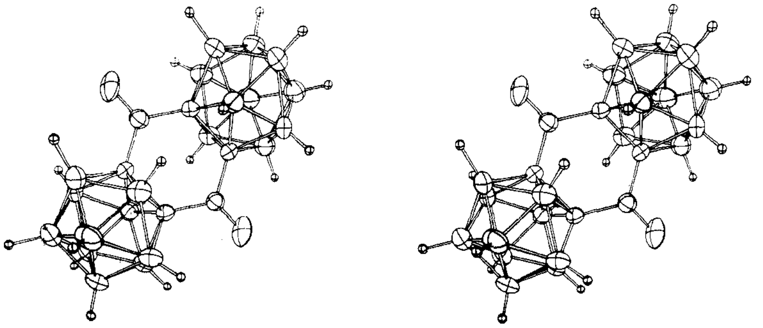

Figure 2.—Stereoscopic representation of the molecular structure and vibrational ellipsoids of the atoms.

cycles of least squares including the hydrogen atoms were carried out reducing the nonzero data residual to 7.6%. The data were checked for blunders in data collection and several errors were found. These data were remeasured and two more cycles of least squares brought the residual[5] to R_1 (including zeros) = 0.087, R_1 (excluding zeros) = 0.071, weighted R_2 (including zeros) = 0.064, and weighted R_2 (excluding zeros) = 0.063.

The error terms were all on the order of 2 and 3 times the parameter shifts at this time and the refinement was considered complete.

Observed and computed structure factors are presented in Table III. Atom position and thermal parameters are listed in Table IV.

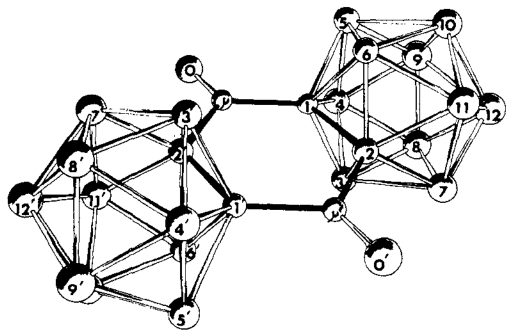

Figure 3.—Atom numbering convention. Hydrogen atoms are omitted for clarity.

Discussion

The packing arrangement of the crystal is shown in perspective in Figure 1. The configuration of the molecule can be better seen in the stereoscopic diagram (Figure 2) which includes the vibrational ellipsoids of the atoms. The atom numbering scheme is given in Figure 3. Bond distances are listed in Table V and selected bond angles are given in Table VI.

The "icosahedral" bond distances (Table V) are averaged in terms of equivalent bonds based on an

TABLE V

BOND DISTANCES[a]

Bond	Distances, Å	Av[b]
C(μ)–O	1.217 (4)	1.217 (4)
	C–C	
1–μ	1.523 (5)	1.520 (5)
2–μ	1.517 (5)	
	C–C	
1–2	1.645 (5)	1.645 (5)
	C–B	
1–3	1.742 (5)	1.745 (5)
1–6	1.754 (5)	
2–3	1.738 (5)	
2–6	1.745 (5)	
	C–B	
1–4	1.715 (5)	1.715 (10)
1–5	1.729 (5)	
2–7	1.711 (5)	
2–11	1.705 (5)	
	B–B	
4–5	1.779 (6)	1.771 (8)
7–11	1.763 (6)	
	B–B	
3–8	1.764 (6)	1.760 (6)
6–10	1.755 (6)	
	B–B	
3–4	1.796 (6)	1.792 (7)
3–7	1.791 (6)	
5–6	1.799 (6)	
6–11	1.782 (6)	
	B–B	
4–8	1.767 (6)	1.781 (6)
5–10	1.790 (6)	
7–8	1.788 (6)	
10–11	1.779 (6)	
	B–B	
8–9	1.769 (6)	1.785 (11)
8–12	1.783 (6)	
9–10	1.790 (6)	
10–12	1.798 (6)	
	B–B	
4–9	1.762 (6)	1.767 (6)
5–9	1.761 (6)	
7–12	1.774 (6)	
11–12	1.769 (10)	
	B–B	
9–12	1.782 (6)	1.782 (6)
	B–H	
3–3′	1.09 (3)	1.09 (5)
4–4′	1.14 (3)	
5–5′	1.09 (3)	
6–6′	1.13 (3)	
7–7′	1.11 (3)	
8–8′	1.01 (3)	
9–9′	0.97 (3)	
10–10′	1.08 (3)	
11–11′	1.14 (3)	
12–12′	1.13 (3)	

[a] Corrections for thermal motion were made only for C(μ)–O. [b] If the rms error of the average bond length was greater than the standard deviations of the values averaged, it is listed in parentheses for the least significant figure.

TABLE VI

SELECTED BOND ANGLES

Bonded atoms		Angle, deg
C(1)–C(μ)–C(2′)		120.2 (4)
C(1)–C(μ)–O		119.7 (3)
C(2′)–C(μ)–O		120.1 (3)
C(μ)–C(1)–C(2)		120.0 (4)
C(μ′)–C(2)–C(1)		119.8 (4)
Polyhedral bond type	Av angle,[a] deg	No. of determns
B–B–B	60.0 (6)	36
B–B–C	58.7 (7)	12
B–C–B	62.3 (4)	6
B–C–C	61.9 (4)	4
C–B–C	56.2 (4)	2
Bonded atoms[b]		
	C–C–B	
1–2–7	111.3 (3)	4
	B–C–B	
3–1–6	115.1 (3)	2
3–1–5	114.1 (3)	4
	C–B–B	
1–4–9	104.7 (4)	4
1–4–8	104.8 (6)	4
1–3–8	104.2 (5)	4
1–3–7	103.3 (4)	4
	B–B–B	
4–3–7	107.5 (4)	2
4–8–7	108.5 (4)	2
8–9–10	108.2 (5)	2
4–5–10	108.4 (7)	4
4–9–12	108.3 (7)	4
4–9–10	108.4 (4)	4
4–8–12	107.5 (8)	4
3–4–5	109.1 (5)	4
3–4–9	108.0 (5)	4
3–8–9	108.6 (4)	4

[a] If the rms error of the average bond angle was greater than the standard deviations of the values averaged, it is listed in parentheses for the least significant figure. [b] In the case of the polyhedral angles near 108°, the values are averaged in terms of equivalent angles based on an idealized C_{2v} symmetry for the $B_{10}C_2$ moiety. The atom numbers for a typical angle of an equivalent set are listed.

idealized C_{2v} symmetry for the $B_{10}C_2$ moiety.[10] The distances within the polyhedron compare favorably with other *o*-carborane distances previously reported.[11–15]

The B–H distances also compare favorably with those found[15] for 1-dicarba-*closo*-dodecaboran(12)-yl-1,2-dicarba-*closo*-dodecaborane(12), $(C_2B_{10}H_{11})_2$. A B–H distance of 1.2 Å has been assumed in the refinement of some[10,13,14] *o*-carborane structures.

The C–O bond distance calculated without correction for thermal motion was 1.188 ± 0.004 Å; however calculation of this distance assuming a "riding" mo-

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tion[16] of oxygen on carbon yielded the tabulated value of 1.217 (4) Å which appears to be a normal carbonyl length. Similar calculations for other skeletal bonds gave only insignificant corrections in length.

The bridging carbon atoms and the oxygen atoms lie ±0.013 (5) and ±0.032 (4) Å, respectively, from the plane defined by the four carbon atoms in the polyhedra [C(1), C(1′), C(2), and C(2′)]. Thus the six cabon atom ring is not strictly planar but has a very slight "chair" conformation.

The polyhderal bond angles are summarized in Table VI. Although the listed angles approximate those of 60.0 and 108.0° for a regular icosahedron, a distortion which might be described as a compression of the carbon atoms along the twofold axis of the *o*-carborane moiety is evident. The latter distortion is also apparent in the relative shortness of the polyhedral bond lengths involving carbon (Table V).

Disorder as is commonly found in the icosahedral positions of carboranes[13,15] is not possible in the present *doubly* connected bis *o*-carborane. More subtly, however, the carbonyl groups might be tilted above and below the C(1)–C(2)–C(1′)–C(2′) plane so as to give the six carbon atom ring a chair-like configuration. The latter disorder could average to give the observed planar carbon atom ring without destroying the crystallographically demanded molecular inversion center. However, all the atom positions were well defined, the thermal ellipsoid diagram (Figure 3) showed no irregularities, and the difference Fourier map showed no residual electron density in the carbonyl vicinity. Therefore, we exclude the possibility of disorder.

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Molecular and Crystal Structure of Dimethyl-1,6-dicarba-*closo*-decaborane(10)

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A three-dimensional single-crystal X-ray diffraction study at −20 to −35° shows the molecule of dimethyl-1,6-dicarba-*closo*-decaborane(10), $B_8H_8C_2(CH_3)_2$, to have essentially C_s symmetry. The B_8C_2 unit is a bicapped square antiprism only slightly distorted from full D_{4d} symmetry. The charges on the B atoms, determined by LCAO–MO methods, become more positive in the order B8 (attached to no C atoms) < B10, B7, B9, B3, B4 (attached to one C) < B2, B5 (attached to two C atoms). The compound crystallizes in the orthorhombic space group Pbca with eight molecules in a cell of dimensions $a = 11.36 \pm 0.01$, $b = 11.81 \pm 0.01$, and $c = 14.74 \pm 0.01$ Å. A density of 0.997 g/cm³ was calculated from these cell dimensions. The 1615 X-ray reflections observed on film were refined to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.084$.

Introduction

The 1,6 isomer of $B_8H_8C_2(CH_3)_2$ is produced,[1] along with $B_6H_6C_2(CH_3)_2$ and $B_7H_7C_2(CH_3)_2$, when $B_7C_2H_{11}(CH_3)_2$ is pyrolyzed near 200° in the presence of diphenyl ether. The ^{11}B nuclear magnetic resonance spectrum[1] of this molecule at 19.3 Mc shows two peaks: a doublet of area 1 at low field and a complex peak of area 7 at high field. The doublet at low field was assigned[1] to an apical BH position, like that previously assigned[2] for $B_{10}H_{10}^{2-}$, and all others were assigned to equatorial positions on a bicapped square-antiprism cage. Our X-ray study, as described below, proves that the C atoms are in the nonadjacent 1 and 6 positions, not in the adjacent 1 and 2 positions which would also be consistent with the ^{11}B nmr spectrum. Thus, the 1 and 6 assignment for C atoms, considered more plausible on chemical grounds, has been confirmed by our study. In addition a detailed molecular geometry which is suitable for theoretical study is established below.

Experimental Section

Liquid 1,6-$B_8H_8C_2(CH_3)_2$ (mp 1.0–1.6°) was sealed into Pyrex capillaries having uniform wall thickness and inside diameter about 0.7 mm. The sample size was regulated to yield crystals, grown in a cold stream of N_2,[3] which were roughly equal in all dimensions. X-Ray data were collected between −20 and −35°. Crystals were stable for periods of up to 4 months when maintained in this temperature range, and all necessary data were collected from two crystals. Reciprocal lattice symmetry D_{2h} and systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd indicated that the space group is Pbca. Unit cell parameters of $a = 11.36 \pm 0.01$, $b = 11.81 \pm 0.01$, and $c = 14.74 \pm 0.01$ Å were obtained from Weissenberg photographs calibrated by the superposition of a powder diffraction pattern of Al, using 4.04916 Å for the Al cell constant and λ 1.54178 Å for Cu Kα. The cell dimensions were refined by a previously described least-squares procedure[4] using as data 2θ values for 50 reflections. Assuming eight molecules in the unit cell, a reason-

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