

The MM3 force field for 12-vertex boranes and carboranes¹

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Received 5 August 1996; accepted 3 October 1996

Abstract

A model and parameters were developed which allow conformational calculations to be carried out on the 12-vertex boranes, carboranes and their derivatives, within the framework of the MM3 force field. In order to avoid description of all the bond angles, the molecule was represented as a superposition of two rings and two cap groups. The valence bonds between these moieties were described by a Buckingham potential. The statistical analysis of carborane molecules found in the Cambridge Structural Database has been carried out in order to find the mean values of the bond lengths and angles for these molecules. A parameter set was developed and used for the calculations on substituted carboranes, and the results show good agreement with the experimental data. © 1997 Elsevier Science S.A.

Keywords: Molecular mechanics; Boron; 12-Vertex boranes; 12-Vertex carboranes; Ab initio

1. Introduction

Molecular mechanics has become a powerful tool for modeling the structure of polymers, biopolymers, and materials, as well as for many of their properties. So, it is quite useful and interesting to apply this method to molecules that have not been described until recently within the framework of molecular mechanics, such as metal complexes, metal clusters, carboranes and other compounds with variable atomic coordination. The use of the standard molecular mechanics procedures is not straightforward for these compounds. The usual connectivity methods are unsatisfactory, as far too many valence bonds and bond angles would need to be described around atoms with high coordination numbers.

Several ways to solve this problem have been described in the literature. First, one can delete the bond angle bending terms, and keep only bond lengths. The bond angles around highly coordinated atoms will then be the 'natural' result of the interligand non-bonded

interactions [1,2]. A second way to circumvent this problem is to reduce the number of valence bonds, for example using a dummy atom for symmetrical ligands such as cyclopentadienyl (Cp) and phenyl (Ph) [3–6]. The third way is to describe valence bonds within the molecular mechanics framework as interactions of a (non-directional) van der Waals [7,8] or Coulomb type [9,10]. This allows one to avoid program changes, and to avoid using connectivity files to reproduce the molecular graph for atoms with non-standard coordination types. We earlier used the latter option for a description of Cp-sandwich molecules, and for seven-vertex carboranes and metallocarboranes. The details of these models can be found in reviews [11,12].

To our knowledge there are only a few reported attempts to describe carborane molecules within the framework of molecular mechanics [13–15]. Two of the approximations mentioned above have been used for the modeling of carborane molecules: usage of bond length terms without the bond angle description [13], and usage of Buckingham or Hill-like potential for a description of valence bonds [14,15].

In this work we describe a model and parameter set that allow conformational calculations of 12-vertex boranes and carboranes to be carried out with the MM3(94) program [16] in a way analogous to that used earlier for seven-vertex carboranes [14,15]. Four main types of

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¹ To the memory of our teacher and colleague Professor Yuri T. Struchkov. Three of us (TVT, AIY, and KYUS) worked with Professor Struchkov for many years, and it was certainly his devotion and example that stimulated our interest in structural organometallic chemistry.

12-vertex boron cage compound were investigated: $B_{12}H_{12}^{2-}$ (I), 1,2- $C_2B_{10}H_{12}$ (*ortho*-) (II), 1,7- $C_2B_{10}H_{12}$ (*meta*-) (III), 1,12- $C_2B_{10}H_{12}$ (*para*-) (IV) dicarbocloso-dodecaboranes. To test the resulting model and parameter set, the conformational calculations on several substituted *closo*-carboranes were then carried out. The results of conformational calculations of metallo-carboranes, where a ligand substituted metal atom takes the place of one of the vertices, will be described in a subsequent publication.

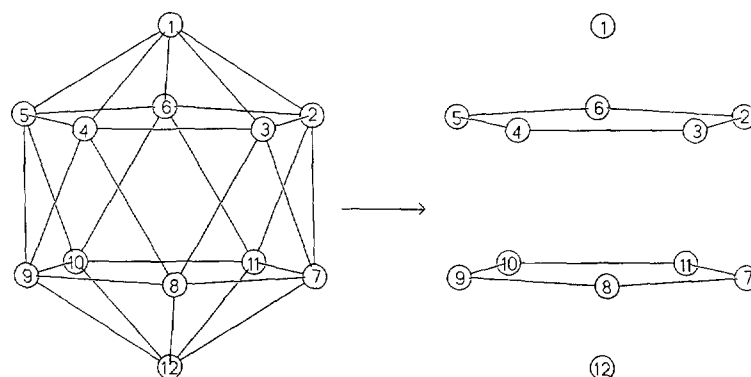
1.1. Model and method of calculation

The cages of molecules I–IV can be described as ideal or distorted icosahedrons. The coordination number of every heavy atom is equal to 6, and consists of five neighbors in the cage plus one substituent. To use a molecular graph for description of these cages, the simplest case (molecule I) would require four angle types around every boron atom, and in order to do that we would have to identify equivalent boron atoms with different atom-type identifiers. Since it is difficult to use connectivity files in the MM3 program for atoms that have more than four neighbors, we used a special model that allows us to avoid these problems, and to use the MM3(94) program without any alterations. We are also hopeful that such a molecular description will correspond to physical reality. That is, the geometry in such a system is assumed to be dependent on the van der Waals interactions present, and to be insensitive to the bond and dihedral angles. There is previous evidence that this is a good approximation [14,15].

Borane and carborane 12-vertex cages were represented as a superposition of four formally independent parts: two rings and two cap groups (Scheme 1).

Earlier, a similar model (one central ring and two caps) was used for a description of seven-vertex carborane cages [14,15]. Some hints as to the potential usefulness of such molecular partitioning are available from quantum chemical descriptions of cap–ring interactions in molecules of this type [17–19].

Interactions within a cap or ring group are presented



Scheme 1.

Table 1
Carbon atom positions according to Scheme 1 corresponding to carborane cage description

	1st way	2nd way	3rd way
<i>ortho</i> -carborane	2 and 3	2 and 7	1 and 2
<i>meta</i> -carborane	1 and 7	2 and 8	3 and 5
<i>para</i> -carborane	1 and 12	5 and 7	—

as those within ordinary organic molecules, for instance as in the heterocycles, by bond stretch, angle bend, torsion, and other energy terms [16]. Ring–ring and ring–cap interactions (valence bonds) are described by Hill-like potentials, as normally used for a description of non-bonded intra- and intermolecular interactions. For such bonds, energies are represented by the equation

$$E_b = \varepsilon_b / D (1.84 \times 10^5 \exp(-12.0R/R_b) - 2.25R^6/R_b^6),$$

where ε_b is close to the bond dissociation energy, R_b is an ideal valence bond distance, and D is the dielectric constant. The possibility of using such potentials for bond energy description has been known for a long time, but they have not often been used. Recently, several non-standard descriptions of bond stretching have been discussed and applied to conformational problems [20].

The applicability of this model is confirmed by the correct reproduction of the bond lengths, bond angles and conformational peculiarities of the molecules under consideration. It should be mentioned that *meta*- and *ortho*-carborane molecules can be described within the framework of this model in three similar, but non-equivalent, ways, and that *para*-carborane can be described in two ways. The ways of describing molecules II–IV are shown in Table 1.

1.2. Force field parameters for boranes and carboranes

To carry out conformational calculations on boranes and carboranes we used the standard parameter set from

Table 2
Stretching parameters inside ring and cap groups: L_0 (Å), K_s (mdyn Å⁻¹)

Bond	<i>ortho</i> -Carborane (1st way)		<i>ortho</i> -Carborane (2nd way)		<i>meta</i> -Carborane		<i>para</i> -Carborane		Borane	
	L_0	K_s	L_0	K_s	L_0	K_s	L_0	K_s	L_0	K_s
B–C	1.704	3.0	1.715	3.0	1.704	3.0	—	—	—	—
B–B	1.765	3.0	1.768	3.0	1.764	3.0	1.763	3.0	1.787	3.0
C–C	1.681	3.0	—	—	—	—	—	—	—	—
C–H	1.100	5.35	1.100	5.35	1.100	5.35	—	—	—	—
B–H	1.185	3.85	1.185	3.85	1.185	3.85	1.185	3.85	1.185	3.85
B–H ^a	1.185	4.0	1.185	4.0	1.185	4.0	—	—	1.185	4.0
C–H ^a	—	—	—	—	—	—	1.100	4.0	—	—

^a Bonds inside cap groups.

Table 3
Parameters of ring–ring, ring–cap and cap–cap interactions (valence bonds): R_b (Å), ϵ (kcal mol⁻¹)

Bond	<i>ortho</i> -Carborane (1st way)		<i>ortho</i> -Carborane (2nd way)		<i>meta</i> -Carborane		<i>para</i> -Carborane		Borane	
	R_b	ϵ	R_b	ϵ	R_b	ϵ	R_b	ϵ	R_b	ϵ
B–B ^a	1.785	20.0	1.786	20.0	1.786	20.0	1.766	20.0	1.782	20.0
B–C ^a	1.719	20.0	1.725	20.0	1.720	20.0	—	—	—	—
C–C ^a	—	—	1.669	20.0	—	—	—	—	—	—
B–B ^b	1.780	35.0	1.782	35.0	1.782	35.0	—	—	1.783	35.0
B–C ^b	1.730	35.0	1.719	35.0	1.715	35.0	—	—	—	—
C–B	—	—	—	—	—	—	1.717	35.0	—	—
B...B ^c	2.350	0.01	2.350	0.01	2.350	0.01	—	—	2.350	0.01
C...C ^c	—	—	—	—	—	—	2.350	0.01	—	—

^a Ring–ring interactions.

^b Ring–cap interactions.

^c Cap–cap interactions.

the MM3(94) program [16] (available to all users from Tripos Associates, 1699 S. Hanley Road, St. Louis, MO 63144 and to academic users only from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405), augmented with additional parameters for these molecules. We determined standard bond lengths and angles by analyzing the results of the X-ray investigations of these molecules, as reported in the Cambridge Structural Database [21]. We took into consideration the symmetries of the unsubstituted carborane cages in the process of statistical analysis.

The differences between bond angles of the same

type were found to be not larger than 2–4°. The situation with the bond lengths was not the same. A wide range of bond lengths was found, and we were not able to describe this effect by the systematic influence of the substituents. It is very likely that the large dispersion results from both the non-precise experimental bond length determinations due to the significant thermal motion of the carborane nuclei, and/or flexibility of bonds in carborane cages.

We did not find identifiable regularities for bond lengths of the same type, with only one exception.

Table 4
Bending parameters inside rings

Angle	θ_0 (°)	K_θ (mdyn Å rad ⁻¹)
B–B–B	104.0	0.3
B–B–C	103.0	0.3
B–C–B	115.0	0.4
B–C–C	115.0	0.4
C–B–C	100.0	0.3
B–B–H	130.0	0.3
B–C–H	122.0	0.3
C–B–H	130.0	0.3
C–C–H	122.0	0.3

Table 5
Torsion parameters inside rings (kcal mol⁻¹)

Angle	V_1	V_2	V_3
B–B–C–C	0.0	3.0	0.0
B–B–B–C	0.0	3.0	0.0
B–C–C–B	0.0	7.0	0.0
B–B–B–B	0.0	3.0	0.0
B–B–C–B	0.0	3.0	0.0
B–C–B–C	0.0	3.0	0.0
C–B–B–C	0.0	3.0	0.0
H–B–B–H	0.0	3.0	0.0
H–C–C–H	0.0	11.5	0.0
H–B–C–H	0.0	7.0	0.0

Histograms of C–B bonds in *ortho*-carboranes found in the Cambridge Structural Database, in which there are two types of such bond, allow us to conclude that the bonds of one type (1–3, 1–6, 2–3, 2–6) are ca. 0.02 Å shorter than the bonds of the other type (1–4, 1–5, 2–7, 2–11) (see Scheme 1; for those compounds in which the C atoms are considered to be in the 1 and 2 positions).

We chose the values of the ideal bond lengths and bond angles so as to reproduce as well as possible the mean values of geometries according to the Cambridge Structural Database. Force constants were taken as for seven-vertex carboranes, investigated earlier [14,15].

The parameter set developed in the present work is given in Tables 2–5. The torsion parameters of all exocyclic angles X–X–X–Y and X–X–Y–Y (X = B or C belonging to the carborane cage, Y = H or another atom of the substituent attached to a cage) are equal to zero, and not shown in Tables 2–5.

2. Results and discussion

The model described above was used for conformational calculations of unsubstituted molecules I–IV, as well as for several substituted *ortho*-, *meta*-, and *para*-carboranes, for which molecular structures in crystals were previously reported.

To characterize the unsubstituted *ortho*-carborane molecule we used the first description in Table 1. For *meta*-carborane the third way was used, in order to put both carbon atoms inside one ‘heterocyclic’ ring. The first way was used for *para*-carborane, and in this case carbon atoms are situated in the cap positions.

The calculated values of the bond lengths of molecules I–IV have been compared with the mean values of these parameters from the results of X-ray analysis [21], with gas electron diffraction data [22], and with the results of ab initio calculations at the STO-3G

Table 6

Mean X-ray (CSD, L_x) [21], MM3 calculated (L_{calc}), gas electron diffraction (L_{ged}) [22] and ab initio calculated (L_{quant}) [23] values of the bond lengths in *ortho*-carborane II (Å)

Bond type ^a	Standard numbering [24]	Numbering according to model	L_x	L_{calc}	$\Delta = L_x - L_{calc}$	L_{ged}	L_{quant}
B _(c) –C _(r)	2–6	1–2	1.722	1.722	0.000	1.707	1.728
	1–6	1–3	1.722	1.722	0.000	1.707	1.729
B _(c) –B _(r)	6–11	1–6	1.773	1.775	0.002	1.800	1.781
	6–5	1–4	1.773	1.775	0.002	1.800	1.782
	6–10	1–5	1.765	1.765	0.000	1.787	1.755
	8–9	12–9	1.781	1.770	0.011	1.787	1.791
	8–12	12–10	1.781	1.770	0.011	1.787	1.790
	4–8	12–8	1.773	1.769	0.004	1.787	1.777
	7–8	12–11	1.773	1.769	0.004	1.787	1.777
	3–8	12–7	1.765	1.770	0.005	1.787	1.755
C _(r) –C _(r)	1–2	2–3	1.676	1.678	0.000	1.651	1.634
B _(r) –C _(r)	2–3	2–7	1.722	1.716	0.006	1.707	1.728
	1–3	3–7	1.722	1.716	0.006	1.707	1.729
	1–4	3–8	1.707	1.712	0.005	1.707	1.700
	2–7	2–11	1.707	1.712	0.005	1.707	1.701
	2–11	2–6	1.707	1.707	0.000	1.707	1.701
	1–5	3–4	1.707	1.707	0.000	1.707	1.700
B _(r) –C _(r)	4–5	4–8	1.774	1.774	0.000	1.800	1.789
	7–11	6–11	1.774	1.774	0.000	1.800	1.785
	5–9	4–9	1.772	1.774	0.002	1.787	1.772
	11–12	6–10	1.772	1.774	0.002	1.787	1.772
	9–10	5–9	1.781	1.771	0.010	1.787	1.791
	10–12	5–10	1.781	1.771	0.010	1.787	1.790
	5–10	4–5	1.773	1.782	0.009	1.787	1.777
	10–11	6–5	1.773	1.782	0.009	1.787	1.782
	3–4	7–8	1.773	1.772	0.001	1.800	1.782
	3–7	7–11	1.773	1.772	0.001	1.800	1.781
	4–9	8–9	1.772	1.769	0.003	1.787	1.772
	7–12	11–10	1.772	1.769	0.003	1.787	1.772
9–12	9–10	1.771	1.770	0.001	1.787	1.779	

^a Ring atoms marked (r), cap atoms (c).

The bond lengths in this table are given as determined, and they are different (r_α , r_g , r_c) depending on the type of calculation or measurement. In order to quantitatively compare them, they would have to be converted to a common basis. The details of how this may be done are given in Ref. [25].

level [23]. The mean deviations of calculated bond lengths from the mean crystallographic values are equal to zero for highly symmetrical borane and *para*-carborane. For molecules with lower symmetry we have some deviations, 0.004 Å for *ortho*- and 0.005 Å for *meta*-carborane. We show the calculated results for *ortho*-carborane **II** in comparison with the above mentioned methods in Table 6. We should note that the other (second) way of description gives quite good agreement between computed and X-ray results (mean deviation 0.004 Å). Thus it is reasonable to use either the first or the second way for description of the substituted *ortho*-carboranes, depending on the substituent positions. So, we can see that the deviations between calculated and mean X-ray values are much less than the bond length distribution for carboranes in crystals, according to the data from the CSD, which can be more than 0.1–0.2 Å, and the mean deviations are of the same magnitude as standard deviations of the bond lengths from the results of X-ray analysis of carborane molecules. The endocyclic bond angle deviations have been found to be small within heterocyclic rings, and between rings as well.

In order to compare calculated and experimental results for the exocyclic torsion angles, we chose experimental data from the CSD on carboranes without steric interference between substituents, i.e. with one or two substituents on the carborane nuclei. The following mean values of torsion angles were found for these molecules: X–X–B–H 149°, X–X–C–H 147°, and the individual experimental values of these angles were found to vary from 136 to 160°. The calculated values of the torsion angles are within this range. Calculated torsion angles for angles including cap and ring atoms (molecules **I–IV**) are in the range 141–152°, and for those describing only ring angles, 151–158°. Our calculations also show that torsion angles of X–X–C–H type are 1–3° smaller than angles of X–X–B–H type, in agreement with experimental data from the CSD [21].

The isolated molecule 2,3,4,5,6,7,8,9,10,11-decaiodo-1,12-dicarbo-*closo*-dodecaborane (**V**) has D_{5d} symmetry, but in the crystal, which consists of two systems of symmetry independent molecules **A** and **B** [26], both of these molecules have C_i symmetry. So, in

Table 7

Comparison of some calculated and X-ray ^a [26] geometry parameters for molecule **V**, distances (Å), angles (°)

Geometry parameter	X-ray		MM3	Molecule IV ^b
	Molecule A	Molecule B		
C–B	1.69	1.70	1.71	—
	1.66–1.74	1.65–1.73		
B2–B7 ^c	1.77	1.79	1.76	—
	1.72–1.80	1.74–1.86		
B2–B3 ^d	1.78	1.79	1.79	—
	1.73–1.81	1.74–1.85		
C–B–I	124.2	124.3	124.9	131.9
	122.5–126.0	122.8–126.2		
B–B–B–I ^e	144.9	145.3	146.2	156.0
	143.5–148.4	143.7–147.4		
I...I ^f	3.96	3.96	4.05	—
	3.92–4.01	3.92–3.97		
I...I ^g	4.16	4.15	4.15	—
	4.12–4.18	4.10–4.20		

^a For X-ray data mean values and distribution are shown.

^b C–B–H and B–B–B–H angles are shown.

^c Ring–ring bond.

^d Bond inside ring.

^e Exocyclic angle in boron ring.

^f Non-bonded distance between iodines connected with boron atoms located inside one ring.

^g Non-bonded distance between iodines connected with boron atoms located in different rings.

the isolated *p*-carborane molecule there are three bond types in the carborane cage, and 15 bond types (according to symmetry) in the crystal. The first description (Table 1) was used for this molecule, therefore the molecule consists of two iodine substituted five-membered boron rings (belts), and two unsubstituted carbon caps. The calculated bond lengths show the same trend as the mean experimental bond length values in molecules **A** and **B** (Table 7). The experimental bond length distribution (inside a wide range of ca. 0.08 Å) shows that it is difficult to compare experimental X-ray and calculated bond lengths in detail. It should be mentioned that for every such comparison of X-ray and calculated data we will face the same problem. For calculated geometric parameters we will deal with mean statistical values of the parameters, and for experimental data in crystals we will deal with data influenced by

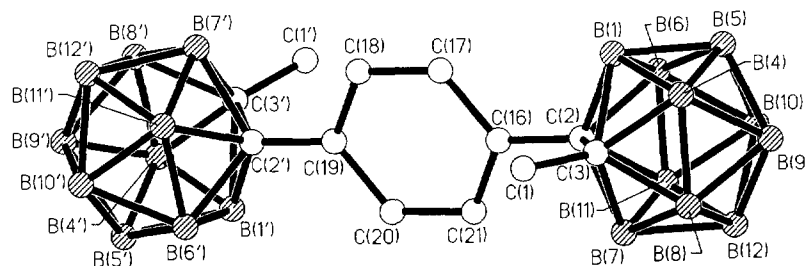


Fig. 1. Molecule of 1,4-bis-(2-methyl-1,2-dicarbadodecaboran-1-yl)benzene (**VII**); in order to simplify this and other figures, hydrogen atoms are not shown.

Table 8

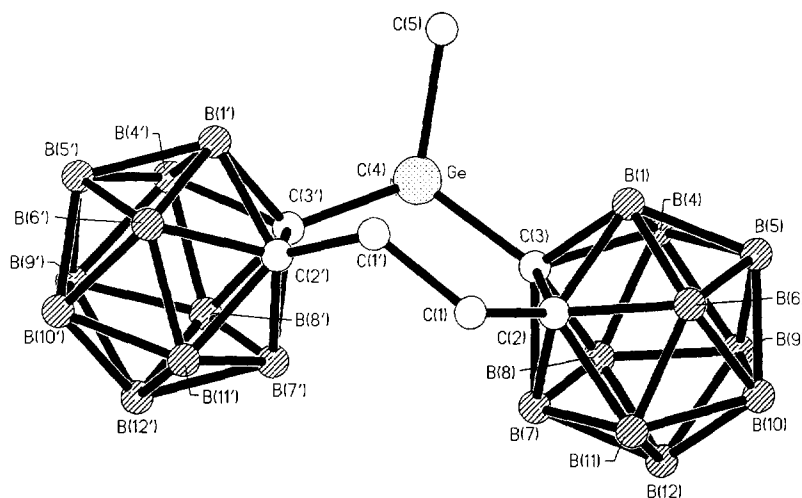
Comparison of calculated (L_{calc}) and experimental (L_x) bond lengths for molecules VI [27] and VII [28] (Å)

Bond type ^a	Standard numbering [24]	Numbering according to model	Molecule VI			Molecule VII ^b		
			L_x	L_{calc}	$\Delta = L_x - L_{\text{calc}}$	L_x	L_{calc}	$\Delta = L_x - L_{\text{calc}}$
$B_{(c)}-C_{(r)}$	2-6	1-2	1.740	1.727	0.013	1.726	1.725	0.001
	1-6	1-3	1.697	1.717	0.020	1.709	1.720	0.011
$B_{(c)}-B_{(r)}$	6-11	1-6	1.777	1.769	0.008	1.785	1.772	0.013
	6-5	1-4	1.782	1.774	0.008	1.755	1.770	0.015
	6-10	1-5	1.771	1.764	0.007	1.756	1.763	0.007
	8-9	12-9	1.773	1.770	0.003	1.774	1.769	0.005
	8-12	12-10	1.779	1.769	0.010	1.771	1.770	0.001
	4-8	12-8	1.771	1.769	0.002	1.772	1.769	0.003
	7-8	12-11	1.791	1.170	0.021	1.758	1.769	0.011
	3-8	12-7	1.773	1.770	0.003	1.761	1.770	0.009
$C_{(r)}-C_{(r)}$	1-2	2-3	1.670	1.696	0.026	1.685	1.694	0.009
$B_{(r)}-C_{(r)}$	2-3	2-7	1.735	1.729	0.006	1.721	1.727	0.006
	1-3	3-7	1.708	1.705	0.003	1.717	1.707	0.010
$B_{(r)}-B_{(r)}$	1-4	3-8	1.695	1.715	0.020	1.694	1.718	0.024
	2-7	2-11	1.721	1.724	0.003	1.704	1.724	0.020
	2-11	2-6	1.717	1.730	0.013	1.711	1.719	0.008
	1-5	3-4	1.693	1.709	0.016	1.701	1.719	0.018
	4-5	4-8	1.777	1.770	0.007	1.769	1.766	0.003
	7-11	6-11	1.775	1.763	0.012	1.769	1.766	0.003
	5-9	4-9	1.776	1.774	0.002	1.774	1.774	0.000
	11-12	6-10	1.776	1.775	0.001	1.770	1.776	0.006
	9-10	5-9	1.791	1.771	0.020	1.777	1.770	0.007
	10-12	5-10	1.782	1.768	0.014	1.784	1.767	0.017
	5-10	4-5	1.770	1.778	0.008	1.758	1.783	0.025
	10-11	5-6	1.783	1.783	0.000	1.776	1.784	0.012
	3-4	7-8	1.788	1.771	0.016	1.772	1.767	0.005
	3-7	7-11	1.766	1.764	0.002	1.758	1.767	0.009
	4-9	8-9	1.772	1.769	0.003	1.776	1.770	0.006
	7-12	10-11	1.769	1.768	0.001	1.769	1.768	0.001
9-12	9-10	1.780	1.170	0.010	1.758	1.771	0.013	

^a Ring atoms marked (r), cap atoms (c).^b Mean bond lengths for two carborane cages are shown.

thermal motions and packing conditions, i.e. symmetry, intermolecular interactions, and so on. Calculated and mean experimental bond angles for this molecule are also in reasonable agreement (Table 7).

According to experiment [26], in molecule V the iodines in the two iodo substituted five-membered rings are slightly moved apart relative to the unsubstituted apical positions. So the mean non-bonded I...I dis-

Fig. 2. Molecule of 1,1-(dimethyl)germano-2,3,6,7-[bis(*o*-carborane)]cycloheptane (VIII).

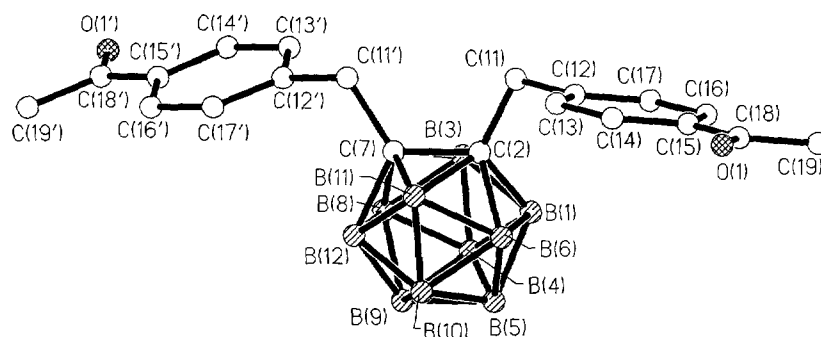


Fig. 3. Molecule of 1,2-bis-(4-acetylbenzyl)-1,2-dicarba-closo-dodecaborane (**IX**).

tances inside the five-membered belts are shorter than those between belts. Our calculation reproduces this peculiarity of molecule **V** (Table 7). The same effect can be seen if we compare bond and torsion angles for unsubstituted (**IV**) and substituted (**V**) *p*-carboranes (Table 7).

Some results of our computations and X-ray data for mono- and disubstituted *ortho*-carborane molecules, 1-(*tert*-butyl)-1,2-dicarba-closo-dodecaborane (**VI**) [27] and 1,4-bis-(2-methyl-1,2-dicarbadoecaboran-1-yl)benzene (**VII**) [28] are compared in Table 8. For these molecules, the first *ortho*-carborane cage description was used. Experimental and calculated bond angles for these molecules are in good agreement. Mean experimental and calculated bond angles respectively are as follow: B–B–C 104.6, 105.8 (**VI**); 105.6, 106.0 (**VII**); B–C–C 110.7, 110.1 (**VI**); 110.2, 110.1 (**VII**); B–C–B 115.8, 112.9 (**VI**); 113.2, 111.9 (**VII**); B–B–B 108.0, 107.9 (**VI**); 108.0, 108.0° (**VII**). The results are not so good for the bond lengths (Table 8), as far as the ideal parameters of the bond lengths were taken as a mean value from the results of X-ray analysis. However, the level of the results (mean experimental/calculated bond length difference 0.009 Å in **VI** and **VII**) is perhaps

adequate for conformational analysis of organic molecules with carborane residues.

There are two carborane nuclei with a benzene bridge in molecule **VII** (Fig. 1). According to our calculations, the conformations with pseudo-*trans* (as in crystal) and pseudo-*cis* orientations of methyl substituents around the pseudo-bond between two carborane nuclei are energetically equivalent. The calculated value of the barrier to *cis*–*trans* rotation is calculated to be 3.9 kcal mol⁻¹.

The main aim of the calculations on the cyclic molecule with two *ortho*-carborane nuclei (1,1-(dimethyl)germano-2,3,6,7-[bis(*o*-carborane)]cycloheptane (**VIII**) [29] was to compare the experimental and computational data on the conformation. For molecule **VIII**, the first *ortho*-carborane description was used. In Table 9, the main conformational parameters (torsion and bond angles) of molecule **VIII** from the results of X-ray analysis and molecular mechanics calculations are listed. The atoms are numbered as in Fig. 2. For molecule **VIII** [29], the authors pointed out that the bond angles are slightly distorted in the seven-membered ring between two carborane cages, and that this ring is not symmetrical. The same trend was found from molecular mechanics calculations. However, the values of these param-

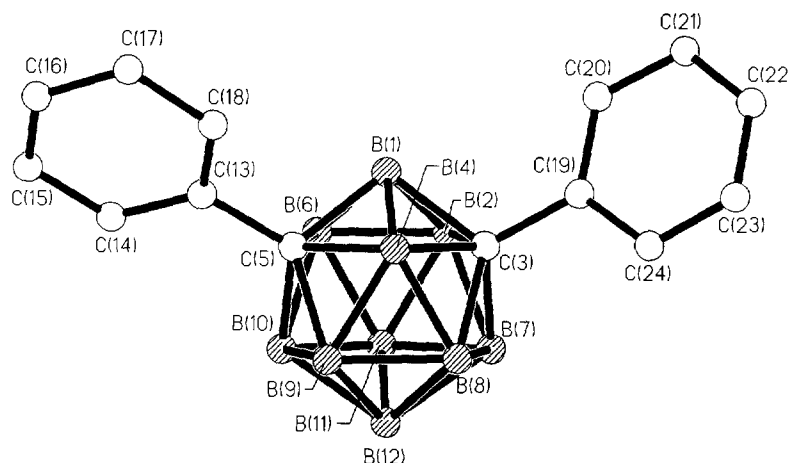


Fig. 4. Molecule of *meta*-carborane 1,7-diphenyl-*m*-carborane (**X**).

Table 9
Comparison of calculated (θ_{calc}) and experimental (θ_x) angles for molecules VIII [29], IX [30], and X [31] ($^\circ$)

Molecule	Angle	θ_x	θ_{calc}
VIII	C(3')–C(2')–C(1')–C(1)	22.6	29.8
	C(3)–C(2)–C(1)–C(1)	74.5	75.7
	C(2')–C(1')–C(1)–C(2)	–74.1	–84.9
	C(2')–C(3')–Ge–C(3)	42.8	25.1
	C(2)–C(3)–Ge–C(3')	–49.4	–43.1
	C(1')–C(2')–C(3')–Ge	–13.4	–2.2
	C(1)–C(2)–C(3)–Ge	–3.3	0.8
IX	C(7)–C(2)–C(11)–C(12)	151.8	151.8
	C(2)–C(11)–C(12)–C(13)	92.8	92.4
	C(11)–C(2)–C(7)–C(11')	–0.9	–1.0
	C(7)–C(2)–C(11)	119.9	120.7
	C(2)–C(11)–C(12)	112.4	112.4
X	B(4)–C(3)–C(19)–C(24)	82.4	81.1
	B(4)–C(5)–C(13)–C(18)	21.1	20.3

ters are different, and this difference may be due to the influence of the crystal field on the molecular geometry.

For disubstituted *ortho*-1,2-bis-(4-acetylbenzyl)-1,2-dicarba-*closo*-dodecaborane (IX) [30] and *meta*-carborane 1,7-diphenyl-*m*-carborane (X) [31] (Figs. 3 and 4), the relative orientations of the substituents are characterized in Table 9. For molecules IX and X the second and third types of description were used (Table 1). It can be seen that orientations of the substituents in the crystal are close to those calculated for the isolated molecules. It should be mentioned that the reorientations of the substituents in molecule X are not sterically hindered.

The results of the calculations show that the model developed can be used for a description of the conformations of molecules containing the 12-vertex carborane moiety. In our previous work [14,15] the Hill-like potential was used only for a description of valence bonds between ring and cap fragments (seven-vertex molecule with one ring and two cap fragments), in this work it has been shown that it is possible to apply the same description for ring–ring valence interactions in 12-vertex carboranes. It should be mentioned that the other models can be applied to molecules of this type, as reported earlier [13].

Acknowledgements

We are grateful to the International Science Foundation (Grant MP5300) and the National Science Foundation (Grant CHE 9222655) for support of this work.

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