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Molecular Structure of 1-Thia-*closo*-dodecaborane(11) Studied by Electron Diffraction Complemented by ab Initio Calculations

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The molecular structure of 1-thia-*closo*-dodecaborane(11), 1-$SB_{11}H_{11}$, has been determined by gas-phase electron diffraction. A model assuming C_{5v} symmetry lead to a determination of the distortions from a regular icosahedron consisting mainly in the substantial expansion of the pentagonal belt adjacent to sulfur, with $r_g(B–B) = 1.905 \pm 0.004$ Å. Well-determined parameters are the S–B and $(B–H)_{mean}$ distances, $r_g = 2.010 \pm 0.005$ and 1.190 ± 0.003 Å, respectively. The geometric parameters calculated at the ab initio 3-21G(*) level, as well as the IGLO calculations (individual gauge for localized orbitals) ^{11}B chemical shifts, are in overall agreement with the experimental findings.

Introduction

Very little is known about the structures of thiaboranes. For example, the structure of the dimeric form of 1-thia-*closo*-decaborane(9), 2,2′-(1-SB_9H_8)$_2$, has been determined by X-ray diffraction.[1] A short B–B bond links the two bicapped square antiprismatic frameworks of the SB_9H_8 moieties. 1-SB_9H_9 is isoelectronic with $B_{10}H_{10}^{2-}$. In accord with Wade's rules,[2] S formally replaces a $[BH]^{2-}$ unit,[3] but causes a substantial lengthening of the nearest B–B bonds. In another investigation,[4] the photoelectron spectra of the 1-SB_9H_9 monomer and some other thiaboranes, including 1-$SB_{11}H_{11}$, have been reported and analyzed in terms of a simple approach known as the equatorial-apex model. The PES data of 1-SB_9H_9 have been assigned by means of MNDO calculations, which also revealed the cluster-bonding molecular orbitals (constructed from a B_9H_9 unit and a sulfur atom).[5] The MNDO-optimized structure also was reported, but the electronic structure of 1-$SB_{11}H_{11}$ was analyzed using an assumed molecular geometry. In order to obtain the structure of 1-$SB_{11}H_{11}$, we now report the results of an electron diffraction study (GED) complemented by ab initio calculations on the geometry and ^{11}B NMR chemical shifts.

Experimental Section

The sample of 1-thia-*closo*-dodecaborane(11) (purity >98% as assessed by TLC) was prepared by Dr. J. Plešek according to literature procedures.[6]

The electron diffraction patterns were recorded in Budapest with a modified EG-100A unit,[7] using a membrane nozzle system.[8] The nozzle temperature was about 110 °C. The accelerating voltage of the electron beam was 60 kV. Eight photographic plates were used for both camera distances (50, 19 cm), respectively. The ranges of intensity data used in the analysis were $2.0 \le s \le 13.875$ Å^{-1} and $9.50 \le s \le 33.0$ Å^{-1} with data intervals 0.125 and 0.25 Å^{-1} [$s = (4\pi/\lambda) \sin(\theta/2)$, where λ, the electron wave length, is 0.049132 Å for both camera distances and θ is the scattering angle]. The method of data treatment is described elsewhere.[9] The structure analysis was based on least-squares refinement of molecular intensities.[10] Literature coherent[11] and incoherent[12] scattering factors were employed. The final experimental and calculated molecular intensities and radial distributions are shown in Figures 1 and 2, respectively.

Structure Analysis

The 1-thia-*closo*-dodecaborane(11) molecule was assumed to have C_{5v} symmetry. The following independent parameters were used for the description of the geometry (see Figure 2): the B_3–B_7, B_7–B_8, B_7–B_{12} and $(B–H)_{mean}$ distances and the differences between S–B and B_3–B_7 (Dif_1) and B_2–B_3 and B_3–B_7 (Dif_2), as well as the S–B–H and B_{12}–B_7–H bond angles. In some refinements only the bond lengths within the cage as independent parameters (without Dif_1 and Dif_2) were used. Since no vibrational spectroscopic data were available, the vibrational parameters for 1,12-$C_2B_{10}H_{12}$[13] provided the initial values for the refinements. The vibrational amplitudes of similar distances were coupled by fixing the differences between them. Shrinkage effects were neglected.

Refinements using different starting values of S–B and B–B bonds, or using various Dif_1 and Dif_2 values converged to the same minimum without affecting the geometric parameters. Nevertheless, various refinement conditions for vibrational amplitudes may produce a strong influence on the results. Since theoretical calculations for getting better starting values of vibrational amplitudes could not be performed due to the lack of force field, a lot of refinements with various starting *l* values

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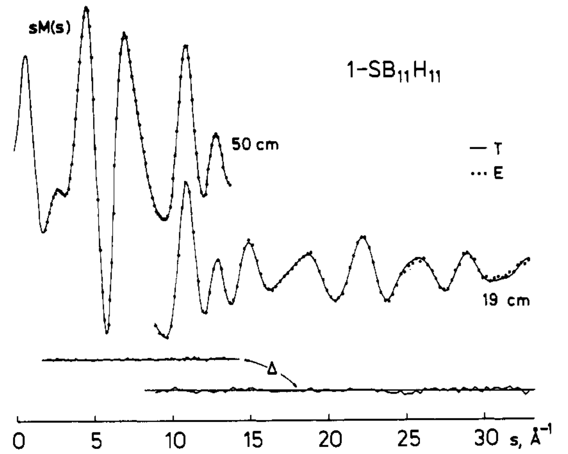

Figure 1. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical for the model obtained from refinement A). The difference curves (experimental–theoretical) are also shown.

Table I. Final Molecular Parameters[a] for 1-Thia-*closo*-dodecaborane(11) As Obtained from Refinement A

(a) Distances $r_a{}^b$ and $r_g{}^c$ and Mean Amplitudes of Vibration (Å)[b]

atomic pair	multiplicity	r_g	r_a	l^i
S–B	5	2.010 (5)	$2.007\ (1)^d$	$0.0706\ (4)^{\mathrm{i}}$
B_2–B_3	5	1.905 (4)	$1.904\ (1)^d$	0.0506^{i}
B_3–B_7	10	1.783 (8)	1.781 (2)	
B_7–B_8	5	1.780 (11)	1.778 (2)	0.0606^{i}
B_7–B_{12}	5	1.777 (6)	1.775 (2)	
B_2–H_{13} (av)	5	1.190 (3)	1.187 (1)	$0.062\ (1)^{\mathrm{ii}}$
B_7–H_{18} (av)	5			
B_{12}–H_{23} (av)	1			
S···B_7	5		$3.075\ (1)^d$	$0.072\ (1)^{\mathrm{iii}}$
S···B_{12}	1		$3.606\ (4)^d$	$0.058\ (3)^{\mathrm{iv}}$
B_2···B_9	5		$3.469\ (1)^d$	0.068^{iv}
B_2···B_8	10		$2.941\ (1)^d$	0.069^{iii}
B_2···B_4	5		$3.081\ (1)^d$	
B_7···B_9	5		$2.877\ (3)^d$	
B_2···B_{12}	5		$2.912\ (3)^d$	
S···H_{13}	5		$2.801\ (7)^d$	0.130^{iii}
S···H_{18}	5		$4.082\ (7)^d$	$0.111\ (3)^{\mathrm{v}}$
S···H_{23}	1		$4.793\ (4)^d$	$0.138\ (12)^{\mathrm{vi}}$
$(B\cdots H)^e$	4 × 10 + 2 × 5		2.538–2.734^d	0.100^{iii}
$(B\cdots H)^f$	4 × 10 + 2 × 5		3.954–4.157^d	$(0.083$–$0.111)^{\mathrm{v}}$
$(B\cdots H)^g$	2 × 5		4.656^d	0.118^{vi}

(b) Bond Angles (deg) and Differences between Bond Distances (Å)

parameter	value	
$\angle_a$S–B–H	120.3 (40)	120.3 (5)
$\angle_a B_{12}$–B_7–H	125.3 (25)	125.3 (7)
$\mathrm{Dif}_1{}^h$		0.227 (2)
$\mathrm{Dif}_2{}^j$		0.124 (1)

[a] The H···H distances were included in the refinement but they are not listed here. Their amplitudes were within the range 0.086–0.20 Å. [b] Least-squares standard deviations in the last digit are given in parentheses. [c] Total errors for r_g bonds and for $\angle_a$ bond angles were calculated according to ref 29. [d] Dependent parameter. [e] Two bonds removed. [f] Three bonds removed. [g] Diametrically opposite. [h] $\mathrm{Dif}_1 = r(S\text{–}B) - r(B_2\text{–}B_3)$. [i] i–vi are the key to the coupling scheme. [j] $\mathrm{Dif}_2 = r(B_2\text{–}B_3) - r(B_3\text{–}B_7)$.

Table II. Geometric Parameters[a] and *R* Factors for 1-Thia-*closo*-dodecaborane(11) As Obtained from the Various Refinements

parameter	model A[b]	model B	model C	model D[c]
$\mathrm{Dif}_1{}^d$	0.227 (2)	0.234	0.219	
$\mathrm{Dif}_2{}^e$	0.124 (1)	0.130	0.119	
$r(S\text{–}B)^f$	2.007 (1)	2.008	2.005	2.008
$r(B_2\text{–}B_3)^f$	1.904 (1)	1.903	1.905	1.904
$r(B_3\text{–}B_7)$	1.781 (2)	1.774	1.786	(av) 1.779
$r(B_7\text{–}B_8)$	1.778 (2)	1.795	1.775	
$r(B_7\text{–}B_{12})$	1.775 (2)	1.773	1.770	
$r(B\text{–}H)_{\mathrm{mean}}$	1.187 (1)	1.187	1.188	1.187
∠S–B–H	120.3 (5)	120.3	120.7	120.0
$\angle B_{12}$–B_7–H	125.3 (7)	127.7	125.7	124.9
R factor	0.0249	0.0261	0.0260	0.0253

[a] Bond lengths (r_a) are given in Å; angles, in degrees. [b] Least-squares standard deviations in the last digit are given in parentheses. [c] All the cage distances were refined as independent parameters. [d] $\mathrm{Dif}_1 = r(S\text{–}B) - r(B_3\text{–}B_7)$. [e] $\mathrm{Dif}_2 = r(B_2\text{–}B_3) - r(B_3\text{–}B_7)$. [f] Dependent parameter.

Table III. Elements of the Correlation Matrix Exceeding 0.6 in Absolute Value

i	*j*	$\rho_{ij}(i \neq j)$
$\mathrm{Dif}_1{}^a$	$\mathrm{Dif}_2{}^b$	0.871
	$r(B_3\text{–}B_7)$	–0.969
	$r(B_7\text{–}B_8)$	0.793
	$r(B_7\text{–}B_{12})$	0.779
$\mathrm{Dif}_2{}^b$	$r(B_3\text{–}B_7)$	–0.852
	$r(B_7\text{–}B_8)$	0.710
	$r(B_7\text{–}B_{12})$	0.661
$r(B_3\text{–}B_7)$	$r(B_7\text{–}B_8)$	–0.826
	$r(B_7\text{–}B_{12})$	–0.786
$\mathrm{SC}_1{}^c$	$l(B\text{–}H)_{\mathrm{mean}}$	0.647

[a] $\mathrm{Dif}_1 = r(S\text{–}B) - r(B_3\text{–}B_7)$. [b] $\mathrm{Dif}_2 = r(B_2\text{–}B_3) - r(B_3\text{–}B_7)$. [c] SC_1 is the scale factor for the short camera distance.

of close-lying distances, and various differences between them, also were carried out. Thus the geometric consequences of the choice of $\Delta_1 l = l(B_2\text{–}B_3) - l(B\text{–}B)_{\mathrm{rest}}$, $\Delta_2 l = l(S\text{–}B) - l(B\text{–}B)_{\mathrm{rest}}$, $\Delta_3 l = l(S\text{–}B) - l(B_2\text{–}B_3)$, $\Delta_4 l = l(S\cdots B_7) - l(B\cdots B)_{\mathrm{all}}$, and $\Delta_5 l = l(S\cdots B_{12}) - l(B_2\cdots B_9)$ were thoroughly tested. [A single vibrational amplitude, $l(B\text{–}B)_{\mathrm{rest}}$, was found to characterize the vibration of the B–B bonds excluding $r(B_2\text{–}B_3)$, whereas $l(B\cdots B)_{\mathrm{all}}$ are the vibrational amplitudes of the next-nearest-neighbor boron atoms, which were supposed to be equal.] The geometric parameters of the heavy-atom skeleton were found to be quite sensitive to the choice of $\Delta_n l$ (n = 1–4). Interestingly, although the results were relatively invariant to changes in $\Delta_5 l$, the values of these body-diagonal amplitudes influenced the results strongly. The optimal $\Delta_n l$ (n = 1–5) values from fitting the experimental data can be deduced from Table I (same as model A in Table II).

The effect of the different initial values of both bond angles was found to be negligible. The agreement between calculated and experimental intensities became worse when these parameters were fixed at particular values; e.g., $\angle B_{12}$–B_7–H = 121.7° (the angle in a regular icosahedron) or 123.2° [the 3-21G(*) value], and ∠S–B–H = 110.5° [the 3-21G(*) value]. Larger starting values of $l(S\cdots H_{13})$ and $l(B\cdots H)^e$ [for $l(B\cdots H)^e$ see Table I] always worsened the agreement due to the simultaneous closing of both bond angles. On the other hand, the difference $l(S\cdots H_{13}) - l(B\cdots H)^e$ appeared to have only marginal effects on these angles.

The results of the least-square refinements are given in Table I. Note that $l(S\cdots B_{12}) < l(S\text{–}B)$. The fact that vibrational amplitudes of some nonbonded distances are close to, or even smaller than, amplitudes for bonding ones is very common for *closo*-carboranes. This has been confirmed by theoretical calculations based on known force fields.[14] This situation may be ascribed to the specific internal motion within such rigid closo systems.

Due to the lack of calculated l values for $1\text{-}SB_{11}H_{11}$ we considered a second model (B in Table II), in which $\Delta_4 l$ was increased (to 0.004 Å) as well as the initial values of the corresponding vibrational amplitudes. This resulted in $l(S\text{–}B) < l(S\cdots B_7) < l(S\cdots B_{12})$ and $l(S\cdots B_{12}) = 0.079$ (3) Å. Model B follows the general observation that vibrational amplitudes are nearly proportional to the corresponding internuclear distances.[15,16] In Table II the geometric parameters of two additional models are also included. These were obtained either by supposing $l(B_2\text{–}B_3) = l(B\text{–}B)_{\mathrm{rest}}$ (model C), or by refining $r(S\text{–}B)$, $r(B_2\text{–}B_3)$, and the mean value of the remaining boron–boron bond lengths (model D). The minimum *R* factor values for the models A–D are also presented in Table II.

Although we favor model A, other models cannot be rejected completely, and they were used to obtain more realistic error estimates (see Table I, ref 29).

The elements of the correlation matrix exceeding 0.6 in absolute value are given in Table III. Several of these elements show a strong corre-

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Table IV. Ab Initio Optimized Geometries and IGLO ^{11}B Chemical Shifts for 1-$SB_{11}H_{11}$

(a) Bond Lengths (Å)

	S–B	B_2–B_3	B_3–B_7	B_7–B_8	B_7–B_{12}	B_2–H_{13}	B_7–H_{18}	B_{12}–H_{23}
3-21G[a]	2.129	1.975	1.771	1.813	1.800	1.172	1.179	1.178
3-21G(*)	2.050	1.929	1.778	1.812	1.802	1.174	1.179	1.178
GED[b]	*2.007*	*1.904*	*1.781*	*1.778*	*1.775*		*1.187*	

(b) Bond Angles (deg)

	S–B–H	B_{12}–B_7–H		S–B–H	B_{12}–B_7–H
3-21G[a]	109.4	122.2	*GED*[b]	*120.3*	*125.3*
3-21G(*)	110.5	123.2			

(c) δ(^{11}B) in ppm[c]

	B_{2-6}	B_{7-11}	B_{12}		B_{2-6}	B_{7-11}	B_{12}
DZ//3-21G(*)	1.8	−9.8	24.7	*expt*[d]	*−6.7*	*−4.2*	*18.4*
DZ//GED	0.5	−8.0	24.5	*expt*[e]	*−5.8*	*−3.2*	*19.2*

[a] Reference 22. [b] r_a and $\angle_a$ values based on model A; for r_g values, see Table I. [c] Relative to BF_3·OEt_2. [d] $CHCl_3$ solution: Heřmánek, S. Personal communication. [e] Benzene solution: Pretzer, W. R.; Rudolph, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1441.

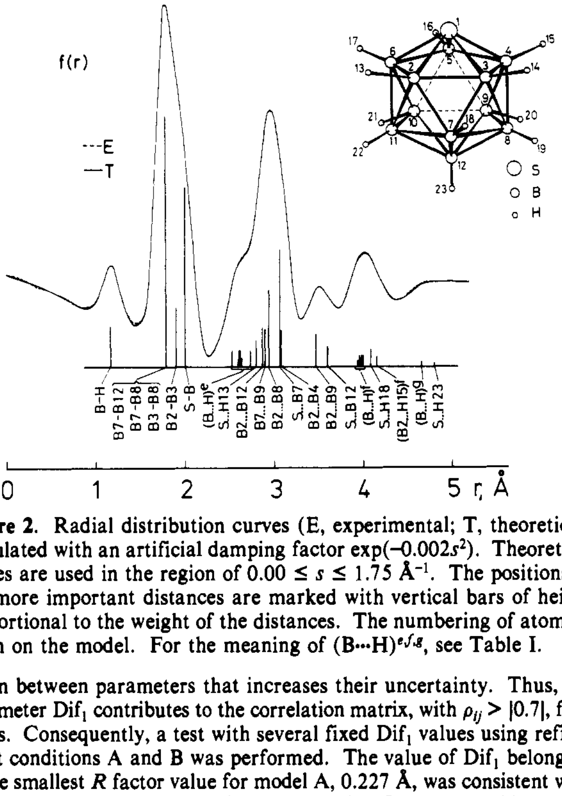

Figure 2. Radial distribution curves (E, experimental; T, theoretical) calculated with an artificial damping factor exp(−0.002s^2). Theoretical values are used in the region of $0.00 \leq s \leq 1.75$ Å^{-1}. The positions of the more important distances are marked with vertical bars of height proportional to the weight of the distances. The numbering of atoms is given on the model. For the meaning of (B···H)^{e,f,g}, see Table I.

lation between parameters that increases their uncertainty. Thus, the parameter Dif_1 contributes to the correlation matrix, with $\rho_{ij} > |0.7|$, four times. Consequently, a test with several fixed Dif_1 values using refinement conditions A and B was performed. The value of Dif_1 belonging to the smallest *R* factor value for model A, 0.227 Å, was consistent with that achieved by the virtual refinement of Dif_1. In contrast, this test for model B gave Dif_1 = 0.226–0.228 Å, belonging to the minimum *R* factor value. The parameters in this minimum were practically identical with those determined for model A.

Ab Initio Calculations

The geometry was fully optimized in C_{5v} symmetry with the CADPAC program[17] employing the standard 3-21G(*) basis set (same as 3-21G, but augmented with one set of polarization functions on sulfur[18]). ^{11}B chemical shifts were calculated with the IGLO (individual gauge for localized orbitals) program[19,20] employing a DZ basis set of Huzinaga[21] Gaussian lobes contracted as follows:[19b] B 7s3p (4111, 21); S 10s6p (511111, 3111); H 3s (21). The results, as well as the geometry optimized at the 3-21G level,[22] are summarized in Table IV.

Discussion

The most accurate parameters determined are the S–B and B_2–B_3 bond lengths and the mean value of the B–H bonds [$(B–H)_{mean}$].

The S–B bond length is the first one established in the gas phase for this class of compounds. The B_2–B_3 separation is the longest B–B bond in the molecule. Moreover, it belongs to the group of the longest B–B bonds in boranes and heteroboranes investigated in the gas phase, e.g. 1.98 and 1.99 Å for 1,6-$C_2B_7H_9$.[23]

The axial sulfur placement leads to a substantial lengthening of the B–B linkages in the pentagonal belt adjacent to sulfur. This also is obvious in the theoretical structures (see Table IV). As is found generally, the distances involving sulfur are too long at the 3-21G level [cf. r_e(S–B) = 2.129 Å (3-21G); r_g(S–B) = 2.010 Å (GED)]. Inclusion of polarization functions on sulfur [i.e. the 3-21G(*) level] improves the situation considerably: r_e(S–B) = 2.050 Å. At that level, the B–B bonds including $r(B_2–B_3)$ agree with experimental values within ca. 1.9%.[24] The magnitude of the B_2–B_3 elongation is especially noteworthy in comparison to the related 1,12-$XYB_{10}H_{11}$ series (see Table V). For example, since As has a larger atomic radius than S, one might expect a stronger perturbation of the boron skeleton in 1,12-$AsCB_{10}H_{11}$. However, the B_2–B_3 bond for the latter (1.886 Å) is shorter than that determined for 1-$SB_{11}H_{11}$.

The other B–B bonds are closely spaced and, consequently, could not be distinguished reliably by electron diffraction. The computed mean distance for B_3–B_7, B_7–B_8, and B_7–B_{12} [r_e = 1.797 Å at the 3-21G(*) level] compares well to the experimental mean, r_g = 1.780 Å.

The $(B–H)_{mean}$ bond length does not show any substantial deviations from its usual value determined for a variety of boron clusters.[25,26] This applies to the theoretical values calculated on

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Table V. Molecular Geometry of the 1,12-$XYB_{10}H_{11}$ Molecules so Far Studied by Gas-Electron Diffraction[a]

parameter	X = C–H Y = C	X = P Y = C	X = As Y = C	X = S Y = B
r_X	0.77	1.10	1.21	1.03
$r_X + r_B$	1.62	1.95	2.06	1.88
r(B–X)	1.710 (11)	2.052 (7)	2.137 (3)	2.010 (5)
$r(B_2–B_3)$	1.792 (7)	1.862 (16)	1.886 (6)	1.905 (4)
$r(B_3–B_7)$	1.772 (13)	1.773 (29)	1.778 (11)	1.783 (8)
$r(B_7–B_8)$	1.792 (7)	1.796 (23)	1.785 (11)	1.780 (11)
$r(B_7–Y_{12})$	1.710 (11)	1.709 (24)	1.708 (14)	1.777 (6)
ref	13	27	27	*b*

[a] For $B_{12}H_{12}^{2-}$, r(B–B) = 1.77 Å as determined by X-ray diffraction technique.[30] In reality there are 6 B–B bonds of 1.755 Å and 24 B–B bonds of 1.78 Å, giving the mean value of 1.77 Å; this is ascribed to specific steric interactions of hydrogen atoms and cations (K^+) in the crystal packing. r_B and r_X are taken from ref 31. [b] Present work.

various levels as well.[20c] The three kinds of computed B–H distances differ only by less than 0.01 Å. Consequently, inclusion of some ΔBH constraints would not be expected to improve the agreement.

The largest discrepancy in the geometric parameters is found for the S–B–H bond angle [3-21G(*), 110.5°; GED, 120.3°]. However, the experimental value is strongly influenced by the starting values of some vibrational amplitudes and thus is rather uncertain.

We also performed IGLO ^{11}B chemical shifts calculations employing both theoretical [3-21G(*)] and experimental (GED) structures. The $\delta(^{11}B)$ values computed for both geometries are virtually identical and are qualitatively in accord with the experimentally known chemical shifts (see Table IV). The largest discrepancy between the theoretical and experimental $\delta(^{11}B)$ values, ca. 7 ppm, is found for boron atoms B_{2-6} adjacent to sulfur. A better description of these borons, however, would require a larger basis set on sulfur for which the DZ basis is probably not sufficient.[28]

A shift to high frequency of B_{12} ($\delta(^{11}B)$ = 19.2 ppm) with respect to the "parent" $B_{12}H_{12}^{2-}$ is well reproduced by the calculations (IGLO DZ: 24.5 ppm). A more detailed discussion of this "antipodal effect"[32] will be published elsewhere.

Note Added in Proof. We were not aware of the 6-31G* geometry[22] when the present contribution had gone to press. The results are as follows (in Å): r(S–B), 2.018; $r(B_2–B_3)$, 1.904; $r(B_3–B_7)$, 1.771; $r(B_7–B_8)$, 1.804; $r(B_7–B_{12})$, 1.794; $r(B_2–H_{13})$, 1.177; $r(B_7–H_{18})$ and $r(B_{12}–H_{23})$, 1.182. There is an excellent agreement of the first two parameters with the corresponding GED ones. The IGLO values (DZ//6-31G*, in ppm) are (B_{2-6}) −0.7, (B_{7-11}) −10.0, and (B_{12}) 23.1 ppm, quite similar to the DZ//GED and DZ//3-21G(*) results.

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Supplementary Material Available: Listings of total electron diffraction intensities for both camera distances (2 pages). Ordering information is given on any current masthead page.

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Transition Metal Carbonyl Clusters. A Molecular Mechanics Approach to Ligand Stereochemistry

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The surface force field for molecular mechanics simulation of the ligand structure in transition metal carbonyl clusters, originally developed by Lauher, is redesigned and implemented in the common MM2 Allinger's program. The equal potential surface (EPS) for a cluster is built by patchwork using patches whose shape depends on Crabtree and Lavin's reaction path for the terminal/μ_2-bridging/terminal interconversion. The CO ligands can float on the EPS even in the presence of a clear connectivity pattern (necessary for the energy minimization within the MM2 scheme) because their connectivity is periodically redetermined. *A CO ligand is assumed to be locally connected to the metals used to generate the patches to which the ligand belongs.* The program is a powerful modeler and can be used as a *source of sterically reasonable geometries.* The dominant contribution to the computed steric energies arises from the nonbonded interactions; hence, the comparison of modeled and experimental structures should lead to the recognition of other forces at work. Consideration is given to the case of octahedral metal carbonyl clusters with stoichiometries ranging from $M_6(CO)_{12}$ to $M_6(CO)_{20}$, and since "real" structures are only occasionally found in the global minimum of the "steric" potential energy surface, *it would appear that intramolecular steric interactions are not the leading term in determining the metal carbonyl cluster stereogeometries in the solid state.* It is only the interplay between many different factors (inter- and intramolecular steric interactions, charge and local bookkeeping equilization, and more specific electronic effects) that determines the real structure. *Steric energies are properly used only to justify small distortions around a given geometry or to exclude a particularly crowded stereoisomer rather than to foresee the correct one.*

The cornerstone of all rationale concerning carbonyl clusters[1-4] is the assumption that the number of ligands and their stereochemistry do not affect the overall number of cluster valence electrons (CVEs), the only relevant factor being the metal cluster

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