$C_2B_7H_9$: Snapshots of a Rearranging Carborane

Arnout Ceulemans,* Geert Goijens, and Minh Tho Nguyen

Department of Chemistry, Katholieke Universiteit Leuven
Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received April 4, 1994

closo-Nonaborane $B_9H_9^{2-}$ has a tricapped trigonal prismatic structure.[1] Of the six possible isomers of the corresponding carborane $C_2B_7H_9$, only one is known experimentally. It has the two C atoms in capping positions of the prism (Figure 1a). Qualitative charge stabilization considerations[2] and *ab initio* calculations[3,4] indicate that this cap–cap form is the most stable isomer. It is speculated that the other possible structures can easily rearrange to the cap–cap global minimum. Gimarc and Ott[5] have shown that Lipscomb's single diamond–square–diamond (dsd) rearrangement[6] is forbidden by the principle of conservation of orbital symmetry,[7] but a double dsd process is allowed. The critical edges involved are required to be mutually perpendicular relative to the conserved mirror plane.[8] In this paper we report the result of a more detailed *ab initio* study which proves that the $C_2B_7H_9$ carborane is fluxional along a *closo–nido* opening mode and can indeed rearrange via a consecutive double dsd mechanism.

Previously Gimarc et al. have calculated all $C_2B_7H_9$ isomers at the HF/STO-3G level.[3,4] Optimized geometries were of the *closo* type, although one isomer was reported[3] to have an "odd" structure with some unusually long B–B and C–B bonds. Using a vibrational analysis we have found that the published *closo* structures are in fact saddle points rather than minima as assumed. The true minima for all six isomers have open structures, at both the HF/STO-3G and HF/6-31G* levels of calculation.[9] In each case the geometry is of the *nido* type, with a triangle under a nonplanar hexagon, as shown in Figure 1b. The opening of the trigonal prismatic cage is stereospecific: one of the triangular faces expands and forms together with the three capping atoms an open hexagonal face in a chairlike conformation. For those carborane isomers where the upper and lower triangle of the prism are inequivalent, the triangle which expands always corresponds to the one carrying the carbon substituents. In the D_{3h} point group of the unsubstituted cage this opening mode has a_2'' symmetry and conserves a C_{3v} subgroup. The HF/4-31G* calculated frequency[10] for the a_2'' mode in $B_9H_9^{2-}$ is only 139 cm^{-1}.

For three of the isomers the opening mode lowers the effective point group symmetry. In these cases symmetry constraints allow a separate geometry optimization of *closo* and *nido* forms. In Table 1 the energies of the three *closo* transition structures and of all six *nido* equilibrium structures are listed. Table 2 contains a selection of bond lengths for the two cap–cap structures shown in Figure 1. For one of the isomers, the so-called triangular edge form, the cage opening was followed by a further relaxation to yield the same open structure as the cap–cap isomer. This offers an unexpected opportunity to take snapshots of the carborane framework during its isomerization (*vide infra*). The relative stabilities of the remaining isomers comply with the earlier results by Gimarc et al.[3,4]

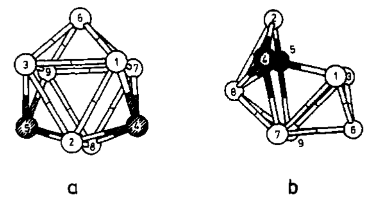

Figure 1. Two alternative ground state geometries for the cap–cap isomer of $C_2B_7H_9$ where darkened circles denote the C atoms. H atoms are not shown. Form a is the *closo* form with C_{2v} symmetry, and form b is the *nido* form with C_s symmetry.

Table 1. Total Energies (in Hartrees) of the Six $C_2B_7H_9$ Isomers Calculated at the HF/6-31G* Level

isomer[a]	transition structure (*closo*)	equilibrium structure (*nido*)
cc	C_{2v} –253.782 42	C_s –253.784 68
cfv		C_s –253.750 54
cnv		C_1 –253.719 69
rd	C_2 –253.699 84	C_1 –253.702 25
te		C_s[b] –253.784 68
re	C_{2v} –253.680 86	C_s –253.684 13

[a] Isomer labeling refers to the substituent positions in a tricapped triangular prism; cc, cap–cap; cfv, cap–far vertex; rd, rectangular diagonal; te, triangular edge; and re, rectangular edge. [b] This form collapses to the cc minimum following geometry optimization.

Table 2. Bond Lengths (Å) for C_{2v} and C_s Conformations of the Cap–Cap Isomer, Calculated at the HF/6-31G* Level

bonds[a]	C_{2v}	C_s
B_1B_2	1.999	2.218
B_1B_3	2.010	2.204
B_1C_4	1.615	1.593
B_1B_6	1.713	1.680
B_1B_7	1.787	1.798
B_2C_4	1.599	1.569
B_2B_8	1.804	1.816
C_4B_7	1.615	1.667
C_4B_8	1.599	1.650
B_6B_7	1.713	1.760
B_7B_8	1.999	1.837
B_7B_9	2.010	1.856
B_1H	1.180	1.180
B_2H	1.177	1.178
C_4H	1.071	1.072
B_6H	1.181	1.182
B_7H	1.180	1.180
B_8H	1.177	1.177

[a] All atoms are numbered as in Figure 1a (C_{2v}) and Figure 1b (C_s).

As Table 1 shows, the stabilizing effect of the cage opening is only a few kilocalories/mole. One expects that the Hartree–Fock approximation slightly favors open structures. For this reason more refined calculations at the MP4SDQ/6-31G* level were performed for both *closo* and *nido* forms of the most stable cap–cap isomer using HF/6-31G* optimized parameters. The total energy of the C_{2v} *closo* form is –254.721 12 au, as compared to –254.720 06 au for the C_s *open* form. Hence it is indeed true that inclusion of electron correlation corrections reverses the relative stability of the two structures, the *closo* configuration now being 0.7 kcal/mol more stable than the *nido* form. This result reproduces the experimental *closo* structure[11] for the dimethyl compound $C_2(CH_3)_2B_7H_7$. Calculated bond lengths

---

(1) Guggenberger, L. J. *Inorg. Chem.* **1968**, *7*, 2260.
(2) Ott, J. J.; Gimarc, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4303.
(3) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673.
(4) Gimarc, B. M.; Dai, B.; Ott, J. J. *J. Comput. Chem.* **1989**, *10*, 14.
(5) Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 2708.
(6) Lipscomb, W. N. *Science* **1966**, *153*, 373.
(7) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.
(8) Wales, D. J.; Mingos, D. M. P.; Zhenyang, L. *Inorg. Chem.* **1989**, *28*, 2754.
(9) *Gaussian92*, Revision A: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1992.
(10) Brint, P.; Sangchakr, B.; Fowler, P. W.; Weldon, V. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2253.
(11) Koetzle, T. F.; Scarbrough, F. E.; Lipscomb, W. N. *Inorg. Chem.* **1968**, *7*, 1076.

0002-7863/94/1516-9395$04.50/0

for the C_{2v} structure are in excellent agreement with the experimental distances.

Our *ab initio* calculations thus indicate that the *closo* structures are probably at the bottom of a very flat potential well along a specific cage opening coordinate. On the orbital level the facile opening of the cage, involving the breaking of no fewer than three triangular edge bonds, can be explained by the interaction between frontier orbitals. Using the nomenclature of the tensor surface harmonic model[12–14] for cluster bonding, the active orbitals can be identified as an occupied D^{π} orbital and an empty $\bar{F}^{\pi}$ orbital. Their symmetries in the D_{3h} point group of the parent $B_9H_9^{2-}$ are a_1' and a_2'', respectively, giving rise to the observed promoting mode of a_2'' symmetry.[15] In this scheme the appearance of an orbital component with F parentage is not accidental. Indeed nonaborane is the first member of the borane series with cluster orbitals of F type. The introduction of a new shell is characterized by a small HOMO–LUMO gap[16,17] and may thus rationalize the pronounced frontier orbital interactions. In comparison open intermediates are not expected to be equally important in the case of the dodecaborane framework where the HOMO–LUMO gap is much larger.[18,19]

As indicated in Table 1, a gradient driven geometry optimization of the triangular edge isomer induced a spontaneous rearrangement to the cap–cap minimum. This observation demonstrates that the nonacarborane framework can indeed isomerize and allows the corresponding mechanism to be deduced. A few intermediate steps on the isomerization path are shown in Figure 2. The starting point in Figure 2a is the *nido* form of the triangular edge structure, which is calculated as a local minimum at the HF/STO-3G level but is unstable when calculated at the HF/6-31G* level. The initial stage of the isomerization is characterized by a collapse of the original hexagonal face. Eventually in Figure 2b a structure is formed which has a square face. This structure may be viewed as the transition structure of a dsd process involving the cleavage of a triangular edge. In Figure 2c a new bond is indeed formed perpendicular to the original edge, but in the same time an adjacent diamond set is converted into a square. The switching edge[20] of this second dsd process is the opposite rectangular edge. In the final stage of Figure 2d this square opens up to the hexagonal face of the cap–cap product. The isomerization pathway is thus readily identified as a double dsd process superimposed on the fluxional *closo–nido* opening mode. The intimate nature of this double dsd process appears to be consecutive rather than concerted.

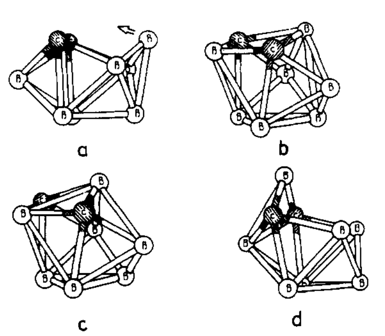

Figure 2. Snapshots of rearranging $C_2B_7H_9$. Form a is the unstable *nido* form of the triangular edge isomer. This isomer starts to rearrange *via* the inward motion of a B atom as indicated; form b corresponds to the square intermediate of a single dsd rotation of the triangular edge joining the two C atoms; in form c a square face is formed by breaking the opposite rectangular edge. Form d is the stable *nido* form of the cap–cap product.

It seems therefore that the rearrangement of most carborane cages is initiated by a single dsd process.[21] In principle in the present cluster the switching edge of such a process could be the rectangular or the triangular edge. However, due to orbital selection rules only the triangular edge can be attacked. The actual switching of this edge increases the degree of the near vertex from 5 to 6. This induces the second dsd process involving the opposite rectangular edge. The mechanism may thus be understood as a cascade of single dsd processes. The initial dsd switch creates a defect which propagates through the cluster until vertices with degree 6 have been removed.

These conclusions are based on the analysis of structures generated during the geometry optimization of an unstable isomer. They form the first computational proof for the proposed[5] double diamond–square–diamond mechanism; they will greatly facilitate the search for transition states on the rearrangement pathways between stable isomers.

Acknowledgment. Financial support from the Belgian National Science Foundation (NFWO) and the Belgian Government (Ministerie voor Programmatie van het Wetenschapsbeleid) is gratefully acknowledged. G.G. is indebted to the IWONL Institute for a research fellowship and also thanks L. Landuyt for helpful discussion.

---

[12] Stone, A. J. *J. Mol. Phys.* **1980**, *41*, 1339.

[13] Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563.

[14] Stone, A. J.; Alderton, M. J. *Inorg. Chem.* **1982**, *21*, 2297.

[15] The odd $\bar{F}^{\pi}_{3s}$ and even F^{π}_{0} harmonic generate the same a_2'' LUMO. *Vice versa* the a_2' HOMO can be obtained from the even F^{π}_{3s} or from the odd $\bar{F}^{\pi}_{0}$. In view of this ambiguity TSH imposes an even harmonic parentage for the bonding orbital (a_2', F^{π}_{3s}) and an odd harmonic parentage for its antibonding partner (a_2'', $\bar{F}^{\pi}_{3s}$).

[16] Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*: Prentice-Hall Int. Ed.: Englewood Cliffs, NJ, 1990.

[17] Fowler, P. W.; Porterfield, W. W. *Inorg. Chem.* **1985**, *24*, 3511.

[18] Wales, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 1557.

[19] Johnson, B. F. G.; Roberts, Y. V.; Parisin, E. *Inorg. Chim. Acta* **1993**, *221*, 17.

[20] King, R. B. *Inorg. Chim. Acta* **1981**, *49*, 237.

[21] Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 1388.