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Fluxional Behavior in $B_{11}H_{11}^{2-}$. A Theoretical Study

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Molecular orbital calculations in the approximation of partial retention of diatomic differential overlap (PRDDO) have been done for various geometries of $B_{11}H_{11}^{2-}$ in order to study its fluxional behavior. The energies of the C_{5v} isomers are 20, 44, and 66 kcal/mol above the C_{2v} isomer for the $^3A_2$, $^1E_2$, and $^1A_1$ states, respectively. Rearrangement is not predicted to proceed through this high-energy path. A low-energy path for the rearrangement with a barrier of 1–3 kcal/mol has been obtained with the linear synchronous transit approach. The low-energy path connects C_s and C_{2v} geometries. Due to the small energy differences between the C_s, C_1, and C_{2v} structures, it is not possible to choose between these geometries for the ground state.

Fluxional molecules, such as cyclopentane,[1] PF_5,[2] complexes of iron tricarbonyl with cyclooctatetraene,[3] $B_3H_8^-$ ion,[4] and bullvalene[5] are early examples of a class[6] which is defined by the time scale of observations. Usually, these molecules undergo degenerate rearrangements at room, or lower, temperatures, and most frequently the geometrical structures are equivalent on an NMR time scale. Few theoretical studies of fluxional systems have been made because, in common with chemical reactions, an exploration of the "potential" energy surface is required. With the advent of fast yet accurate molecular orbital methods such as PRDDO and of schemes for defining reaction paths such as the synchronous transit approach,[8] a wide range of chemical systems of moderate complexity can be studied. Using these two methods, we have begun studying the fluxional behavior of a variety of molecules such as bullvalene,[9] $B_3H_8^-$ ion,[10] and the excited states of trimethylenemethane.[11] In this note we present a theoretical study of the fluxional behavior of $B_{11}H_{11}^{2-}$ as part of our continuing study of boron hydrides[12] and their rearrangements.[8a,10]

Spontaneous isomerization of $B_{11}H_{11}^{2-}$ at low temperature (−70 °C) has been observed to occur rapidly on the NMR time scale.[13] Only a single ^{11}B Peak is observed in the proton-decoupled NMR spectrum. Thus, all of the boron atoms are NMR equivalent. A number of polytopal rearrangements which would permute all of the borons have been suggested[13-15] to account for the fluxional behavior. These proposals for the detailed motions (Figure 1) have assumed that the C_{2v} structure is the most stable and that the transition state (or intermediate) has C_s or C_{5v} symmetry. We have investigated the energetics of rearrangement for both possibilities.

Initial coordinates for the C_{5v} structure were obtained from the optimized coordinates[12b] of $B_{12}H_{12}^{2-}$ by removing one apex B–H group from the icosahedron. The starting coordinates for the C_{2v} structure were then generated by rotating boron 11 and its associated hydrogen about an axis passing through the midpoint of borons 6 and 2 and through the midpoint of borons 4 and 9 (Figure 2). The C_{2v} structure was then partially optimized by varying the position of B(11) along the C_2 axis, followed by optimization of the B(6)–B(9), B(7)–B(8), B(5)–B(10), B(5)–B(7), and B(8)–B(10) distances subject to the restriction of C_{2v} symmetry.[16] The total energy of $B_{11}H_{11}^{2-}$ is given in Table I.

The C_{5v} structure has an open-shell configuration which gives rise to three electronic states: $^3A_2$, $^1E_2$, $^1A_1$. Using the C_{5v} geometry described above, we find that the energies of these three states relative to the C_{2v} geometry are $^3A_2$ (20 kcal/mol), $^1E_2$ (44 kcal/mol), and $^1A_1$ (66 kcal/mol).[17] The $^1E_2$ state is, of course, orbitally degenerate and thus will be subject to Jahn–Teller distortion. Upon distortion of the C_{5v} structure as illustrated in Figure 2, the components of the $^1E_2$ state are expected to split into $^1A''$ and $^1A'$ states of the C_s structure, the latter ultimately correlating with the $^1A_1$ ground state of the C_{2v} structure. The calculated energies of all of the C_{5v} states are too high for any of these states to be important in the polytopal rearrangements. The ground state of the C_{5v} isomer is a triplet. Even if the energy were lower, it is unlikely that rearrangement would proceed via this intermediate because *two* intersystem crossings $C_{2v}(^1A_1) \rightarrow C_{5v}(^3A_2) \rightarrow C_{2v}(^1A_1)$ must be invoked to explain the process.

Table I. Energies of the Various Isomers

A. Comparison of C_{2v} and C_{5v}

State[a]	Energy,[b] kcal/mol	State[a]	Energy,[b] kcal/mol
$C_{2v}(^1A_1)$	0	$C_{5v}(^1E_2)$	44
$C_{5v}(^3A_2)$	20	$C_{5v}(^1A_1)$	66

B. Path Containing C_s Transition State

Path coordinate[c]	Energy,[b] kcal/mol	Path coordinate[c]	Energy,[b] kcal/mol
0.0 (C_{2v})	0.0	0.3 (C_1)	−1.3
0.05 (C_1)	−0.9	0.4 (C_1)	−0.1
0.1 (C_1)	−2.6	0.5 (C_s)	0.2
0.2 (C_1)	−2.1		

[a] Symmetry type and state. [b] All energies are given relative to the energy of the C_{2v} isomer, −277.823 au. Positive energies show less stable states, and negative energies show more stable states. [c] For the definition of path coordinate, see ref 8.

The above calculations demonstrate that the C_{5v} structure is not a viable intermediate or transition state for the rearrangement. The C_{5v} structure can also be eliminated as a transition state following the rules of McIver.[18] Since the C_{5v} structure can distort in more than one degenerate way to products, it cannot serve as the transition state. A linear synchronous transit path (near least motion path) constructed between two C_{2v} structures traverses a C_s geometry at the half-way point. The change in geometric parameters along the path is given in Table II.

The C_s structure can be viewed as arising from the Jahn–Teller distortion of the C_{5v} structure[20] but corresponds to a closed-shell state rather than to an open-shell state. The energy of this C_s isomer is less than 1 kcal/mol above the energy of the C_{2v} isomer. Calculations at earlier points along the path (Table I) show that the energy decreased to a value slightly below that of the C_s geometry, and thus a shallow minimum occurs along this path. This can be attributed either to artifacts arising from incomplete optimization of the C_{2v} structure or to the possibility that the most stable structure of $B_{11}H_{11}^{2-}$ belongs to the C_1 point group. A more likely explanation is that the C_s structure traversed on the synchronous transit path is less well optimized than the limiting C_{2v} structures. In fact, optimization of the 11–8, 11–7, 10–4, 10–1, and 11–10 dis-

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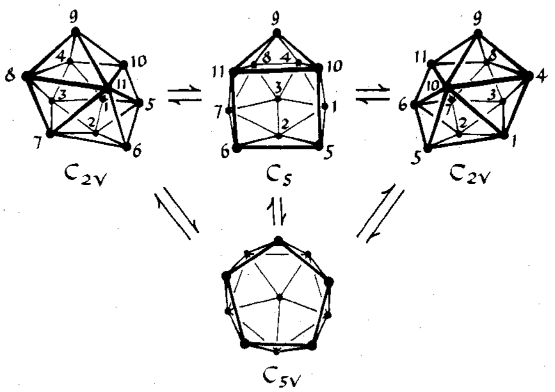

Figure 1. Polytopal rearrangements for interconverting two C_{2v} isomers by proceeding through a C_s structure or through a C_{5v} structure.

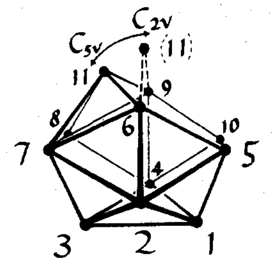

Figure 2. Interconversion of C_{5v} and C_{2v} structures showing the generation of the C_{2v} coordinates from those of the C_{5v} polytope.

Table II. Variation in Selected Bond Distances and Bond Angles[a,c] during the $C_{2v} \rightarrow C_s$ Synchronous Transit

	R[b]					
	0.0 (C_{2v})	0.1	0.2	0.3	0.4	0.5 (C_s)
11-10	4.17	4.17	4.17	4.17	4.17	4.17
11-9	3.01	3.02	3.04	3.05	3.07	3.09
11-8	4.17	4.08	3.98	3.88	3.77	3.67
11-7	4.17	4.08	4.00	3.90	3.81	3.72
11-6	3.01	3.04	3.08	3.11	3.15	3.19
11-5	4.17	4.31	4.45	4.58	4.71	4.84
10-9	3.20	3.18	3.15	3.13	3.11	3.09
10-6	5.40	5.31	5.20	5.09	4.97	4.84
10-5	3.42	3.37	3.32	3.28	3.23	3.19
10-4	3.17	3.27	3.37	3.47	3.57	3.67
10-1	3.29	3.37	3.46	3.54	3.63	3.72
9-8	3.20	3.21	3.21	3.22	3.23	3.24
9-4	3.29	3.28	3.27	3.26	3.25	3.24
6-7	3.20	3.21	3.22	3.23	3.24	3.25
6-5	3.20	3.20	3.19	3.19	3.19	3.19
6-2	3.29	3.27	3.26	3.24	3.23	3.22
5-2	3.17	3.18	3.19	3.20	3.21	3.22
5-1	3.29	3.28	3.27	3.26	3.25	3.24
6-11-9	133	132	131	129	127	124
6-11-10	96	93	91	87	84	81
11-10-5	66	69	72	75	78	81
11-10-9	46	46	47	47	47	48
11-10-4	89	89	87	85	84	82
11-9-10	84	84	85	85	85	85
11-8-4	89	91	93	94	96	98
11-6-5	84	87	90	93	96	99
10-5-6	109	108	106	104	101	99
10-11-8	75	76	78	79	81	82

[a] Angles are expressed in degrees and distances in au. [b] Distance along linear synchronous path connecting limiting C_{2v} structures. [c] Some distances which do not change more than 0.06 au are not included in this table. In the C_{2v} structure these bond distances are 8-3, 7-3, 4-3, 4-1, 3-1, 3-2, and 2-1 which all equal 3.28 au and 8-7 = 3.42 au and 8-4 = 7-2 = 3.17 au.

tances stabilized the C_s structure by about 3 kcal/mol so that a synchronous transit path to the partially optimized C_s structure would probably proceed monotonically downhill. However, at this level of approximation we cannot predict whether the C_s or C_{2v} structure is the most stable, but our calculations are consistent with a very low barrier (less than 3 kcal/mol) for a rearrangement traversing both C_s and C_{2v} structures.

Interestingly, the thermal rearrangements of $B_{11}H_{11}^{2-}$ are in contrast to the thermal rearrangement of methylenecyclopropane.[11,19] This latter rearrangement proceeds through a C_{2v} structure formed by a distortion of the idealized D_{3h} geometry of trimethylenemethane. The ground state for this transitional structure correlates with a component of the ^1E state which is split upon distortion. Both rearrangements proceed through a structure arising from a Jahn–Teller distortion of an idealized geometry of high symmetry. However, the character of the wave function is quite different as the methylenecyclopropane rearrangement proceeds through an open-shell transition state while the $B_{11}H_{11}^{2-}$ rearrangement remains on a closed-shell surface containing the C_s structure. The two orbitals in the diradical transition state of the methylenecyclopropane rearrangement remain localized and do not interact. Consequently the transition state retains its open-shell character. For the $B_{11}H_{11}^{2-}$ rearrangement, these orbitals interact strongly leading to a large energy splitting. Thus, it is lower in energy for the two electrons to pair up in a closed-shell configuration with a C_s geometry.

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Registry No. $B_{11}H_{11}^{2-}$ (C_{5v}), 12430-44-3; $B_{11}H_{11}^{2-}$ (C_s), 64475-50-9; $B_{11}H_{11}^{2-}$ (C_{2v}), 64475-49-6.

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