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Vibrational Spectrum and Electronic Structure of the $[B_{11}H_{11}]^{2-}$ Dianion

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The vibrational spectrum, geometrical structure and electron-density distribution (EDD) of the formally *closo* (2*n*+2)-electron cluster species $[B_{11}H_{11}]^{2-}$ have been studied. The presence of two low-frequency vibrational modes is evidence of cluster nonrigidity. A rationale for this lies in the results of EDD calculations which show that the polyhedron lacks two-centre edge-localized B–B bonds of the 6**k**–5**k** type and that its surface exhibits two six-membered rings with low electron density. Thus, the polyhedron does not consist of deltahedral faces only and therefore does not have a genuine *closo* structure. The data obtained also allow further elucidation of the "diamond-square-diamond" mechanism as commonly applied to the fluxionality of $[B_{11}H_{11}]^{2-}$ in solution.

Introduction

The eleven-vertex *closo* boranes and *closo* carbaboranes differ from their twelve-vertex and ten-vertex *closo* congeners in that (i) their cages contain a boron atom with the highest cluster connectivity of six, designated 6**k** in Williams' notation,[1] and in that (ii) they exhibit unusual NMR spectroscopic and chemical properties.[2–7]

Recently we studied the vibrational spectra of two representatives of the eleven-vertex *closo*-carbaborane family, namely the neutral molecule 2,3-$C_2B_9H_{11}$ (**1**) and the $[2\text{-}CB_{10}H_{11}]^-$ anion (**2**) (see Figure 1 for atom numbering), and showed that both species exhibited two low-frequency large-amplitude vibrational modes, at ca. 200 and ca. 300 cm^{-1}.[8,9] In this regard they contrast to all of the previously studied[10–12] unsubstituted twelve-, ten-, and six-vertex *closo*-boranes and *closo*-carbaboranes, which exhibit **no** normal modes with frequencies lower than 450 cm^{-1}. This lack of low-frequency modes is a consequence of the rigidity of the latter polyhedral cages. The cage rigidity, when present, permits the treatment of a *closo*-carbaboranyl moiety as a *pseudo*-atom, "Cb", and this model approach has worked well for the interpretation of the vibrational spectra of Cb–Cb and Cb–X molecules.[10,13,14]

By contrast, the presence of the low-frequency "soft modes" in the vibrational spectra of both **1** and **2** suggested cage nonrigidity, which, we surmised, was associated with the 6**k** feature. Based on the analysis of the published experimental and computed data on interboron distances in the structures of **1** and **2**, together with the results of the topological analysis of the electron-density distribution in both species, we thence concluded[8,9] that each of the polyhedra **1** and **2** does not actually have the deltahedral *closo* structure traditionally associated with them by the formal [2*n*+2] electron-count.[1,15]

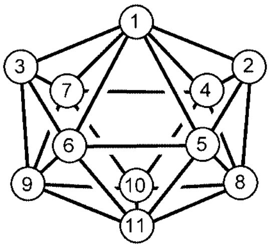

Figure 1. A traditional representation of the $\{B_{11}\}$ *closo* polyhedron depicting the atom numbering.

It was of interest similarly to investigate the other principal representative of the eleven-vertex *closo* polyhedral class, the $[B_{11}H_{11}]^{2-}$ boron cluster dianion (**3**), of which a well-known and interesting characteristic is its very simple, averaged ^{11}B NMR spectrum in solution, which was first reported by Tolpin and Lipscomb in 1973,[2] and which arises from a fluxionality due to a rapid polyhedral rearrangement.[2,6]

In this paper we present the Raman and IR spectra of **3** as its di-K^+ and di-Cs^+ salts and the Raman data on an aqueous solution of the di-Cs^+ salt. These vibrational spectra of **3** are previously unreported. Quantum-chemical DFT B3LYP calculations of the geometry of the undistorted dianion **3** and its vibrational mode frequencies and eigenvec-

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tors are also reported, and the electron density distribution (EDD) in **3** has been reconstructed using Bader's theory of "atoms in molecules" (AIM),[16] based on the optimized structure arising from DFT calculations. The results are related to the mechanism of the fluxionality of the anion.

Results and Discussion

Synthesis

A sample of $K_2[B_{11}H_{11}]$ (**3a**) was synthesized essentially according to a literature method.[6] The cation exchange reaction, substituting Cs^+ for K^+, between **3a** and a solution in methanol of CsCl, did not lead to $Cs_2[B_{11}H_{11}]$ (**3b**) but to a mixed salt of which the elemental analysis was consistent with the formulation $Cs_2[B_{11}H_{11}]·CsCl$ (**3c**). Here it may be noted that an analogous double salt has been obtained for the $[B_{12}H_{12}]^{2-}$ dianion.[17] Subsequent attempts to prepare the simple di-Cs^+ salt of **3** using CsCl were made by variation of the concentrations of the reagents and by changing the order of reagent addition, but, in both cases, only the mixed salt **3c** with a 1:1 $Cs_2[B_{11}H_{11}]$: CsCl ratio was obtained. Use of CsF, however, did yield $Cs_2[B_{11}H_{11}]$ (**3b**). The Raman spectra of both Cs^+ salts **3b** and **3c** were almost identical, as were the IR spectra; the presence of Cl^- anions in **3c** resulted only in small shifts of several bands in the spectrum of solid **3c** (Table 1).

Table 1. Vibrational spectrum of the $[B_{11}H_{11}]^{2-}$ anion.[a]

Calculated frequency [cm^{-1}]	IR intensity (arbitrary units)	Experimental frequencies [cm^{-1}]: IR spectrum of the solid salt $Cs_2B_{11}H_{11}·CsCl$	Raman spectrum of the salt $Cs_2B_{11}H_{11}·CsCl$: solid sample	Raman spectrum of the salt $Cs_2B_{11}H_{11}·CsCl$: aqueous solution	Raman spectra of the solid salts: $Cs_2B_{11}H_{11}$	Raman spectra of the solid salts: $K_2B_{11}H_{11}$	Symmetry species	Assignment
2526	0		2517 vs	2511 s p	2514 vs	2516 vs br	A_1	
2497, 2492	10.0	2498 vvs						
2482, 2475	9.0	2480 vs	2484 s br	2475 w				νBH
2465		2463 vvs	2461 s br	2460 m dp	2474 s sh	2467 vs br	A_1, B_2	
2450	0.3					2429 sh		
		1208 vw						
		1168 sh						
1066	0.3	1154 m						
1049	0.2	1076 m					B_1	
1037	0.2	1059 s	1061 m	1064 mw p	1062 m	1070 mw	A_1 B_2	
			1040 vw			1035 vw		δBH
		1024 sh						
942	0.1	960 m br	963 m	950 mw p	952 m	948 m	A_1	
941	0.1	942 sh					B_2	
921	0					914 vw		
893	0	891 vw	905 mw	879 m p	871 sh	873 m	A_1	
860	0.1	863 sh					B_2	δBH
862	0.0	851 mw	856 vs	843 s p	845 s	841 s	A_1,B_1	+νBB
832	0.1	812 mw	814 vw				A_1,B_2	
822	0						A_2	
802	0	806 sh					B_1	
786	0.1						B_1	
781	0	769 w					B_2	
751	0.04		748 vs	749 s p	746 vs	751 vs	A_1	cage stretch
740	0.04	730 sh						
717, 726	0.04	725 sh	726 s	725 s p	732 s sh	724 s	A_1	cage stretch
695	0.02	680 w	683 vw			689 vw	B_2	νBB+δBBB
675	0.01	664 vw	661 vw		662 w	664 vw	A_1	
640	2.0					638 sh	B_2	
617	1.0	631 vw	627 m	626 m p	626 m	623 m	A_1,B_1	
			608 w		612 w sh			
598	0		594 m	594 w dp	592 m	594 m	B_2	
579	0						B_1	δBBB
546	2.0		575 m	577 w p	575 m	578 m	A_1	cage
539	0		541 m	543 w dp	541 m	541 m	A_2	deformations
495	2.0	510 w	519 m	518 w p	514 m	525 m	A_1	
473	7.0	460 vw	464 mw	466 m dp	465 m	459 mw	B_2	
282	0.02	310 vvw ?	300 w br		312 mw br	310 mw	B_2	wB1
173	0		210 m		212 m br	220 m	A_2	δB(4,5,6,7)

[a] s: strong, m: medium, w: weak, sh: shoulder, br: broad, p: polarized, dp: depolarized.

Vibrational Spectra and Electronic Structure

The undistorted dianion $[B_{11}H_{11}]^{2-}$ belongs to the C_{2v} symmetry point group; its 60 normal modes are distributed among the symmetry species as follows:

$\Gamma = 19\ A_1 + 11\ A_2 + 16\ B_1 + 14\ B_2$

The vibrations of the A_1, B_1 and B_2 species are both IR-active and Raman-active, whereas the A_2 ones are only Raman-active. The spectra obtained are given in Figure 2 and Table 1. The latter also presents the calculated, unscaled harmonic frequencies and IR intensities of some normal modes, along with band assignment. The assignment was based on the Raman and IR activities, depolarization ratios of the Raman lines and on the results of normal-coordinate analysis. Previously, the low-resolution IR spectrum of the Nujol mull of the di-Cs^+ salt has been presented as a picture in ref.[18], where its Raman spectrum was also mentioned, but no particularly specific data were reported.

As is seen from Figure 2 and Table 1, the number of spectral features is much less than the theoretical value of 60. This observation can be rationalized in terms of the results of the normal-coordinate analysis, which shows that the frequencies of some normal modes, having close displacement eigenvectors but belonging to different symmetry species, nearly coincide (Table 1). An analogous situation was also observed for the spectra of both **1** and **2**.[8,9] It is of interest that the calculation for **3** reproduces the frequencies of ν(BH) stretching vibrations quite well without any scaling, unlike in the cases of the carbaboranes **1** and **2**, for which the computed ν(BH) frequencies were highly overvalued.

The vibrational spectrum of **3** is as specific as those of **1** and **2** in that it also exhibits two low-frequency modes at about 200 and 300 cm^{-1}. The exact frequency values of these modes depend slightly on the nature of the cation. The normal-coordinate analysis for the free anion **3** reproduces these low-frequency modes, but with somewhat lowered frequencies compared to the experimental values, as if they are now free from cation influences. Notably, by contrast, in the spectra of the two rigid-cage species $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ there are no frequencies lower than 588 cm^{-1} [19] and 515 cm^{-1},[20] respectively. However, all the rest of the salient spectral features, for example the ν(BH) frequencies or the cage breathing modes, are very much alike for all three borane dianions $[B_nH_n]^{2-}$, where n is 12, 11 and 10.[10] There are two totally symmetric cage vibrations in the spectra of all of the salts of **3**, to which very intense Raman lines at ca. 725 cm^{-1} and ca. 750 cm^{-1} correspond.

The incidence of low frequencies in the spectrum of **3**, as for those of **1** and **2**, is explained by the nonrigidity of the cage that is caused by the peculiarities of geometrical and electronic structure of the eleven-vertex polyhedron. To the best of our knowledge, three molecular structures, as determined by X-ray crystallography, are available for salts containing $\{B_{11}\}$ cluster anions. These are for $A_2[B_{11}H_{11}]$, where A is $[Li(thp)_3]$ (**4**) or $[NBzlEt_3]$ (**5**),[6b] and for $[NEt_4][4\text{-}(SMe_2)B_{11}H_{10}]$ (**6**).[21] Short interionic contacts in the crystal structure of **4** strongly distort the symmetry of the anion from regular C_{2v}. However, the less interactive ammonium cations in **5** and **6** leave the geometry of the anion closer to the idealized one. Dimensions derived by X-

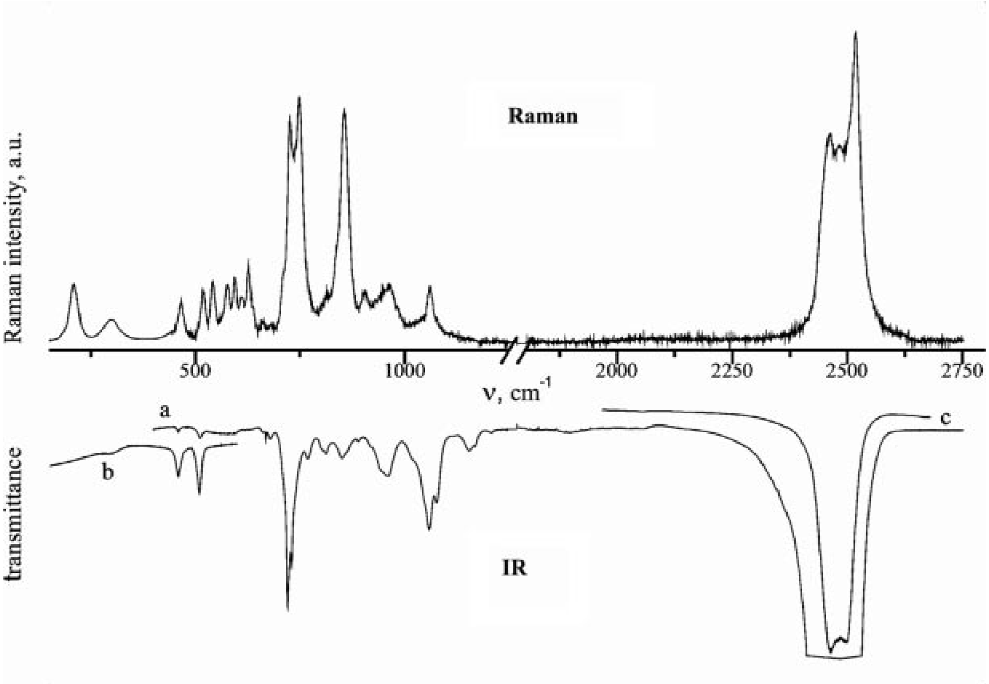


Figure 2. The Raman and IR spectra of solid $Cs_2[B_{11}H_{11}]\cdot CsCl$. The IR spectra: (a) KBr pellet, (b) polyethylene pellet, (c) Nujol mull.

Table 2. Interatomic distances and bond electron density $\rho_b(\mathbf{r})$ inside the $\{B_{11}\}$ polyhedron of the $[B_{11}H_{11}]^{2-}$ dianion (**3**).

Pairs of cage atoms	Interatomic distances [Å]						Presence of the (3,–1) bond critical points in **3**	$\rho_b(\mathbf{r})$ a.u.
	X-ray data for **5**[a][6b]	for **6**[a][21]	X-ray data [23]	[22]	calculated for isolated **3** [6]	this work		
B(1)B(2) = B(1)B(3)	1.747, 1.744	1.768, 1.722	1.746	1.726	1.745	1.745	+	0.117
B(2)B(8) = B(3)B(9)	1.743, 1.746	1.786, 1.757	1.753	1.746	1.760	1.759	+	0.120
B(2)B(4) = B(2)B(5) = B(3)B(6) = B(3)B(7)	1.658, 1.660, 1.665, 1.664	1.650, 1.662, 1.632, 1.677	1.670	1.634	1.672	1.670	+	0.142
B(1)B(4) = B(1)B(5) = B(1)B(6) = B(1)B(7)	2.024, 1.999, 2.026, 1.988	2.001, 2.025, 2.048, 1.971	2.004	1.990	2.026	2.028	–	
B(8)B(10) = B(8)B(11) = B(9)B(10) = B(9)B(11)	1.767, 1.781, 1.772, 1.775	1.804, 1.757, 1.731, 1.772	1.785	1.760	1.790	1.789	+	0.116
B(4)B(7) = B(5)B(6)	1.861, 1.846	1.806, 1.901	1.856	1.847	1.871	1.873	–	
B(4)B(10) = B(5)B(11) = B(6)B(11) = B(7)B(10)	1.779, 1.775, 1.770, 1.784	1.759, 1.812, 1.775, 1.795	1.780	1.775	1.786	1.785	+	0.116
B(4)B(8) = B(5)B(8) = B(6)B(9) = B(7)B(9)	1.761, 1.783, 1.785, 1.795	1.791, 1.797, 1.757, 1.782	1.791	1.783	1.796	1.794	+	0.117
B(10)B(11)	1.809	1.781	1.814	1.821	1.830	1.830	+	0.108

[a] The corresponding B–B interatomic distances in **5** and **6** are crystallographically non-equivalent as well as being subject to differing cation and substituent influences.

ray crystallography for **5** and **6**,[6b,21] as well as the results of geometry optimization for the undistorted **3**, both as reported previously[6a,22,23] and as obtained in this study, are given in Table 2. Both the experimental data and the computed data show that the interatomic distances between the B(1) and the B(4), B(5), B(6) and B(7) boron atoms, that average at 2.02 Å, are anomalously long for B–B bonds in *closo*-boranes, which typically vary from 1.58 to 1.99 Å.[22] Analogously long 6**k**–5**k** distances are similarly observed for **1** and **2**.[8,9] It is pertinent to mention here that Wade estimated the 6**k**–5**k** type of B–B interatomic distance to be 1.95 Å on the basis of fractional bond order.[15b] Long interboron connectivities have been recognized in some "disobedient" *closo* clusters to be typical for "fragile" structures.[24]

Explanation for these peculiar properties of the eleven-vertex *closo* polyhedra can be attempted by means of a topological analysis of the electron-density function according to Bader's "atoms in molecules" (AIM) approach.[16] This method has proven to be a useful and successful tool in understanding several other electron-deficient borane and carbaborane structures.[25,26] The results of such calculations for the $[B_{11}H_{11}]^{2-}$ anion **3** are given in Table 2. The corresponding molecular graph is presented in Figure 3, where the bond critical points are indicated and denoted by small circles.

The electron density values $\rho_b(\mathbf{r})$ for the (3,–1) critical points [i.e. bond critical points (BCPs)] of the BH and BB two-centre bonds lie in the intervals 0.166–0.162 and 0.142–0.108 a.u., respectively. These values are close to those obtained for the $[B_{12}H_{12}]^{2-}$ dianion.[25a] The electron-density values $\rho_r(\mathbf{r})$ for the (3,+1) critical points [i.e. ring critical points (RCPs)] that characterize the three-membered rings are as follows: for the eqivalent B(3,9,6) = B(3,9,7) = B(2,5,8) = B(2,4,8) faces: 0.116 a.u., for the equivalent B(6,9,11) = B(5,8,11) = B(4,8,10) = B(7,9,10) faces: 0.109 a.u., for the equivalent B(9,10,11) = B(8,10,11) faces: 0.105 a.u.

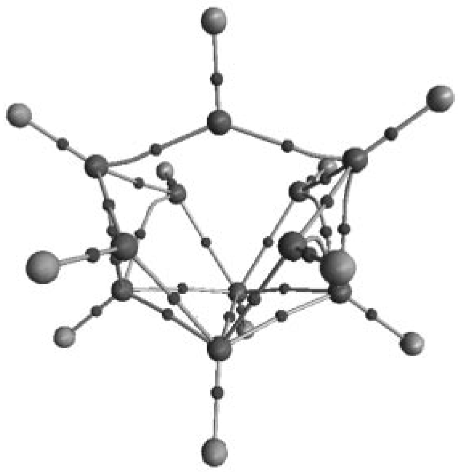


Figure 3. Molecular graph of the $[B_{11}H_{11}]^{2-}$ dianion **3** obtained as a result of the AIM topological analysis of electron-density distribution.

It is evident from these data that the $\rho_r(\mathbf{r})$ values for the above-mentioned three-membered rings in the structure of **3** are of comparable magnitude to those of $\rho_b(\mathbf{r})$ for the pairwise B–B interactions (Table 2). This is typical for boron polyhedra[25,26] and shows that the three-centre bonding plays almost the same role as the two-centre bonding; in other words, stabilization of the cage is attained both by the accumulation of electron density along the edge-localized bond paths and by its delocalization over the triangular polyhedral faces. There is a (3,+3) critical point in the cage interior: this is consistent with the essentially closed volume of **3**. The electron density value $\rho_c(\mathbf{r})$ in the centre of the cage **3** is low, at 0.0196 a.u., close to those[8,9] of the other eleven-vertex cages, for **1** at 0.0211 a.u. and for **2** at 0.0195 a.u.

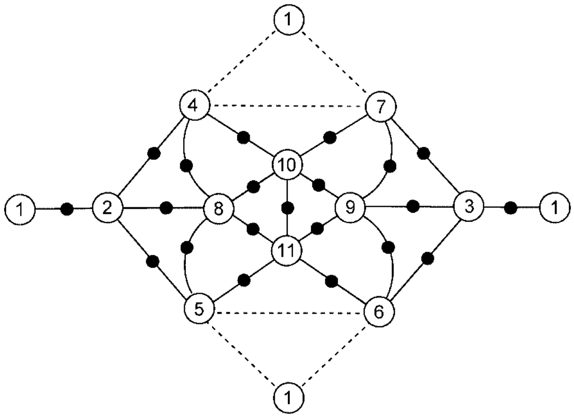
However, the results also show that there are no (3,–1) BCPs between members of each of the following pairs of boron atoms: B(1)–B(4), B(1)–B(5), B(1)–B(6) and B(1)–B(7); that is, there are no edge-localized two-centre 6**k**–5**k** bonds in the bonding network of **3**. This obviously leads to the longer interatomic distances from the B(1) atom to B(4), B(5), B(6) and B(7). Also, however, no BCPs were found between the B(5) and B(6) atoms, or between the B(4) and B(7) atoms, for which the interboron distances, which average at 1.86 Å, are significantly shorter than the 1.99 Å upper limit mentioned above, although elongated compared to the typical expected value of 1.79 Å[15b] for a 5**k**–5**k** cluster interboron linkage. The reason for this is not clear yet; the atoms in each of the B(4)–B(7) and B(5)–B(6) pairs would seem to be drawn together by the whole delocalized bonding system of the cage **3**. An analogous situation occurs for the *closo*-1,5-$C_2B_3H_5$ molecule, for which the AIM treatment, both theoretical[25a] and experimental,[26b] reveals no B–B bond paths, although the corresponding experimental B–B interatomic distances are also of closely similar magnitude, at 1.853 Å.

Thus, according to the analysis of the topology of electron density with AIM, six of the 27 edges of the octadecahedron of **3**, specifically B(1)–B(4), B(1)–B(5), B(1)–B(6) and B(1)–B(7), together with B(5)–B(6) and B(4)–B(7), do not correspond to two-centre bond paths. The absence of these leads to the presence in the structure of **3** of two equivalent six-membered rings encompassing the B(1,2,5,11,6,3) and B(1,2,4,10,7,3) atoms. These rings are characterized by two (3,+1) RCPs with low values for the electron density $\rho_r(\mathbf{r})$ of 0.070 a.u. The $\rho_r(\mathbf{r})$ values for the RCPs of the three-membered rings are much higher (see above), all being greater than 0.105 a.u. Thus in the structure of **3**, multicentre bonding in the six-membered rings is significantly weakened. These rings can therefore be regarded to some extent as "open faces", although it is pertinent to mention here that, according to our computations, the $\rho_r(\mathbf{r})$ value for a conventionally recognized five-membered open face, as in the *nido*-dicarbaborane anion [7,8-$C_2B_9H_{12}]^-$, is much lower, at 0.020 a.u.

The weaker bonding interaction between the B(1) and the B(4), B(5), B(6) and B(7) atoms (compared to those between other pairs of boron atoms) inevitably gives a freer mobility to these atoms, and thus accounts for the low frequencies and large amplitudes of the corresponding vibrational "soft modes" that involve this set of boron atoms. The normal-coordinate analysis shows that the mode at ca. 200 cm^{-1} is of the A_2 type and involves mainly displacements of equivalent B(4), B(5), B(6) and B(7) atoms. During this vibration, atoms B(4) and B(6) are approaching B(1) whereas atoms B(5) and B(7) are moving away from it. The mode at ca. 300 cm^{-1} of the B_2 type is a wagging of the 6**k** B(1) atom in the B(2)B(1)B(3) "handle" back and forth in the symmetry plane defined by the B(1), B(10) and B(11) atoms.

Hence, all the data presented here and in the previous papers on 2,3-$C_2B_9H_{11}$ (**1**) and $[2\text{-}CB_{10}H_{11}]^-$ (**2**)[8,9] suggest that the formally closed eleven-vertex polyhedra **1**, **2** and **3** are **not formed by triangular faces only**, and therefore do not have genuine *closo* structures, in spite of having (2*n*+2) skeletal bonding electrons. It is obvious that they can be regarded as belonging to a category of "disobedient skeletons".[24]

It is of interest to attempt to reconcile the molecular graph that emerges from Bader's AIM approach with a more familiar Lipscomb-type "semi-localised" bonding diagram, which is based on two-electron two-centre and two-electron three-centre bonds. A schematic as in **I** (Scheme 1) below may be sketched as a representation of the bond paths and bond critical points of the molecular graph presented in Figure 3. In this diagram the hatched lines from B(1) to the B(4), B(7), B(5) and B(6) atoms, as well as from the B(4) to B(7) and from the B(5) to B(6) atoms, correspond to the "missing" two-centre bond paths and point to the thinning of the bonding "electronic glue" layer in these regions of the cage surface.

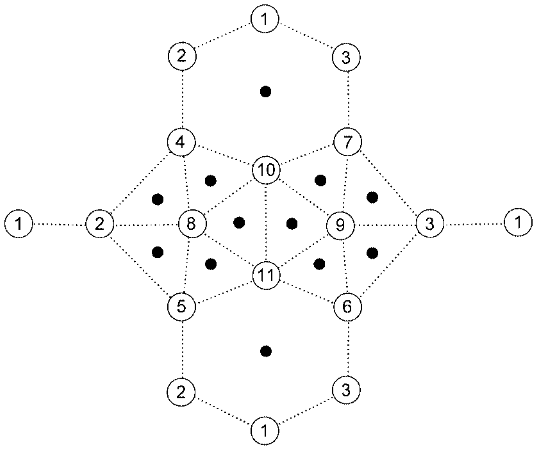


Scheme 1.

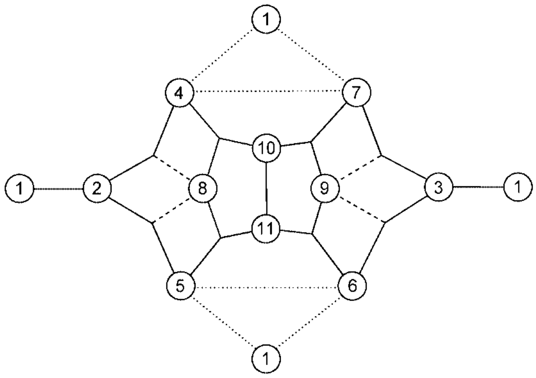
This schematic **I** can be supplemented by a schematic **II** (Scheme 2) to approximately reflect the rings and ring critical points of the molecular graph.

A corresponding classical Lipscomb-type semi-localized diagram, which seems to be a reasonable approximation of the electron density in terms of a factorization into localised two-electron bonding units, may be sketched as in schematic **III** (Scheme 3): this accommodates the 2*n*+2 cluster electrons required for a formal *closo* cluster-electron count if the dotted lines among the B(1), B(4), B(7), B(5) and B(6) atoms are taken to account for an overall total two-electron bonding interaction between B(1) and the B(4)B(7)B(5)B(6)B(10)B(11) region of the molecule.

The bonding representations involving the hatched lines, between B(2), B(4) and B(8), and also at the other three equivalent sites, B(2)B(5)B(8), B(3)B(6)B(9), and B(3)B(7)B(9), represent Lipscomb's semi-localised "partial-three-



Scheme 2.



Scheme 3.

centre bonds". Which of these two approaches to a description of the bonding is adopted is a matter of taste and habit.

The data obtained also shed new light on the long-recognized phenomenon of the very facile fluxionality of anion **3**, which mutually "scrambles" all the cluster vertices. A Lipscomb diamond-square-diamond (*dsd*) mechanism is reasonably established for the dynamic framework rearrangements in the 11-vertex *closo* polyhedra.[3a,6] Repeated *dsd* processes, involving the B(1)B(2)B(5)B(6) quadrangle or one of the three other equivalent units, lead to the time-average equivalence of all the boron atoms in **3** in the ^{11}B NMR spectrum in solution.[2,3,6] On the presumption that each of the quadrangles consists of two deltahedral faces, the *dsd* mechanism requires that, in its initiating diamond-to-square stage, a 6**k**–5**k** linkage [e.g. B(1)–B(5)] be broken, thus generating a square face, and then the nearest boron atoms undergo a slight rotation, and in the final square-to-diamond stage a new interboron linkage is formed, between B(2) and B(6). The B(6) atom thereby becomes a 6**k** vertex [instead of B(1)], and by repetition of this process, the 6**k** and all the 5**k** and 4**k** positions move over the whole polyhedron. However, the present results suggest that 6**k**–5**k** two-centre edge-localized bonds from B(1) to the B(4), B(5), B(6) and B(7) atoms are in fact absent, and, further, that multicentre bonding between B(1) and the B(4)B(5)B(6)B(7) quartet is weak. This bonding perception, together with the vibrational analysis, indicates that the process for the permutation of the 6**k** position can be regarded as being initiated simply via large-amplitude vibrations entailing the B(1) and the B(4), B(5), B(6), and B(7) atoms. Hence there is no need for a "*deus ex machina*" initially to "break" a (non-existent) 6**k**–5**k** linkage in the process of this cluster rearrangement.

These factors imply a very low activation energy for this process. Indeed, Paetzold and co-workers have calculated this value as 9.1 kJ mol^{-1}.[6] Incidental to this present work we have also obtained a similarly low calculated activation energy. This low value is clearly in accord with the experimental finding that fluxionality cannot be slowed sufficiently for individual resonances to be observed in the solution-state ^{11}B NMR spectrum down to 200 K,[2] which implies an experimental activation energy upper limit of ca. 30 kJ·mol^{-1}. The low activation energy adds further to the perception that distortions away from the C_{2v} ideal should be frequently observable in solid-state structures, since asymmetric crystal packing forces of even a few kJ mol^{-1} will easily force distortions along the *dsd* rearrangement coordinate. This last phenomenon is manifested, for example, in the crystallographically determined square-open-faced structure of the interesting fluxional eleven-vertex formally *closo* $[B_{11}H_9(Se_3)]^{2-}$ anion.[27]

Conclusions

Two low-frequency large-amplitude modes (at ca. 200 cm^{-1} and ca. 300 cm^{-1}) in the vibrational spectra of the salts of the $[B_{11}H_{11}]^{2-}$ anion **3** have been found, and these are shown by normal coordinate analysis to involve the 6**k** B(1) and the neighbouring 5**k** B(4), B(5), B(6) and B(7) atoms. A critical review of the published experimental and computed data on the geometry of $[B_{11}H_{11}]^{2-}$ species reveals that the interboron distances between the 6**k** and the 5**k** atoms are greater than the generally accepted interboron bonding limit of 2.0 Å. Calculations of the electron-density distribution in **3**, performed according to Bader's approach and grounded on DFT results, show that there are no two-centre bond paths between the 6**k** B(1) and 5**k** B(4), B(5), B(6), and B(7) atoms; nor are there any between the members of each of the B(4)–B(7) and B(5)–B(6) pairs. Hence the cage of the $[B_{11}H_{11}]^{2-}$ anion **3** contains two six-membered rings with low electron density. These consistent data lead to the conclusion that the eleven-vertex polyhedron of $[B_{11}H_{11}]^{2-}$, although possessing 2*n*+2 skeletal bonding electrons, is not in fact a pure deltahedron and not a straightforward *closo* cluster. A similar conclusion was made previously for the two corresponding eleven-vertex carbaboranes: the neutral 2,3-$C_2B_9H_{11}$ molecule **1** and the $[2\text{-}CB_{10}H_{11}]^-$ monoanion **2**.[8,9] The terminology "*quasi-closo*-polyhedron" has been suggested as a nomenclature to be associated with this interesting phenomenon.[9] Molecules **1**, **2** and **3** can therefore be placed in a category of "disobedient skeletons".[24] The data obtained also allow a refinement of the interpretation of the "diamond-square-diamond" mechanism as commonly applied to the fluxionality of anion **3** in solution.

Overall the results well illustrate the important general point that an allegedly triangulated deltahedron does not necessarily merit such a description when the actual bonding is considered in appropriate detail. More generally, it is important to recognise that the bonding within any cluster may often be much less uniform than a simple consideration of the polyhedral shape of the cluster may be taken to imply.

Experimental Section

Preparation of $Cs_2[B_{11}H_{11}]\cdot CsCl$ (3c). Procedure A: A filtered solution of $K_2[B_{11}H_{11}]$ (0.083 g, 0.4 mmol; prepared essentially as in ref.[6]) in absolute MeOH (2 mL) was added in drops to a stirred solution of CsCl (0.2 g, 1.2 mmol) in the same solvent (5 mL). After 10 min of vigorous stirring, the mother liquid was removed with a pipette from the white precipitate formed. The residue was washed with MeOH (2 × 3 mL) and thoroughly dried in vacuo, affording the mixed salt $Cs_2[B_{11}H_{11}]\cdot CsCl$ (**3c**) (0.15 g, 68%). $B_{11}H_{11}ClCs_3$ (564.20): calcd. B 21.06, H 1.95, Cl 6.29, Cs 70.69; found: B 21.02, H 2.08, Cl 5.76, Cs 70.27.

Procedure B: Analogous to procedure A, but with an inverse order of reagent addition, the same mixed salt $Cs_2[B_{11}H_{11}]\cdot CsCl$ (**3c**) was obtained in 56% yield. $B_{11}H_{11}ClCs_3$ (564.20) calcd. B 21.06, H 1.95, Cl 6.29, Cs 70.69; found: B 21.55, H 2.04, Cl 5.65, Cs 69.21.

Preparation of $Cs_2[B_{11}H_{11}]$ (3b): The salt $Cs_2[B_{11}H_{11}]$ was obtained in the same manner, but using CsF in EtOH instead of CsCl in MeOH.

Vibrational Spectra: Raman spectra for the solid salts sealed in capillaries, and also for a saturated aqueous solution of the salt **3c**, were recorded in the region 30–3500 cm^{-1} using LabRAM and U-1000 Jobin–Yvon laser Raman spectrometers. The spectra were excited by the 632.8 nm line of a He-Ne laser and the 514.5 nm line of an Ar^+ laser (Spectra Physics 2020). Depolarization ratios of the Raman lines in the spectrum of the aqueous solution of **3c** were estimated qualitatively. IR spectra in the region 150–3500 cm^{-1} for the salts **3b** and **3c** pressed with polyethylene, and for their Nujol mulls and KBr pellets, were obtained using a M-82 Carl Zeiss spectrophotometer and a Nicolet Magna-750 FTIR spectrometer.

Computational Details: Geometry optimization and calculations of the vibrational-mode frequencies and eigenvectors for the isolated anion **3** were carried out at the DFT B3LYP/6-31++G(d,p) level, using the G94W program suite.[28] Topological analysis of the theoretical electron-density distribution (based on the results of the DFT calculation) was accomplished using the AIMpac program package.[29] Calculations for the rearrangement process were carried out at the B3LYP/6-31G* level using the Gaussian 98 and Gaussian 03 packages,[30,31] and gave a value of 9.3 $kJ\,mol^{-1}$, comparable to the result of 9.1 $kJ\,mol^{-1}$ reported from a higher-level B3LYP/6-31++G(d,p) calculation.[6]

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