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The Electronic Structures of Polymeric Beryllium Hydride and Polymeric Boron Hydride

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The band structure of linear polymeric beryllium hydride is here calculated by an *ab initio* technique. The doubly-degenerate valence band has π symmetry and is composed of a beryllium p orbital and an antisymmetric combination of the appropriate hydrogen $1s$ orbitals. The Koopmans' ionization potential is calculated to be 16.1 eV and the direct band gap, found at X, is 15.2 eV. The charge distribution shows an electron drift of approximately 0.15 electrons from beryllium to the hydrogen atoms. The total energy calculation indicates that polymeric beryllium hydride is more stable than the monomer while polymeric boron hydride is less stable than the monomeric species. From the polymeric boron hydride system, an alternating-bond model is more stable than a symmetric bond model. The energy band structures of both models reveal that electron delocalization along the polymer chain is weak.

Key words: BeH_2 and BH_2 polymers – Energy band structures in polymeric BeH_2 and BH_2

1. Introduction

The white polymeric solid $[BeH_2]_n$ is prepared by heating $((CH_3)_3C)_2Be$ [1] or by treating $(CH_3)_2Be$ or $BeCl_2$ with lithium aluminium hydride in ethereal solution [2]. The polymer is known to decompose at 125°C. No direct evidence has so far been obtained on its structure: however, the most likely geometry is that of a linear chain of beryllium atoms linked by bridging hydrogen atoms tetrahedrally disposed around the beryllium atoms (Fig. 1). By contrast, there is no evidence for the existence of the analogous polymeric boron hydride $[BH_2]_n$.

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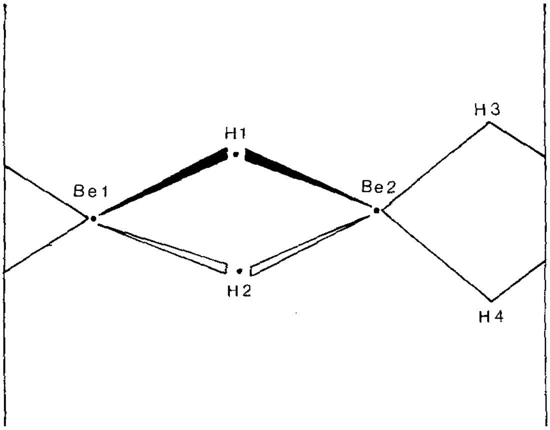

Fig. 1. Geometry of $((BeH_2)_2)_n$

Because of the general interest in the electronic structure of coordination polymers and in the structure of molecular beryllium borohydride [3, 4], we have investigated the above polymers by an *ab initio* solid-state approach [5].

2. Calculational Methods and Results

2.1. Beryllium Hydride Polymer

2.1.1. Optimization of the Beryllium 2*p* Exponent

It was first necessary to obtain a value for the beryllium 2*p* Slater-type-orbital (STO) exponent. In order to achieve this, a series of *ab initio* calculations was performed on an isolated linear BeH_2 molecule. The hydrogen atom 1*s* STO exponent and the beryllium-hydrogen interatomic distance were also optimized in the variational procedure.

The conventional single-zeta STO basis set of Be 1*s*, 2*s*, $2p_{x,y,z}$ and H 1*s* was expanded uniformly as a set of 3 GTO's per STO using the expansion set due to Stewart [6], the values obtained by Clementi [7] being used for the fixed Be 1*s* and 2*s* exponents.

The variational method employed was that of steepest descents, in this case the beryllium 2*p* exponent proving to be the most sensitive parameter. A discrete minimum of the total molecular energy function with respect to all three parameters was obtained. The optimum values of the three variational parameters obtained were: Be 2*p*, 1.114; $R_{\text{Be-H}}$, 2.542 a.u.; H 1*s*, 1.143.

The energy minimum obtained (−15.56786 a.u.) is 98.7% of the value (−15.77243 a.u.) reported by Kaufman [8] in a similar series of calculations in which an attempt was made to obtain thermodynamic data on BeH_2. Our calculated Be—H interatomic distance agrees extremely well with that of 2.54 a.u. (1.344 Å) obtained by Kaufman using a much larger basis set. The value of the hydrogen 1*s* orbital exponent suggests a slightly less diffuse function in the molecular species, although the energy term is found to be less sensitive to this parameter than to the Be 2*p* exponent or to the interatomic distance.

2.1.2. Electronic Band Structure of Polymeric Beryllium Hydride $[(BeH_2)_2]_n$

In the BeH_2 unit cell (Fig. 1) the Be—Be skeleton is linear; H(1) and H(2) are equidistant from Be(1) and Be(2) and lie in the *xy* plane; H(3) and H(4) are equidistant between Be(2) and the translated equivalent of Be(1) in the adjacent cell and are found in the *xz* plane. Thus, a screw axis of symmetry relates any BeH_2 unit to its neighbour in the polymer.

The basis sets employed in this set of calculations were identical in size and origin to the small basis sets employed earlier for polyethylene [9] and for the boron–nitrogen polymers [10], differing only in that the Be 2*p* and H 1*s* STO's used as the optimum values obtained (*vide supra*) in the molecular environment. Each STO was simulated by a linear combination of Gaussian orbitals. The smaller expansion set we used comprises a two-Gaussian expansion for the 1*s*, 2*s*, and 2*p* orbitals of beryllium and a single Gaussian to represent the hydrogen 1*s* orbital. Using our previous notation [9, 10], this is labelled Be(2, 2, 2)H(1). A three-Gaussian expansion, i.e. Be(3, 3, 3)H(3) for the STO's constituted the larger basis set.

Although total energies per unit cell are not given accurately in the nearest-neighbour approximation, a reasonable conformational analysis can be performed with regard to the H—Be—H angle. If the BeH interatomic distance is that obtained in the molecular optimization procedure for BeH_2, then the specification of H—Be—H fixes the geometry of the unit cell and the translation vector. A minimum value of the total energy per unit cell was found using the smaller basis set at a bond angle of 90° ($\pm 2.5°$) and, although no further analysis was carried out, it may be expected that rigorous optimization, if possible, would yield a Be—H distance somewhat different from that obtained for molecular BeH_2. Although we believe our adoption of the nearest-neighbour approximation makes no significant qualitative difference to our results, it does mean, nevertheless, that further optimization of the model via the Be—H distance is unprofitable.

Notwithstanding the latter remarks above, we should reasonably expect to reveal the comparative stabilities of linear monomeric BeH_2 and the polymer chain. We find, on comparing the total energy per unit cell of $[(BeH_2)_2]_n$ with twice that of linear monomeric BeH_2, that the energy of polymerization for the molecule is large and the polymer is stable. The energy changes in the hypothetical process BeH_2 (linear) → BeH_2 (angular) → BeH_2 (unit in polymer) were all calculated within the same basis and show that the linear-angular reorganization process is energetically unfavoured. However, on polymerization, this reorganization energy is more than offset by the new hydrogen bridges formed.

Figure 2 shows the electronic band structure of the polymer generated from the Be(3, 3, 3)H(3) basis using 15 points in the *k*-space. The structure of the valence bands is simple. Two low-lying "non-bonding" bands (not shown) are found at approximately −4.76 a.u., corresponding to the beryllium atomic 1*s* functions.

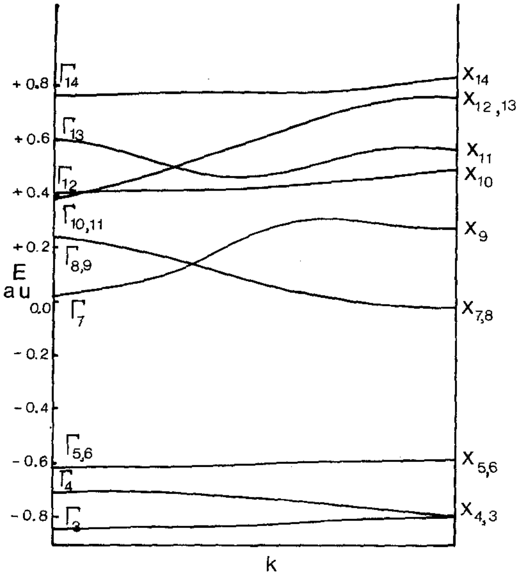

Fig. 2. Band structure for $((BeH_2)_2)_n$ using a Be(3, 3, 3)H(3) basis

Bands 3 and 4 meet at the point $k = \pi/a$ (i.e. X) and arise from localized bonding between pairs of hydrogens and the nearest beryllium atoms. Bands 5 and 6 are degenerate and arise from the orthogonal delocalized "π" bonding schemes involving, on the one hand, the beryllium $2p_y$ orbitals and the antisymmetric combination of the hydrogens in the xy plane and, on the other, the beryllium $2p_z$ orbitals and the antisymmetric combination of the hydrogens in the xz plane. The level nature of the valence band indicates that the hyperconjugative interaction in the polymeric material is weak. The highest point in the band is at the X-point ($k = \pi/a$). Direct transition from this point to the conduction region leads to the corresponding degenerate pair of π "antibonding" bands, which is the lowest conduction energy level.

The Koopmans' ionization potential is 0.592 a.u. (16.1 eV) and the *direct* valence-conduction band gap is 0.559 a.u. (15.2 eV), from which it may be inferred that the solid should be an electronic insulator.

An alternative way of viewing the bonding scheme and energy-band structure is through symmetry. The six possible linear combinations of the following basis functions (i.e. a pair of independent sets of three), Be(1)$2p_y$, Be(2)$2p_y$, [H(1)1s–H(2)1s], Be(1)$2p_z$, Be(2)$2p_z$, [H(3)1s–H(4)1s], define the "π" electronic system of the polymer chain. This means that the Bloch sums arising from these functions correspond to the independent sets of "π"-eigenfunctions of the linear chain, having periodic phase properties in precisely the order given by solution of the Schrödinger equation for a one-dimensional potential well. The eigenfunctions corresponding to the completely bonding combination (having all phase signs the same) give rise to bands 5 and 6 and those corresponding to the totally antibonding combination (alternating phase signs) to bands 10 and 11. The intermediate functions, involving only the legitimate atomic $2p_y$ and $2p_z$ orbitals and having approximately zero "pseudo-p" contribution, correspond to bands 8 and 9.

The sigma (σ) bonding scheme is independent of this. Band 3 is due mainly to the interaction of the beryllium $2p_x$ orbitals along the polymer axis and band 4 comprises a four-centre bonding situation involving the hydrogen 1*s* and sp^3-hybrid orbitals situated on the beryllium atoms. This type of bonding is also manifest in diborane and most of the boron hydrides. From the shape of these bands in Fig. 2, it would appear that the predominant factor which governs the stability of solid beryllium hydride is these σ-orbital-type bands.

2.1.3. Electronic Charge Distribution

The Mulliken population analysis for the minimum-energy case is presented in Table 1.

The inequality of (particularly) the Be(1), Be(2) and the hydrogen (1, 2, 3, 4) charges is a consequence of the nearest-neighbour approximation. Apart from this, the overall tendency is for donation to take place from beryllium to hydrogen, with a net charge of approximately -0.15 e accumulating on the hydrogen atom.

2.2. Boron Hydride Polymer

2.2.1. The Electronic Band Structure of Polymeric Boron Hydride $[(BH_2)_2]_n$

The band structure of the BeH_2 polymer shown in Fig. 2 poses an interesting question with respect to the linear polymer $((BH_2)_2)_n$ of similar geometry. If the band topology were basically the same, the extra two electrons given by boron would have to occupy the first degenerate pair of conduction bands, thus giving a linear metal.

We therefore investigated this geometry for the polymer as well as others based essentially on the polyethylene structure. Preliminary calculations were performed

Table 1. The atomic orbital populations of $[(BeH_2)_2]_n$ obtained from Be(3, 3, 3)H(3) and Be(2, 2, 2)H(1) basis sets

	Be(2, 2, 2)H(1)	Be(3, 3, 3)H(3)
Be (1) *s*	2.42	2.30
$p\sigma$	0.59	0.65
$p\pi$	0.76	0.81
total	3.77	3.76
Be (2) *s*	2.33	2.22
$p\sigma$	0.55	0.62
$p\pi$	0.73	0.78
total	3.61	3.62
H(1), H(2)	1.16	1.16
H(3), H(4)	1.15	1.15

on polyborane to determine the more suitable of these two possible geometries. In the first case a polyethylene-type geometry was employed, with all the interbond angles set at 110° and the B–H bond lengths at 1.195 Å. The B–B bond length was obtained by an energy-minimization technique. In the second geometry, the bridging hydrogen bonds were assigned length 1.329 Å in a model identical to the one employed for $[(BeH_2)_2]_n$; a variation procedure was then employed to determine the HBH angle. A small basis of size B(2, 2, 2)H(1) was employed in the optimization of the geometrical parameters. From these exercises it was found, perhaps surprisingly, that the polyethylene-type geometry with an optimum B—B bond length of 2.25 Å is more stable than the bridging-hydrogen bond model which possesses a HBH angle of 80°. Hence, the former geometry was then adopted as the likely configuration for polyborane. The generated B—B bond is long and is outside the range intuitively expected for stable boron–boron bonds. Even taking into account errors arising from our choice of basis set and from the nearest-neighbour approximation procedure, we can say that only weak bonding will exist between the BH_2 moieties in a regular polymer. This view is reinforced by the fact that the polymerization energy, calculated as the difference between the total energy per unit cell of polyborane and twice the energy of the BH_2 radical computed with the same B—H bond lengths and an optimized HBH angle, is -54 kcal mole^{-1}. A smaller destabilization energy (-27 kcal mole^{-1}) was obtained using a B(3, 3, 3)H(3) basis set.

The energy-band diagram for $[(BH_2)_2]_n$, obtained from the larger basis set calculation, is displayed in Fig. 3. The smaller basis calculation produces bands of similar shape although they are ~0.05 a.u. higher in energy. The highest point of the valence band lies at the Γ point, while the lowest point of the conduction band occurs at X. The calculated indirect band gap is 0.21 a.u. and 0.22 a.u. for the smaller and larger basis set, respectively. This band gap is considerably smaller than that for polyethylene [9]. Bands 1 and 2 (not shown in Fig. 3) consist of the bonding and antibonding combinations of the $1s$ orbitals of the boron atoms. The main constituents of bands 3 and 4 are the boron $2s$ orbitals and the hydrogen orbitals. The boron $2p_y$ orbital and the appropriate combination of hydrogen s orbitals form the main components of the fifth and sixth bonds.

The highest filled band is a bonding combination of the boron $2p_z$ orbitals while the first conduction band consists of the bonding combination of boron $2p_x$ orbitals. In polyethylene the compositions of the bands are rather similar although the ordering is different and the eighth band is, of course, occupied. The shape of this band in polyethylene [9, 11] indicates the delocalized nature of the framework bonding and this accounts partly for the stability of polyethylene. Polyborane, with two fewer electrons per unit cell, has only one occupied band contributing to boron–boron bonding. Hence, the —B—B— chain is weak.

Two significant points of interest arise from the energy-band diagram. Firstly, the bands are flat; this indicates a localized bonding picture of polyborane. Secondly, symmetry dictates that the seventh and the eighth band should be degenerate at the X-point. This clearly does not occur in Fig. 3, and the discrepancy arises from the

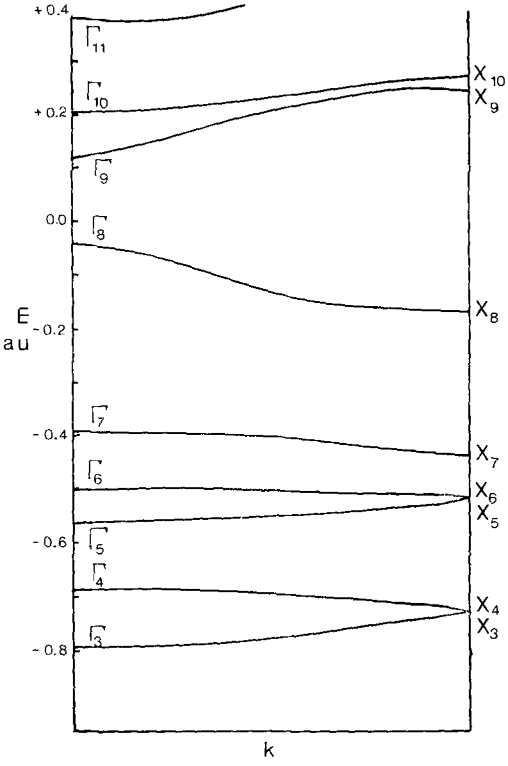

Fig. 3. Band structure for symmetrical $((BH_2)_2)_n$ using a B(3, 3, 3)H(3) basis

use of the restricted Hartree–Fock calculational procedure at the X-point. A similar situation occurs in regular polyene and here it is found that alternation relieves the doubly-degenerate orbital condition. Hence, we also examined an alternating-bond model of polyborane.

2.2.2. Electronic Charge Distribution

The Mulliken Population Analysis for the wavefunction of polyborane calculated using B(2, 2, 2)H(1) and B(3, 3, 3)H(3) basis sets is given in Table 2. The same gross features for the electron distribution are found for both bases. There is a small electron drift from the hydrogen atoms to the boron and a limited electron population in the boron $2p_x$ orbitals; this confirms the weak nature of the framework bonds. The electron distribution for monomeric BH_2 is also detailed for comparison.

2.2.3. The Alternating-Bond Model of Polyborane

The procedure we adopted entailed a systematic lengthening and shortening of the optimized B—B bond length R by a quantity Δ to give alternating-bond lengths $(R + \Delta)$ and $(R - \Delta)$. The total energy per unit cell was calculated using the smaller basis set and an energy minimum occurred when $\Delta = 0.45$ Å. On this basis, the optimum boron–boron bond lengths for the alternating-bond model are, therefore, 1.80 Å and 2.70 Å. The former bond length is within the range expected for stable boron–boron bonds but the latter is, at best, a very weak bond. The stabilization

Table 2. Electron distribution of regular and alternating-bond models of polyborane, BH_2, and B_2H_4

Basis set	B(2, 2, 2)H(1)	B(3, 3, 3)H(3)
a) Regular model of $[(BH_2)_2]_n$		
B1*s*	1.983	1.994
2*s*	1.202	1.173
$2p_x$	0.305	0.257
$2p_y$	1.045	1.001
$2p_z$	0.678	0.683
total	5.213	5.108
H	0.893	0.946
b) Alternating-bond model of $[(BH_2)_2]_n$		
B1*s*	1.982	1.994
2*s*	1.121	1.094
$2p_x$	0.322	0.286
$2p_y$	1.046	1.006
$2p_z$	0.729	0.713
total	5.200	5.094
H	0.900	0.953
c) BH_2		
B1*s*	1.990	1.996
2*s*	1.227	1.164
$2p_x$	0.987	0.941
$2p_y$	0.919	0.900
$2p_z$	0.000	0.000
total	5.123	5.001
H	0.939	0.999
d) B_2H_4		
1*s*	1.984	1.994
2*s*	1.075	1.051
$2p_x$	1.029	0.982
$2p_y$	1.051	1.008
$2p_z$	0.033	0.015
total	5.172	5.050
H	0.914	0.975

energy resulting from the bond alternation amounts to 19.4 kcal mole^{-1} for (B(2, 2, 2)H(1)) and 37.9 kcal mole^{-1} for the (B(3, 3, 3)H(3)) basis set. We prefer, therefore, an alternating-bond model over the regular bond picture for polyborane.

The energy-band diagram for the alternating-bond model (larger basis set) is given in Fig. 4. The smaller basis set gives an almost identical series of bands which are higher in energy by ~0.05 a.u. The highest point of the valence bands occurs at the Γ point while the lowest point of the conduction band is found at X. The calculated indirect band gap is 8.7 eV and the ionization potential obtained from the basis set B(3, 3, 3)H(3) is 12.5 eV. The composition of the bands is the same as those described for regular polyborane. The highest filled band, however, contains a significant proportion of boron–boron $2p_x$–$2p_x$ bonding together with a dominant

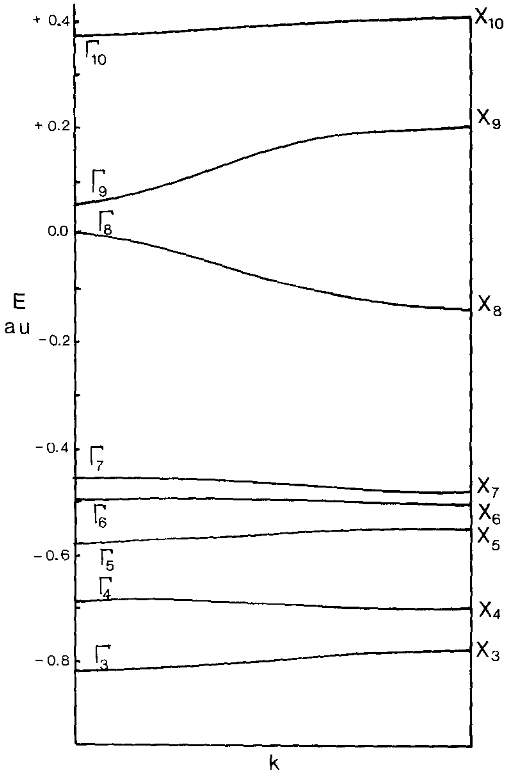

Fig. 4. Band structure for alternating $((BH_2)_2)_n$ using a B(3, 3, 3)H(3) basis

bonding combination from the boron $2p_z$ orbitals. This manifests itself in terms of band stabilization and, at the Γ-point, this band is lowered in energy by 1.77 eV compared with the regular model.

The filled bands show very little variation with the translational vector *k* and, when compared with the bands of regular polyborane, indicate a more localized situation for electrons. We conclude, therefore, from our work, that polyborane should consist of B_2H_4 units inter-connected by very weak boron–boron bonds. It is interesting to effect a comparison through calculation of the relevant *molecular* species using the same basis sets. Thus, for a B(3, 3, 3)H(3) basis, we find the most stable B_2H_4 model is the rotated one with each boron in trigonal site symmetry and 90° rotation angle. Lying 45 kcal mole^{-1} higher in the scale is the reorganized molecule where the geometry is the same as in the alternating polymer and, finally, less stable by 25.5 kcal mole^{-1} is the B_2H_4 unit bonded into the polymer. It seems, therefore, that in such a polymer the lack of two electrons, compared with polyethylene, would cause the system to assume an alternating pattern where the bulk of the available density would reside in alternate B—B bonds. Even this situation would be less stable than a simple molecular solid. Hence, it is clear that the stabilising energy yielded by the new framework bonds is more than offset by the (destabilising) energy required to reorganize B_2H_4 to the polyborane geometry where each boron is fully pyramidal.

2.2.4. The Charge Distribution

The Mulliken Populations for the wavefunction calculated for both bases for the alternating bond model of polyborane is given in Table 2. Bond alternation is seen to alter marginally the electron distribution. The largest change involves the transfer of electron density from the boron $2s$ orbital to the boron $2p_x$ and $2p_z$ orbitals, i.e. the framework orbitals.

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