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On the stability of Met-Car analogue clusters in the solid state

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Abstract

Ab initio density functional plane-wave calculations are performed for a number Met-Car analogue clusters of special stability which are assembled to form hypothetical three-dimensional structures and linear chains. The stabilization energies of various competing structures are determined and their atomic and electronic properties are predicted. Some of the solid phases are found to be metallic (B_8C_{12} and Si_8C_{12}) while others are semiconducting (N_8C_{12}) which suggests a range of new potential applications. The B_8C_{12} phase is also considered to be a possible high- T_c superconductor. The solid phases of P_8C_{12} are not predicted to be stable. The results demonstrate the viability of assembling new solid phases from clusters of various Met-Car analogues.

Met-Cars are an important new class of molecular clusters [1] and there are prospects for their use as building blocks in cluster-assembled materials. The M_8C_{12} cage has been shown to incorporate early transition metal, metal, non-metal and mixed metal atoms in the cluster cage [1] and therefore a range of interesting physical properties can be anticipated. Concurrently C_{20} has been synthesized [2] and its stability in the solid state predicted. Assembled Met-Car analogues of C_{20} with Si [3], N [4, 5], B [6] and P [5] could conceivably form similar stable solids. Interestingly, C_{20} in the cluster-assembled state is considered to be a candidate for showing high- T_c superconductivity [7]. Hence, the Met-Car analogues constitute not only a new class of molecular clusters but could also represent the building blocks of potentially novel materials with unusual electronic properties.

In this work the atomic and electronic structures of M_8C_{12} , $M = (N, B, Si, P)$ and of the C_{20} cluster are determined by an *ab initio* plane-wave method. Several linear chains of Si_8C_{12} clusters with different bonding characteristics are optimized in order to access the dimerization and stabilization energy (SE) of a possible solid phase nucleus. Calculations for linear chains

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of N_8C_{12} and B_8C_{12} clusters are also made to illustrate the conclusions. Finally, the SEs and configurations of several three-dimensional phases assembled from the chains are determined and an analysis of their band structures, bond populations and partial densities of states (PDOS) is performed.

The calculations are carried out using plane-wave density functional theory [8] within the GGA approximation, as parametrized by Perdew and Wang [9] and implemented in the computer code CASTEP [10]. Periodic boundary conditions are used and the pseudopotentials are of the ultrasoft type [11] with a kinetic energy cut-off such that convergence is ensured to less than 0.01 eV/atom and includes s, p and d projectors. Atomic relaxation is performed until all forces are equal to or less than $0.05 \text{ eV } \text{\AA}^{-1}$ for every atom and the total energy is converged to less than $2 \times 10^{-5} \text{ eV}$. The k -point sampling is of the Monkhorst–Pack [12] type and yields a k -point density of 0.06 \AA^{-1} in all calculations. The binding energies (BEs) of the clusters and the assembled solids are calculated with respect to the isolated constituent atoms. The relative stability of the solids is represented by a stabilization energy which is calculated with respect to the isolated clusters. The M ulliken charges, bond populations and PDOS are determined by projecting the eigenstates on to pseudoatomic wavefunctions [13] and are evaluated to less than 2% spilling parameter for all systems.

Following relaxation of the C_{20} cluster, which is a dodecahedron composed of pentagonal rings, the solid phase is assembled and optimized in a primitive orthorhombic structure (orc). In this work only primitive crystal structures are considered including simple cubic (sc) and triclinic (trc) although it is recognized that non-primitive structures with I-centred or F-centred lattices may also lead to stable configurations. The orc structure for the assembled cluster is distinct from those considered previously [15, 16] and its BE is found to be less than that of graphite by 0.873 eV/atom (see table 1) illustrating the feasibility of assembling C_{20} clusters in various stable or metastable crystalline forms [7, 14]. The SE, relative to the cluster, is found to be 5.912 eV/cluster corresponding to 0.49 eV/bond. The chemical bonding is therefore not very strong but the large SE makes the solid viable. The PDOS of the C_{20} solid indicates that it is a metal with a large contribution from p orbitals at the Fermi level. The cluster has three different C–C lengths, 1.39, 1.43 and 1.49  , with the majority being 1.43  . The solid shows a larger diversity of bond lengths with the dominant ones being 1.42, 1.46 and 1.48   corresponding to C–C bonds inside the cluster units. There are also bonds of length 1.35 and 1.61  , corresponding to C=C and C–C bonds between the C_{20} clusters along the [100] and [010] directions respectively. The three distinct types of bond have average bond populations of 1.26 (e), 1.00 (e) and 0.64 (e) in order of increasing bond length. This bond diversity tends to broaden the PDOS at the Fermi level. The M ulliken population analysis shows no significant differences between the cluster and the solid in respect of the charges associated with each carbon atom. The solid phase that is formed contains both open and closed C_{20} cage configurations that have not been previously analysed [15, 16].

The SEs for the Met-Car analogue solids (table 1) show that N_8C_{12} (sc) is the most stable with a remarkable 13.142 eV/cluster. Other high values shown indicate stable condensed phases for Si_8C_{12} (orc) and B_8C_{12} (sc, trc) but not for P_8C_{12} (orc, sc). The linear chains, figure 2, of highest stability tend to favour C–C inter-cluster bonding. The solid structures, figure 1, favour the bonding of C_2 – C_2 units between the clusters at least within the constraints of the primitive assemblies that have been considered. It might be expected that non-primitive assemblies which increase the density of inter-cluster bonding would increase the stability of the solid. However, it also seems to depend on the chemistry of the cluster since, for example, in previous work Ti_8C_{12} (C_{3v}) is found to have a SE of about 1.8 eV/cluster in a face-centred cubic (fcc) lattice [17, 18] and therefore seems unlikely to be very stable in solid form. The SEs for the clusters studied in the present work are 9.58 eV/cluster (or 0.8 eV/bond) for Si_8C_{12} ,

Table 1. Binding energies (BE), relative stabilization energies (SE) and inter-cluster binding energies (ICBE) for several structures. The ICBEs are shown with the atoms involved in the bonding.

System	BE (eV/atom)	SE (eV/cluster)	ICBE (eV/bond)
C graphite	9.467	—	—
C ₂₀ (I _h)	8.299	0	—
C ₂₀ (I _h) (orc)	8.594	5.912	0.493 (C–C)
Si ₈ C ₁₂ (C _{2v})	6.803	0	—
LC1 (C _{2v})	6.929	2.536	0.634 (C–C)
LC2 (C _{2v})	6.981	3.564	0.891 (C–C)
LC3 (C _{2v})	7.079	5.517	1.379 (C–C)
LSi1 (C _{2v})	6.932	2.583	1.292 (Si–Si)
LSi2 (C _{2v})	6.922	2.367	0.592 (Si–Si)
Si ₈ C ₁₂ (C _{2v}) (orc)	7.282	9.575	0.798 (C–C)
Si ₈ C ₁₂ (T _h)	6.768	0	—
Si ₈ C ₁₂ (T _h) (orc)	7.230	9.247	0.771 (C–C)
B ₈ C ₁₂ (T _h)	7.424	0	—
LB1 (T _h)	7.600	3.529	1.765 (B–C)
B ₈ C ₁₂ (T _h) (sc)	7.927	10.059	0.838 (C–C)
B ₈ C ₁₂ (T _h) (trc)	7.895	9.422	0.785 (B–C)
N ₈ C ₁₂ (T _h)	7.871	0	—
LN1 (T _h)	7.832	−0.772	−0.386 (N–N)
N ₈ C ₁₂ (T _h) (sc)	8.528	13.142	1.095 (C–C)
P ₈ C ₁₂ (T _h)	7.249	0	—
P ₈ C ₁₂ (C _{2v}) (orc)	7.258	0.189	0.015 (C–C)
P ₈ C ₁₂ (T _h) (sc)	7.365	2.323	0.193 (C–C)

10.06 eV/cluster (or 0.84 eV/bond) for B₈C₁₂ and 13.14 eV/cluster (or 1.1 eV/bond) for N₈C₁₂. These energies are all higher than that found for the C₂₀ cluster in the orc phase. The SEs for pairs of clusters (dimers) can be estimated from the linear chains and are considered to be generally small in chemical terms (1–3 eV). This suggests that the dimers may be hard to observe in ion mass spectroscopy experiments as is the case for Ti₈C₁₂ [17] since the ionization energies are estimated to be higher. Calculations show that the Ti₈C₁₂ dimer is bound by Ti–C bonds of 1.2 eV/bond [18] with 4.84 eV for the SE of the dimers. This latter value is of the same order as the ionization potential for the dimer.

The solid phases have densities ranging from 2.1 to 2.9 g cm^{−3}. It is found that the Si₈C₁₂ solid has a density of 2.50 g cm^{−3} which is slightly smaller than that of the C₂₀ phase (2.52 g cm^{−3}) and is due to the larger area/volume of the C_{2v} arrangement.

The bond lengths in the Si₈C₁₂ (C_{2v}) cluster are divided into two main groups: C=C (≈1.35 Å) and Si–C (≈1.82–1.91 Å). However, in the solid phase there are significant differences. The C–C bonds are longer (≈1.52–1.60 Å) and the Si–C bonds are more uniform and centred around 1.85 and 1.90 Å. As a result of the C₂–C₂ inter-cluster binding, the C₂ double carbon bonds become single bonds and the Si–C bonds become more uniform in length thus reducing the Jahn–Teller distortions present in the C_{2v} cluster. The C–C inter-cluster bonding is distinct along [100] and [010] due to the symmetry of the cluster. The Mlliken analysis indicates that in the solid phase Si atoms gain electrons (0.15 (e) on average) and C atoms lose electrons (0.1 (e) on average) relative to their populations in the cluster.

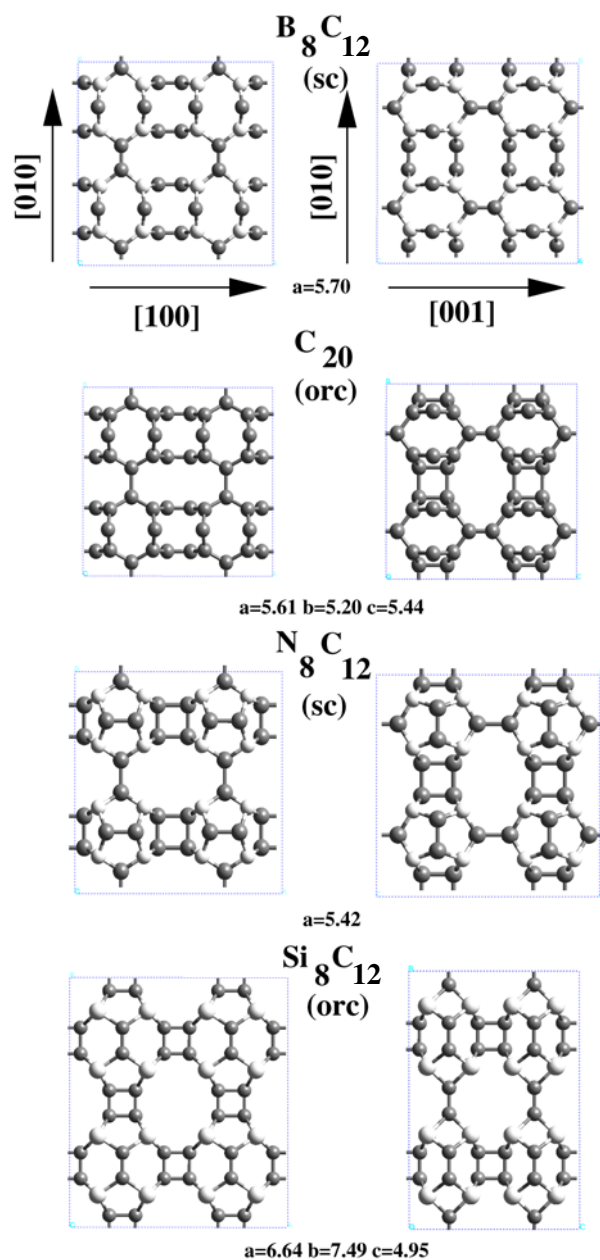


Figure 1. The structures of the four most stable solids. The views on the left and the right are along $[001]$ and $[100]$ respectively. Note the differences in the C–C inter-/intra-cluster bonding between the orc and sc structures. The unit cell parameters are in Å. The carbon atoms are depicted black and the other species white. (This figure is in colour only in the electronic version)

The B_8C_{12} cluster has two distinct bond lengths, 1.37 Å (C=C) and 1.55 Å (B–C), with bond populations of 1.15 (e) and 0.88 (e) respectively. When the sc phase is formed the intra-cluster C_2 (C=C) bonding is broken and replaced by double inter-cluster carbon bonds.

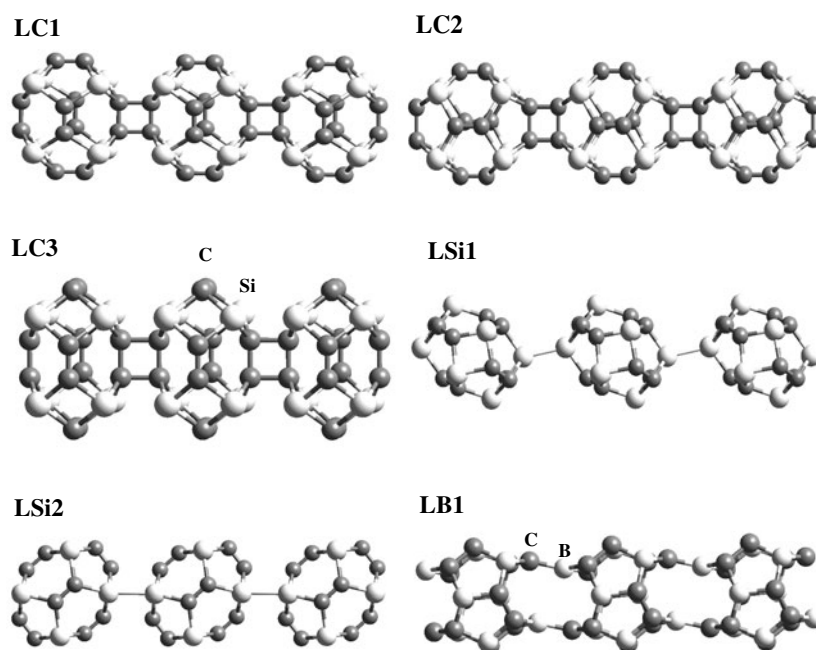


Figure 2. The optimized most stable linear chains. The carbon atoms are black and the other species white. The most stable chain is LC3 and has metallic properties.

The overall effect is that the bond length distribution does not change significantly. The inter-cluster bond lengths are 1.38 Å (C=C) and 1.57 Å (B–C) with bond populations of 1.29 (e) and 0.95 (e) respectively. The Mülliken analysis shows very small electron transfer effects from the C to the B atoms when the solid phase is assembled. The average change in charge for B is 0.04 (e) and for C it is -0.03 (e). The PDOS for the sc structure (figure 3) shows that the density of states at the Fermi level is large and mainly originating from p orbitals.

The triclinic B_8C_{12} solid has B–C inter-cluster bonding. In this case the intra-cluster C=C bonds are not broken and the main difference is the formation of a range of long B–C bonds (2.0–2.2 Å). The non-symmetrical way in which these bonds are distributed gives rise to the trc phase. This phase has metallic properties.

The N_8C_{12} cluster is characterized by three distinct bond lengths, 1.35 Å (C=C), 1.41 Å (N–C) and 1.45 Å (N–C). In the sc solid the average bond length increases significantly with bonds at 1.45 Å (C–C), 1.54 Å (C–C) and 1.58 Å (N–C). This indicates an increase in the number of single C–C bonds (in the sc structure the inter-cluster bonds all have the same approximate length) and in the lengths of N–C bonds. The Mülliken analysis again shows very small changes to the charges on the constituent atoms when the solid is formed. The average charge gain on N atoms is 0.06 (e) and the charge loss on C atoms is -0.04 (e). The intra-cluster C–C bonds are now those with the smallest bond populations (0.61 (e) compared to 1.15 (e) in the isolated cluster). In other words, the inter-cluster C–C bonding is stronger than the intra-cluster C–C bonding as it was for the B_8C_{12} solid phase.

The P_8C_{12} solid phases (sc and orc) have SEs that are small compared to those of the other Met-Car analogues considered in this work and are therefore less likely to form stable materials at least within the constraints of a primitive lattice structure.

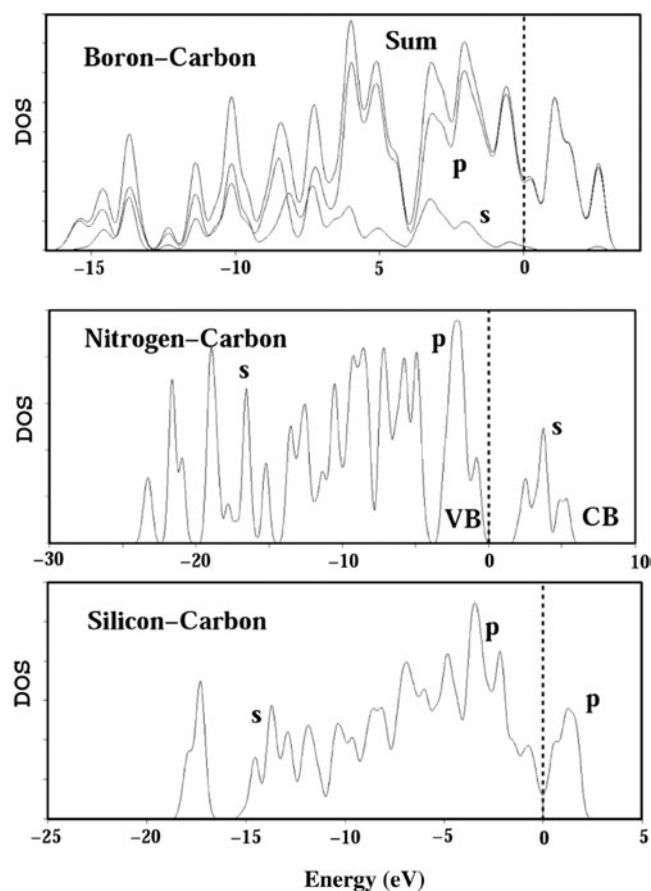


Figure 3. The densities of states for the B_8C_{12} , N_8C_{12} and Si_8C_{12} solid phases. For B_8C_{12} the contributions from s and p orbitals are shown as separate curves. For N_8C_{12} and Si_8C_{12} only the sum of the contributions is shown with some peaks labelled to indicate which orbital is dominant. The B_8C_{12} phase is a metal, N_8C_{12} is a semiconductor with $E_g \approx 1.5$ eV and Si_8C_{12} is a metal with a sharp decrease in the DOS at the Fermi level. All DOS are in arbitrary units and are aligned to the Fermi level at $E = 0$.

The Si_8C_{12} cluster is considered to be a Met-Car analogue of special stability [3]. In the present study the structure of highest BE is found to exhibit C_{2v} symmetry. Linear chains of this optimized structure can be assembled and their SEs and electronic characteristics determined. There are several possibilities for bonding the chains and figure 2 shows the structures of greatest stability. The linear chains of Si_8C_{12} are labelled LC1 (two C–C bonds/cluster), LC2 (two C–C bonds), LC3 (two C–C bonds), LSi1 (one Si–Si bond) and LSi2 (two Si–Si bonds). The N_8C_{12} linear chain is labelled LN1 (one N–C bond/cluster) and the B_8C_{12} linear chain is LB1 (two B–C bonds/cluster). The binding and SEs are given in table 1. The PDOS of the linear chains exhibit a range of electronic characteristics and are interesting in their own right since some of them show metallic behaviour and if assembled can function as quantum wires. Among the chains considered the one that exhibits the largest SE is LB1, followed by LC3 and LSi1. All are good conductors with high densities of states at the Fermi level dominated by p orbitals. When assembly is considered, these are to be the most likely arrangements. The LB1 chain yields an inter-cluster BE of 1.76 eV/bond (B–C) and has metallic

characteristics, but in the solid phase the highest stabilization is achieved with a sc structure in which there are C=C bonds between the clusters and not B–C bonds.

The PDOS for the solids (figure 3) show that the B_8C_{12} (T_h) (sc) and Si_8C_{12} (C_{2v}) (orc) phases are metals and that the N_8C_{12} (T_h) (sc) phase is a semiconductor with a band gap ≈ 1.5 eV. Of these three structures, B_8C_{12} (T_h) (sc) is the most interesting since p orbitals dominate the bonding at the Fermi level. This may indicate that the material is a possible superconductor.

In conclusion, an analysis has been performed of the bonding characteristics of the C_{20} (I_h) (orc) solid phase followed by a study of various Met-Car analogues focusing on their structure and SEs. The origin of the orc or sc structures lies in the types of carbon inter-cluster bond that can form: two types for orc (C–C and C=C with two different C–C lengths) and only one for sc (C=C). Triclinic phases with B–C inter-cluster bonding show evidence of bond distortion.

The SEs are found to be large and therefore lead to the prediction that the solid phases of Si_8C_{12} (orc), B_8C_{12} (sc) and N_8C_{12} (sc) are stable. These energies are considerably higher than that of the C_{20} (orc) solid phase and therefore lead to the conclusion that they are viable materials. In addition, one of the solids (B_8C_{12} (T_h) (orc)) shows metallic characteristics resulting from a large and dominant contribution from p orbitals at the Fermi level. This may be a first indication of superconductivity [19]. The P_8C_{12} assembled structures are found to be relatively less stable.

The electronic structures and SEs of several linear chains of Met-Car analogue clusters are calculated and their small values suggest small dimerization energies for the clusters in the gas phase. Some of the linear chains show metallic character and in this case assembly is more likely. It is proposed that if they can be assembled they can conceivably be used as quantum wires. It is also found that the Si_8C_{12} cluster favours the C_{2v} isomer as opposed to the T_h isomer studied previously [3]. The difference in energy between the two isomers (0.71 eV/cluster) means that the resulting assemblies are competitive. It is noted that both are conducting: Si_8C_{12} (C_{2v}) (orc) is a semiconductor and (T_h) (orc) is a metal.

The possibility of mixed Met-Car analogues adds to the variety of phases that can result from the combination of N, B and Si in C_{20} heterofullerenes. A more detailed study of the properties of mixed clusters is necessary for a better understanding of these processes.

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