ELSEVIER

5 August 1994

Chemical Physics Letters 225 (1994) 448–453

CHEMICAL
PHYSICS
LETTERS

Theoretical study of passivated small fullerenes $C_{24}X_4$ ($X=N$, P, As) and their isoelectronic equivalents $(BN)_{12}X_4$

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Received 5 April 1994; in final form 19 May 1994

Abstract

We present a first-principles theoretical study of complexes formed by combination of C rings and group-V atoms, which are the passivated analogs of the C_{28} fullerene. We study structural and electronic properties of $C_{24}X_4$ clusters, with $X=N$, P, As, in comparison to C_{28} and $C_{28}H_4$. All clusters with group-V atoms are predicted to be stable and chemically passive, with large HOMO–LUMO gaps. The conditions under which these clusters may be formed experimentally are considered. We also study the $(BN)_{12}N_4$ cluster, an isoelectronic equivalent of $C_{28}N_4$, and find a particularly stable and chemically passive isomer.

The study of carbon clusters is quickly advancing from the stage of investigating the properties of 'magic number' structures (such as the 'buckyball' and its derivatives, the fullerenes [1]), to the stage where producing clusters with desired properties and structure seems within reach of experiment. The endohedral complexes of the small fullerene C_{28}, reported recently by Guo et al. [2], may be thought of as examples of structures which are rendered stable artificially by the proper combination of a carbon cage and endohedral atom. The empty C_{28} cage [1] is chemically active, and consequently cannot be produced copiously by the same methods used for C_{60}, C_{70}, etc. When the proper type of atom is included in the reaction components (such as U, Zr, Ti, Hf) the ensuing endohedral complex is produced in amounts comparable to C_{60}. Theoretical studies of the properties of the isolated C_{28} cage and various endohedral compounds [4–9] have provided explanations for the observed stability of these complexes in terms of the interactions between electronic states of the cage and those of the endohedral atoms. It has also been speculated [2,4,8,10], although to our knowledge not yet achieved experimentally, that passivation of the chemically active sites of C_{28} by hydrogen will produce stable compounds.

In this Letter, we investigate theoretically the possibility of producing mixed composition clusters that have essentially the same structure as C_{28}, but are chemically stable without the presence of endohedral atoms. We consider the structure and electronic properties of clusters consisting of 24 C atoms and 4 atoms of group-V elements. This study was motivated by the observation that since the empty C_{28} cluster has four active sites, that is, C atoms with one unpaired electron each, substitution of these 4 C atoms by group-V atoms would produce paired electrons at these sites due to the higher valence of group-V atoms. This chemical substitution leads to a large gap in the electronic spectrum of the cluster between

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[1] The structure of this cluster was first discussed by Kroto [3].

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the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), thus rendering the cluster chemically stable. We use first-principles quantum mechanical calculations to study in detail the systems with 4 N, 4 P and 4 As atoms, and the isoelectronic system $(BN)_{12}N_4$. We also examine the conditions under which these systems may be produced experimentally. Finally, we offer a qualitative discussion of possible uses and applications of these compounds.

Our quantum mechanical calculations of electronic states and structural geometries are based on the density functional theory in the local density approximation (LDA) [11]. We use a Gaussian-orbital basis set for representing the electronic states and an accurate numerical integration scheme in real space to evaluate the cluster total energies [12]. Atomic forces are calculated with the Hellmann–Feynman–Pulay approach [13], and are used together with the energy in a conjugate-gradient scheme to relax the cluster structures. The structures of all the complexes were relaxed until the forces on various atoms vanished to 0.01 au. We have used the recently proposed gradient corrections to the LDA which are known to significantly increase the accuracy of energy comparisons in finite systems [14], in order to calculate reliable cohesive energies and reaction energies. All the geometries we studied have full tetrahedral symmetry.

We begin with a brief review of the structure and electronic properties of the bare C_{28} cluster. The relaxed geometry is shown in Fig. 1 and some of its features are given in more detail in Table 1. In Fig. 2 we show the electronic spectrum of the valence electrons of C_{28}. The splitting of levels in one-, two- and three-fold degeneracies is a result of the overall tetrahedral symmetry of the cluster. The levels near the Fermi energy consist of a triplet t_2 state (which is partially occupied by four electrons in the spin-unpolarized calculation) and an empty singlet a_1 state. In the spin-polarized calculation three spin-up electrons occupy the t_2 level and one spin-up electron occupies the a_1 state, giving rise to a quintet spin ($S=2$) state. These results are in good agreement with the results of Guo et al. [4], which are based on a different methodology, the self-consistent field Hartree–Fock approach (SCF HF): the atomic distances obtained here differ

Table 1
Structural features and electronic properties of C_{28} and related complexes: r_A, r_B, r_C are the distances of sites A, B, C from the center of the cluster (in Å, see also Fig. 1); the HOMO–LUMO gap (in eV); and the binding energy per atom E_B (in eV)

Cluster	r_A	r_B	r_C	Gap	E_B
C_{28}	2.46	2.44	2.40	0.0	7.00
$C_{28}H_4$	2.66	2.43	2.36	2.2	6.50
$C_{24}N_4$	2.51	2.38	2.38	3.1	6.80
$C_{24}P_4$	3.09	2.49	2.39	2.0	6.41
$C_{24}As_4$	3.19	2.52	2.42	2.0	6.33
$(BN)_{12}N_4$	2.57	2.38	2.48	3.1	6.03

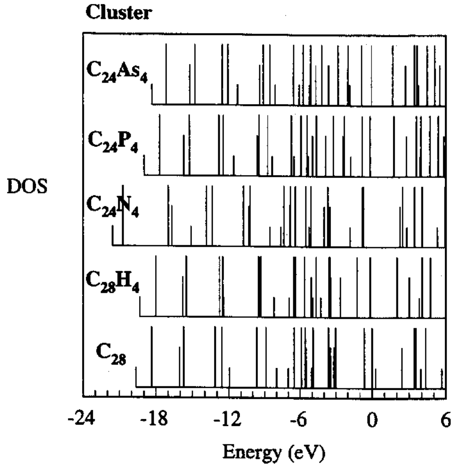

Fig. 2. The electronic spectra of the C_{28} cluster and its derivatives. The zero of energy is the HOMO of the bare C_{28} cluster. Notice the large separation (gap) between HOMO (highest level below 0) and LUMO (lowest level above 0) states in all the derivatives (see also Table 1).

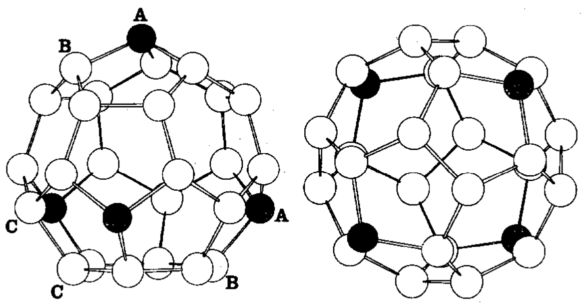

Fig. 1. The structure of the C_{28} cluster and derivatives. Two views are given for better perspective. The three different sites are marked A, B, C (several equivalent sites are marked, in particular those that lie on the plane of Fig. 3). The tetrahedral apex atoms shown shaded are the A sites to which H atoms attach, or which are substituted by group-V atoms.

by less than 2% from the results of Guo et al. [4], while the quantum numbers characterizing the spin-polarized ground state wavefunction are exactly the same. In both the spin-polarized and spin-averaged calculations, the essential physical information is contained in the statement that the Fermi level straddles a partially occupied level. This makes the cluster chemically active, and consequently unstable in an environment where many reactions with other structures are possible. We suggest that this is the primary reason that the bare C_{28} does not survive in the usual experimental conditions for producing fullerenes.

Detailed study of the electronic wavefunctions of the t_2 and a_1 states reveals that they are both heavily concentrated on the four apex atoms (see Fig. 1). Thus, the C_{28} bare cluster is characterized by the presence of four unpaired electrons (also referred to as 'dangling bonds') at the apex atoms. When these atoms are bonded to H atoms, the electronic spectrum and consequently the cluster chemical properties are drastically altered. The changes in the electronic spectrum due to hydrogenation are shown in Fig. 2. A large HOMO–LUMO gap of 2.2 eV opens. This is accompanied by some distortion of the cage geometry, with the apex atoms moving outward, while the rest of the atoms move slightly inward (see Table 1; the 'in' and 'out' directions are defined with respect to the geometric center of the cluster). These results compare well with the structure obtained through SCF HF calculations by Guo et al. [4]: all atomic distances agree to within 1%. It is expected that the $C_{28}H_4$ complex will be chemically unreactive and stable, assuming that it can be formed.

The focus of the present work is to explore ways of achieving the same effect in terms of stability and chemical reactivity with different elements and without the use of endohedral atoms. We have considered the passivation of the dangling bonds in C_{28} by chemical substitution of the C atoms at the active apex sites with group-V atoms, inspired by the passivation of semiconductor surfaces. It is well documented that Si and Ge (111) surfaces on which threefold coordinated atoms have dangling bonds can be passivated by monolayers of group-V atoms, which substitute for the surface atoms [15–18]. The extra valence electron of the group-V atoms results in a surface with all the electrons paired: The group-V atoms have a total of five valence electrons associated with them, three of which participate in covalent bonding with substrate atoms, while the other two form the so-called 'lone-pair' state, a fully occupied electronic level. A band gap separates occupied from unoccupied electronic states. These surfaces are chemically passive and very stable.

We have studied substitution by three kinds of group-V atoms (N, P and As) at the apex positions of C_{28}. All cases resulted in systems with large HOMO–LUMO gaps as seen in Fig. 2 and Table 1. In all cases passivation is achieved by the mechanism described above, i.e. the formation of filled lone-pair orbitals at the group-V atoms. This is shown in Fig. 3 for the case of $C_{24}N_4$. The comparison of charge density distributions in C_{28} and $C_{24}N_4$ clearly demonstrates the larger amount of electronic charge around the N nuclei. This is expected, since N has higher valence and is a more electronegative element than C. This asymmetry in charge distribution also polarizes the covalent bonds. The case of $C_{24}N_4$ is somewhat special: The spectrum of electronic states in this cluster is unusually broad compared to the other cases, as seen in Fig. 2. This can be attributed to the very low energy of the N s atomic level, which gives rise to a state of low energy in the cluster. Similar effects are observed when N is a substitutional defect in bulk diamond, where it gives rise to a 'hyperdeep' defect level [19].

The cluster geometry is significantly affected by the substitution, with similar trends as in the case of the hydrogenated $C_{28}H_4$ cluster (see Table 1): the apex atoms move outward and the rest of the atoms move inward. The amount by which the P and As move outward is very large compared to the case of N and the hydrogenated cluster. This, however, is purely an atomic size effect, since the P and As atoms have significantly larger covalent radii than N and C. It is worthwhile to investigate in some detail the very low energy of the $C_{24}N_4$ cluster (see Table 1). To this end we compare the bond-lengths and bond-angles of the group-V atoms in the $C_{24}X_4$ clusters and in the corresponding trimethyl molecules $(CH_3)_3X$ (X=N, P, As). In those molecules there is more structural freedom in achieving the optimal geometry, since there is no cage to introduce structural constraints, as in the case of the clusters. In Table 2 we present a comparison of the relevant geometrical features of the clusters and trimethyl molecules [20]. This compar-

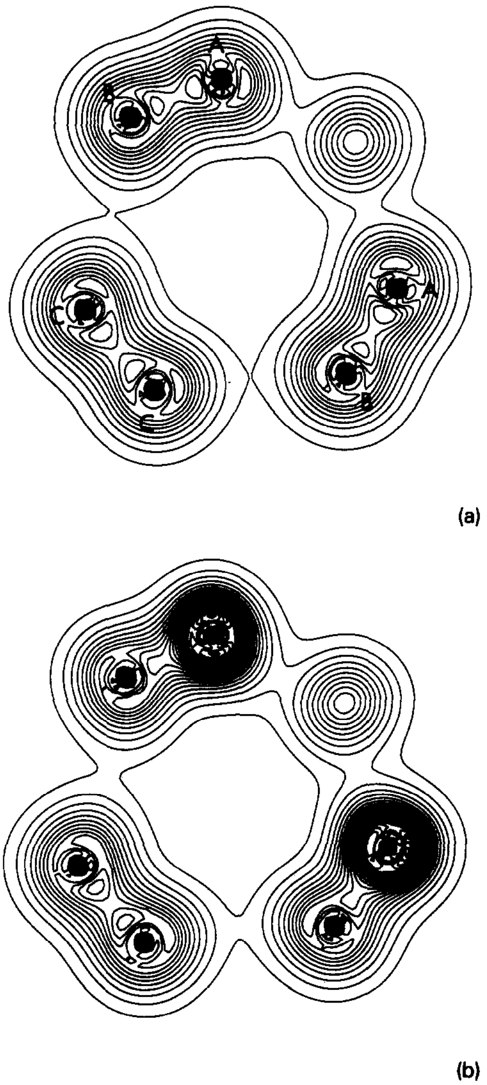

Fig. 3. Comparison of the total valence charge densities for (a) the bare C_{28} cluster and (b) the $C_{24}N_4$ cluster. Notice the polarization of the charge distribution in (b) around the N atoms and the asymmetry in the adjacent bonds.

Table 2
Comparison of structural features in $C_{24}X_4$ clusters and corresponding $(CH_3)_3X$ molecules

X	C–X bond (Å)		C–X–C angle (deg)	
	in $C_{24}X_4$	in $(CH_3)_3X$	in $C_{24}X_4$	in $(CH_3)_3X$
N	1.431	1.458	108.5	110.9
P	1.803	1.847	88.4	98.6
As	1.902	1.979	86.6	98.8

ison reveals that for the cluster and molecule that involve N, the bond-lengths and the bond-angles are very similar. Since the less constrained geometry of the molecule essentially corresponds to the optimal bond-length and bond-angle values, we conclude that the geometry of $C_{24}N_4$ is such that both bond-length and bond-angle requirements can be satisfied in this structure in a near-optimal fashion. In contrast, the bond-angles in the clusters with P or As are considerably smaller than their optimal values in the corresponding molecules. Satisfying bond-length requirements is a more important requirement due to the larger energy cost for bond stretching. However, the larger covalent radii of P and As make it impossible to satisfy simultaneously the bond-length and bond-angle requirements in the $C_{24}P_4$ and $C_{24}As_4$ clusters. As a consequence, while the $C_{24}N_4$ cluster has an almost optimal geometry, the structures of $C_{24}P_4$ and $C_{24}As_4$ involve a certain amount of 'strain' relative to the optimal geometry, which is the result of the closed cage structure.

Although the $C_{24}X_4$ (X=N, P, As) complexes have large cohesive energies and wide HOMO–LUMO gaps, which suggest that they are stable and chemically unreactive systems, it is an open question whether they can be produced experimentally. We address this important question by considering reaction energies under different conditions. We will study the following reaction:

$$\tfrac{24}{28}\,C_{28} + \frac{4}{n}\,X_n \rightarrow C_{24}X_4 + \Delta Q\,, \qquad (1)$$

where X=N, P, As and n is the molecular form that serves as atomic reservoir for the group-V atoms. The justification for this choice is as follows: In the complicated environment that leads to production of carbon clusters of various sizes, the kinetics of cluster formation must be a determining factor, and the clusters that survive are the locally stable and least reactive structures. The relevant issue then is, how does the presence of other elements (such as N, P, As) in the reaction cycle affect the relative stability and reactivity of particular clusters. Since it is not possible to consider all channels of formation and dissociation of the cluster complexes, we shall study the simple choice described by reaction (1). Thus, this reaction will indicate whether formation of the $C_{24}X_4$ clusters is thermodynamically competitive with that of C_{28} clusters. We will also compare the reaction energies of (1) to that of the reaction

$$C_{28}+\frac{4}{n}H_n \rightarrow C_{28}H_4+\Delta Q\,. \qquad (2)$$

We have studied several different choices for the atomic reservoirs, namely $n=1$, 2, 4 and ∞ for the group-V atoms P and As and $n=1$, 2 for N. The reason for these choices is that the most stable molecular forms of group-V atoms are dimers ($n=2$ for N) and tetramers ($n=4$ for P and As). The other two choices correspond to the limiting situations of free atoms ($n=1$) and solids ($n=\infty$). For the cases of N and H, there is no stable solid form at zero pressure. Thus, our choices encompass the widest possible range of chemical potentials for the group-V atoms. For H, we considered the atomic ($n=1$) and molecular ($n=2$) reservoirs. The solid cohesive energies per atom are taken from tabulated values [20], all other values were calculated explicitly. The results of our calculations for ΔQ in reactions (1) and (2) are summarized in Fig. 4. When ΔQ is *negative* the reaction is *exothermic* and will therefore proceed to the right. As seen from Fig. 4, we find that in the case of N and H, any possible atomic reservoir will lead to exothermic reactions, whereas in the case of P and As, only reservoirs involving dimers or free atoms will lead to exothermic reactions. We conclude that no matter how N is supplied to the reaction (1), the reaction will proceed to the right, while P and As have to be broken down to at least their dimer form, before the reaction becomes possible. Similarly, it appears that reaction (2) is always exothermic.

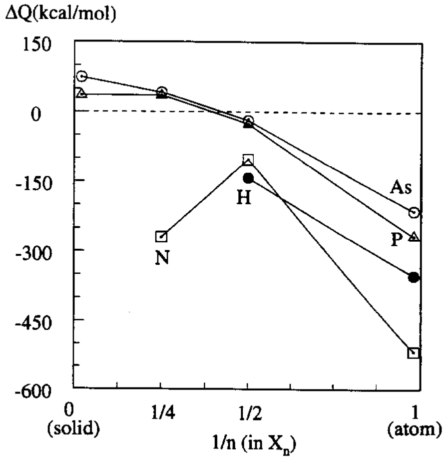

Fig. 4. Energy release (ΔQ) for the reactions (1) and (2). Negative values of ΔQ correspond to exothermic reactions. The abscissa is the inverse of the index n in the molecular form X_n used as the atomic reservoir for the group-V atoms (X = N, P, As) and for H atoms.

In addition to $C_{24}X_4$, chemically passive structures of the same size and of similar properties may be formed by substituting the 24 C atoms by 12 B–N pairs. This substitution is isoelectronic with the $C_{24}X_4$ complexes. There are two possible isomers of this cluster that preserve the tetrahedral symmetry: the first isomer has the 12 B atoms as nearest neighbors of the four apex sites (B sites, see Fig. 1) and the 12 N atoms in the remaining sites (C sites, see Fig. 1); the second isomer has the B and N atoms in B and C sites interchanged. In both isomers the four apex A sites are occupied by group-V atoms, so that the saturation of dangling bonds is effected in the same way as in the $C_{24}X_4$ complexes. We have studied in detail both isomers of the $(BN)_{12}X_4$ cluster with X = N. The first isomer has 36 B–N bonds and 6 N–N bonds; the second isomer has 24 B–N bonds, 12 N–N bonds and 6 B–B bonds. Within our total energy calculations, the first isomer is lower in energy by 17.45 eV. This large energy difference is probably due to the larger number of heteropolar bonds in the first isomer. Since the energy difference between the isomers is very large, we turn our attention to the lower energy structure. With respect to the separated spin-polarized atoms, this isomer has a large binding energy (6.03 eV/atom, see Table 1). It is also an electronically closed shell system, with a t_2–t_1 HOMO–LUMO gap of 3.11 eV (equal to the gap of the $C_{28}N_4$ cluster). The t_2 HOMO level is slightly lower in energy than the corresponding C_{28} level and, as in the case of the isoelectronic $C_{28}H_4$, the intragap a_1 and e levels are swept to higher energies. The stable $(BN)_{12}N_4$ cluster is structurally and electronically quite similar to the passivated cluster $C_{24}N_4$ and even to $C_{28}H_4$ (compare features in Table 1). It is interesting to note that the electronic structure for the second (higher energy) isomer of $(BN)_{12}N_4$ resembles that of the bare C_{28} cluster, i.e. the unoccupied a_1 and e levels have energies close to what is found in the C_{28} spectrum. Using as a chemical reservoir B_2 and N_2 molecules, we find that formation of the stable $(BN)_{12}N_4$ isomer is exothermic by 1433 kcal/mol. If instead we allow for the presence of BN molecules in the reaction, formation of the stable $(BN)_{12}N_4$ isomer is again exothermic, but only by 270 kcal/mol. Formation of the less stable $(BN)_{12}N_4$ isomer is exothermic by 1031 kcal/mol in the first case and endothermic by 132 kcal/mol in the second case.

Finally we discuss some possible advantages of forming these complexes. It is evident that bare C_{28} is difficult to produce and isolate due to its high chemical reactivity. Stabilizing it with endohedral atoms is an interesting possibility that has been demonstrated already [2]. Hydrogenating the cluster is also interesting and potentially useful. We expect that in the hydrogenated cluster the apex atoms should behave similar to sites in fully saturated hydrocarbons. The $C_{24}N_4$ complex, on the other hand, while chemically more inert than C_{28}, is characterized by the presence of lone-pair orbitals at the apex sites, and may exhibit the chemical behavior of an ammonia molecule. Since there are four apex sites in $C_{24}N_4$, this 'super-ammonia' molecule may be amenable to orientation and polarization. By analogy, the $C_{24}P_4$ and $C_{24}As_4$ complexes are expected to behave like 'super-phosphine' and 'super-arsine'. Combinations of the three complexes ($C_{24}X_nY_m$, X and Y=N, P, or As, with $n+m=4$) are also likely to be stable. The mixed complexes may have enhanced polarizabilities and other interesting chemical and physical properties due to the lower symmetry. From our theoretical analysis, it appears that these structures could be as stable as the endohedral complexes and possibly more versatile and interesting than the hydrogenated $C_{28}H_4$ cluster. We also note that $C_{24}N_4$ should be easier to produce than $C_{28}H_4$, when the reservoir is single atoms, as far as exothermicity is concerned ($n=1$ in Fig. 4), while the reverse is true when the reservoir is diatomic molecules ($n=2$ in Fig. 4).

KAJ gratefully acknowledges the support of the Research Corporation and a Research Professorship at Central Michigan University. EK acknowledges support in part by the Materials Research Laboratory of Harvard University, which is funded by the National Science Foundation. MRP acknowledges support in part by the Office of Naval Research.

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