Octacoordinated main-group element centres in a planar cyclic B_8 environment: an *ab initio* study

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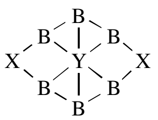
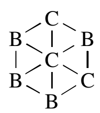
Density functional theory [B3LYP/6-311G(2df)] calculations predict stable planar structures of the nonclassical compounds XB_8 ($X = Si, P^+$) containing central octacoordinated silicon and phosphorus atoms, and a fluxional structure of CB_8 with effective octacoordination of the carbon atom.

Studies of novel stable structures with non-standard geometries formed by hypercoordinated main-group elements are among the most important tasks of contemporary structural chemistry.[1–4] The conditions for stabilization of planar tetracoordinated carbon centres[5] have been realised in a variety of organoelement compounds.[6,7] Novel stable systems **1**–**3** containing planar hexacoordinated carbon[2,4] and boron[8] centres were recently described using *ab initio* calculations.



X = NH, O; Y = C, B^-

1



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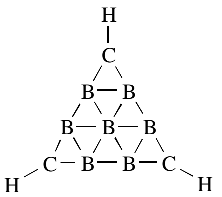

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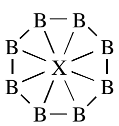
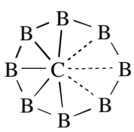
The multicentre bonding type found in **1**–**3** is also expected to be observed in other planar structures with octacoordinated main-group element centres.

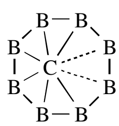
Here, we report on density functional theory [B3LYP/6-311G(2df)] calculations of compounds **4** ($X = Si, P^+$), which contain octacoordinated planar silicon and phosphorus centres, and also of their carbon analogue **4** (X = C), which possesses a fluxional structure with effective octacoordination of the planar carbon atom.



4, D_{8h}



5, C_{2v}



6, C_{2v}

According to the DFT calculations,† compounds **4** ($X = Si, P^+$) possess highly symmetrical D_{8h} planar structures and correspond to the minima ($\lambda = 0$; hereafter, λ designates the number of hessian negative eigenvalues at a given stationary point) on the corresponding potential energy surfaces (PES), whereas the D_{8h} structure of **4** (X = C) corresponds to the hilltop ($\lambda = 2$) on the CB_8 PES. Table 1 and Figure 1 demonstrate their geometry and energy characteristics.

The energy minimum ($\lambda = 0$) for the cyclic structure of CB_8 is represented by the C_{2v} form of **5** with the pentacoordinated central carbon. The lengths of the B–C bonds formed by the central carbon with the peripheral borons in **5** are equal to 1.590, 1.627 and 1.753 Å and are in the range of experimental lengths for a single B–C bond in carboranes.[10] The lengths of the peripheral B–B bonds, which are in the range 1.512–1.548 Å, are shorter than those observed for double B–B bonds (~1.63 Å).[11,12]

† DFT calculations have been performed with B3LYP functional and with 6-311G(2df) basis sets using the Gaussian-98 program package.[9] Geometry optimization was carried out with a 'tight' key-word. Total energies of the structures of **4** (X = C), **5** and **6** were finally calculated by the CCSD/6-311G(2d) method at the B3LYP/6-311G(2df) geometry.

Table 1 Data of DFT and CCSD calculations for compounds **4**–**6**.[a]

Structure, symmetry	Method	E_{tot}	λ	ΔE	ΔE_{ZPE}	$\omega_1/i\omega$
4 (X = C)	B3LYP/6-311G(2df)	–236.578192	2	17.61	14.79	*i*513(e)
D_{8h}	CCSD(fc)/6-311G(2d)	–235.766545	–	18.00	—	—
4 (X = Si) D_{8h}	B3LYP/6-311G(2df)	–488.132109	0	—	—	146
4 ($X = P^+$) D_{8h}	B3LYP/6-311G(2df)	–539.671526	0	—	—	184
5	B3LYP/6-311G(2df)	–236.606253	0	0	0	87.4
C_{2v}	CCSD(fc)/6-311G(2d)	–235.795224	–	0	—	—
6	B3LYP/6-311G(2df)	–236.604204	1	1.29	0.93	*i*149
C_{2v}	CCSD(fc)/6-311G(2d)	–235.791954	–	2.05	—	—

[a] E_{tot} (in a.u.) is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of the negative hessian eigenvalues; ΔE and ΔE_{ZPE} (in kcal mol^{-1}) are relative energies without and with accounting ZPE; $\omega_1/i\omega$ (in cm^{-1}) is the smallest or imaginary harmonic vibration frequency.

The structure of **5** is highly fluxional and undergoes rapid topomerization according to the scheme **5a** ⇄ **6a** ⇄ **5b** ⇄ **6b** ⇄ ⇄ **5c** ⇄ ..., where the structures of **6** with C_{2v} symmetry correspond to saddle points ($\lambda = 1$) on the CB_8 PES and serve as true transition states for the low-energy barrier (1.3 kcal mol^{-1}) process in which internal C–B bonds switch sequentially within the cycle. With the account taken for zero point energy, this barrier decreases to 0.9 kcal mol^{-1}. For the more accurate estimation of relative energies of the structures of **4** (X = C), **5** and **6**, we performed single point CCSD(fc)/6-311G(2d) calculations of these structures at the B3LYP/6-311G(2df) geometries. As can be seen in Table 1, the relative energies obtained by DFT

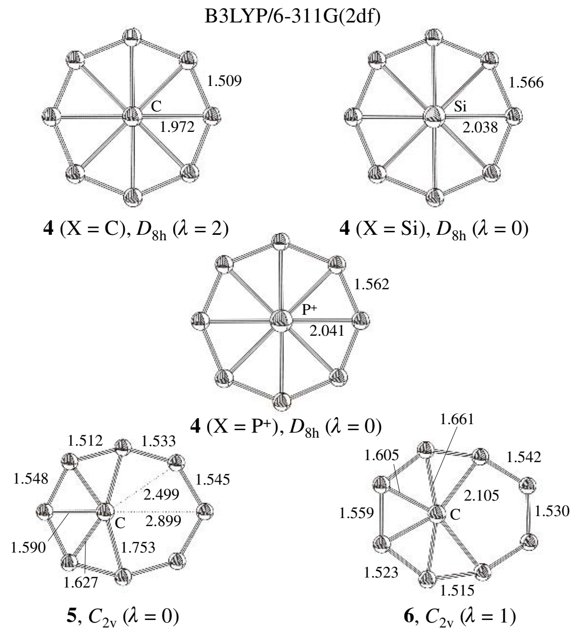
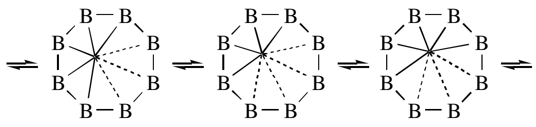
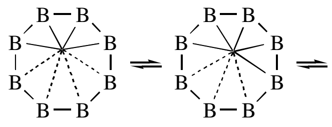


Figure 1 Geometry parameters of the structures of **4**–**6** calculated by the DFT method. The bond lengths are indicated in angström units.



5a **6a** **5b**



6b **5c**

and CCSD(fc)/6-311G(2d) methods agree well. A very small value of the energy barrier for the rearrangement **5a** $\rightleftharpoons$ **6a** $\rightleftharpoons$ $\rightleftharpoons$ **5b** $\rightleftharpoons$ **6b** $\rightleftharpoons$ **5c** $\rightleftharpoons$ ... allows one to consider the fluxional system of **5** as that with the effective octacoordination of the central carbon.

In compounds **4** (X = Si, P^+) with octacoordinated central silicon and phosphorus centres, the lengths of the BSi and BP bonds were calculated to be 2.038 and 2.041 Å. These values exceed slightly the sum of the covalent radii of boron and silicon (1.98 Å) or boron and phosphorus (1.91 Å), which may be explained as a consequence of the multicentre bonding of the central atoms with the surrounding ligating boron atoms.

All compounds **4**–**6** are aromatic 6π-electron systems with three occupied π-orbitals (see Figure 2). According to MO analysis, the π-electron system of **4** contains only 6π electrons, four of which furnishing by boron atoms and the other two by the central atom X.

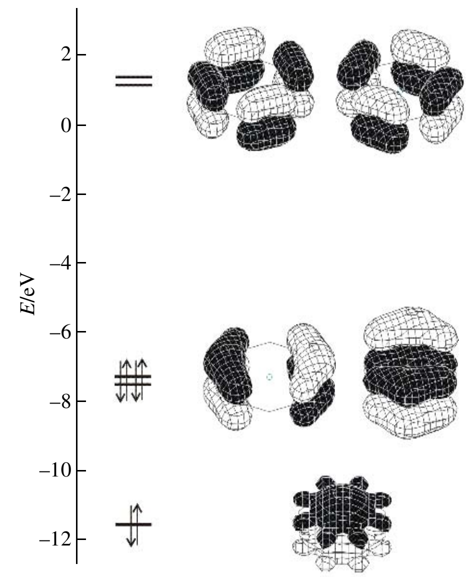


Figure 2 Occupation and shape of π-orbitals in compound **4**.

In conclusion, our DFT calculations showed that the systems of **4** (X = Si, P^+) are the first theoretically predicted examples of stable compounds containing octacoordinated planar silicon and phosphorus atoms. The fluxional structure of **4** (X = C) may be considered as that with an effectively octacoordinated planar carbon centre.

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References

1 V. I. Minkin, R. M. Minyaev and Yu. A. Zhdanov, *Nonclassical Structures of Organic Compounds*, Mir, Moscow, 1987.

2 R. M. Minyaev and T. N. Gribanova, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 786 (*Russ. Chem. Bull.*, 2000, **49**, 783).

3 X. Li, A. E. Kuznetsov, H.-F. Zhang, A. I. Boldyrev and L.-S. Wang, *Science*, 2001, **291**, 859.

4 K. Exner and P. v. R. Schleyer, *Science*, 2000, **290**, 1937.

5 R. Hoffmann, R. W. Alder and C. F. Wilcox Jr., *J. Am. Chem. Soc.*, 1970, **92**, 4992.

6 K. Sorger and P. v. R. Schleyer, *J. Mol. Struct. (Theochem.)*, 1995, **338**, 317.

7 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Collect. Czech. Chem. Commun.*, 1999, **64**, 170.

8 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Mendeleev Commun.*, 2001, 169.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, 1998.

10 M. Hargittai and I. Hargittai, *The Molecular Geometries of Coordination Compounds in Vapour Phase*, Akademia Kiado, Budapest, 1975.

11 P. Power, *Inorg. Chim. Acta*, 1992, **198**–**200**, 443.

12 W. J. Grigsby and P. P. Power, *Chem. Eur. J.*, 1997, **3**, 368.

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