mation in organosilane polymers.

IV. Concluding Remarks

The experimentally unknown mechanism for the formation of the siloxane bond in radiated organosilane polymer solutions has been examined. We have assumed that the residual oxygen or water should be present in the solution, which terminates the radical chain reaction or scavenges the silylene, bringing about the terminal groups SiH and SiOH. Then it follows that the dehydrogenation reaction I would be a candidate for the formation of the siloxane bond, which is studied numerically by using ab initio MO theory. Our computed activation energies for the reactions involving silicon are seen to be lower than those for analogous reactions of carbon by a factor of about $^2/_3$, as is often the case. In particular, our relatively low activation energy for

siloxane formation, 44.2 kcal/mol, supports the Withnal and Andrews reaction scheme.[9] Reaction ergodography for the model reaction system is also examined in order to characterize the course of the reaction pathway.

Superdense Carbon, C$_8$: Supercubane or Analogue of γ-Si?

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Abstract: A new crystalline allotrope of carbon, "C$_8$", which is denser than diamond, has recently been claimed, following research on the plasma deposition of thin carbon films. The reported structure consists of a body-centered cubic array of C$_8$ cubes, forming a lattice previously postulated by Burdett and termed "supercubane". Discrepancies in the crystallographic analysis and the unusual bond length distribution in the reported structure lead us, however, to doubt the validity of the proposed structure of C$_8$. We have found, by means of a structural analysis combined with extended Hückel band calculations, that a likely alternative structure for C$_8$ is the BC-8 structure adopted by the high-pressure γ-Si allotrope. Our calculations indicate that this allotrope of carbon should have a small direct band gap at point H in the Brillouin zone, though a slight structural distortion leads to an increase in the gap. The small band gap is associated with a relatively short (2.18 Å) nonbonded C---C contact in the BC-8 structure. Finally, the BC-8 structure has been compared to a polymer of [1.1.1]propellane.

Diamondlike Films and Hypothetical Carbon Allotropes. In recent years the synthesis and study of "diamondlike" films has become a popular field for chemists, physicists, and materials scientists.[1-5] The term diamondlike generally implies a similarity in structure (i.e. most or all of the carbon atoms are bonded to four others in an approximately tetrahedral fashion), as well as physical properties, to diamond. The properties of diamond that make the synthesis of these films so attractive are its supreme hardness, chemical inertness, high electrical resistivity, and extremely high thermal conductivity. Advances in thin-film technology[5] mean that it is possible to synthesize diamondlike materials with relatively large surface areas for application in the fields of mechanical engineering and electronics.[1b]

The most common methods of generating thin diamondlike films are chemical vapor deposition and ion-beam/plasma deposition of carbon atoms, ions, or molecules generated by pyrolysis, sputtering, electrical discharge, etc., of hydrocarbon or carbon (e.g. graphite) starting materials.[1a,3] The resulting films are usually amorphous, sometimes contain hydrogen, and often possess a mixture of sp^3 and sp^2 carbon (i.e. 4- and 3-connected atoms). Excellent reviews of the field are to be found in the papers of DeVries,[1a,2] Angus,[4] and Weissmantel.[5]

Diamondlike films are generally regarded as metastable,[1a] since the conditions under which they are synthesized are far removed from those (high static pressure and temperature) under which diamond is thermodynamically stable.[6] In the case of ion-beam and plasma deposition synthesis, the formation of metastable phases has been attributed to the extremely rapid collapse (over

a time scale of around 10^{-11} s) of localized (approx. 20 Å radius) thermal spikes caused by the ion/atom impinging on the growing carbon film. In these spikes, the nonequilibrium temperatures (10^3–10^4 K) and pressures (around 10 GPa) can be very high.[3,7]

As mentioned above, diamondlike films are generally amorphous (i.e. possess no long-range order). While the theory of amorphous phases is a fascinating subject,[8-11] there is a certain aesthetic appeal to crystalline matter. In particular, there has been much interest in postulating structures for (and predicting electronic properties of) novel crystalline allotropes of carbon,[12,13] and over the years

(1) (a) For an excellent, thorough historical account of the field, see: DeVries, R. C. *Annu. Rev. Mater. Sci.* **1987**, *17*, 161. (b) A less comprehensive, though quite readable, account can be found in: Simpson, M. *Materials with the Diamond Touch. New Scientist* **1988**, No. 1603, 50.
(2) Badzian, A. R.; DeVries, R. C. *Mater. Res. Bull.* **1988**, *23*, 385.
(3) Klabunde, K. J., Ed. *Thin Films from Free Atoms and Particles*; Academic Press: New York, 1985.
(4) (a) Angus, J. C. *Thin Solid Films* **1986**, *142*, 145. (b) Angus, J. C.; Jansen, F. *J. Vac. Sci. Technol.* **1988**, *A6*, 1778. (c) Angus, J. C.; Hayman, C. C. *Science* **1988**, *241*, 913.
(5) (a) Weissmantel, C.; Breuer, K.; Winde, B. *Thin Solid Films* **1983**, *100*, 383. (b) Weissmantel, C. In Reference 3; Chapter 4, p 153.
(6) For a discussion of the phase diagram of elemental carbon, see: Bundy, F. P. *J. Geophys. Res.* **1980**, *85*, 6930.
(7) Rabelais, J. W.; Kasi, S. *Science* **1988**, *239*, 623.
(8) Brodsky, M. H., Ed. *Amorphous Semiconductors (Top. Appl. Phys. Vol. 36)*; Verlag: Berlin, 1985.
(9) Bicerano, J.; Adler, D. *Pure Appl. Chem.* **1987**, *59*, 102.
(10) Joannopolous, J. D.; Cohen, M. L. *Solid State Phys.* **1976**, *31*, 71.
(11) Robertson, J.; O'Reilly, E. P. *Phys. Rev. B* **1987**, *35*, 2946.
(12) (a) Balaban, A. T.; Rentia, C. C.; Cuipitu, E. *Rev. Roum. Chim.* **1968**, *13*, 231. (b) Baughman, R. H.; Eckhardt, H.; Kertesz, M. *J. Chem. Phys.* **1987**, *87*, 6687.

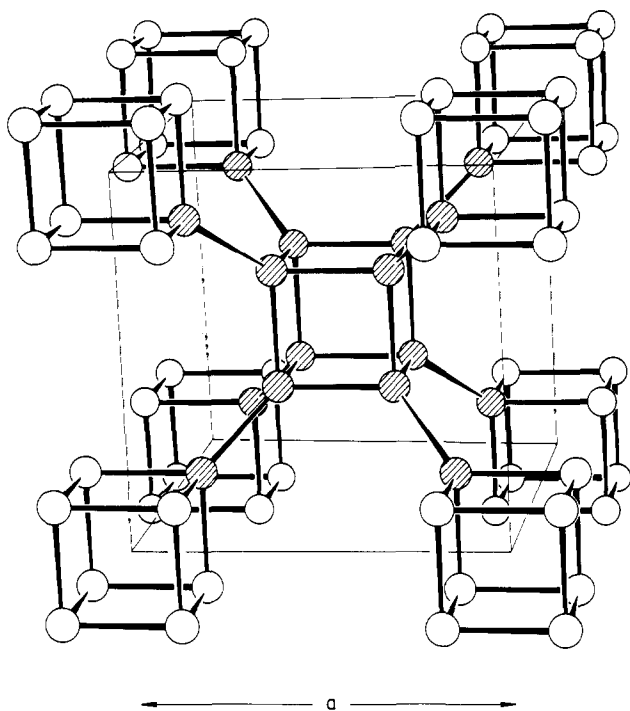[†] SERC/NATO Postdoctoral Fellow 1987–1988.

Figure 1. Fragment of the supercubane structure, including the cubic unit cell (length a). The 16 atoms in this nonprimitive cell are shaded.

we have also maintained an interest in this fascinating subject.[14] It was, therefore, with great interest that we learned (from our correspondence with John Angus) of the reported characterization of plasma-deposited films containing a novel form of crystalline carbon.[15] In this paper, we will concentrate on this phase (known as "C_8"), which raises some points of geometric and electronic interest for organic and solid-state chemists alike.

Superdense Crystalline Carbon, C_8. Ten years ago, a new crystalline form of carbon was reported by Strel'nitskii and co-workers.[15] Single and polycrystalline material was discovered (along with an amorphous phase) in carbon films formed by radio-frequency condensation of carbon plasmas on cooled substrates. From electron diffraction studies, the crystalline phase was indexed in the cubic system with a body-centered cubic (bcc) lattice period of 4.28 Å. The structure was assigned to the space group $Im\bar{3}$ (T_h^5, No. 204), with 16 carbon atoms in the bcc cell in the 16f positions ($x, x, x; \bar{x}, \bar{x}, x; \bar{x}, x, \bar{x}$, etc.; $x = \frac{1}{6}$) with C_3 site symmetry.[15b]

The density of the phase obtained by Strel'nitskii et al. (which was named C_8 because there are 8 carbon atoms in the primitive, rhombohedral unit cell) was calculated to be 4.1 g/cm³, which

is 15% larger than that of cubic or hexagonal diamond (3.51 g/cm³). Since diamond is known to have the highest (atom) number density (ρ_n) of any material (0.295 mol·atoms/cm³) at atmospheric pressure,[17] the C_8 phase ($\rho_n = 0.338$ mol·atoms/cm³), if it really exists, truly deserves to be called "superdense". The very high microhardness of these films, which exceeds even that of the closely packed (111) face of cubic diamond, could indeed be consistent with a new, denser form of carbon.[15b] Strel'nitskii et al. indicated that the 16 equivalent carbon atoms in the proposed C_8 structure have a distorted tetrahedral environment, so, when the above criterion is used, the film is diamondlike in terms of its local structure as well as its physical properties.[15b] It is also interesting to speculate on the relationship between the C_8 phase and the structurally uncharacterized metallic forms of carbon that have been reported.[6,16]

When the structural parameters reported for C_8 are used, the structure, which is shown in Figure 1, can be seen to be a bcc array of C_8 cubes such as that constituting the carbon core of cubane $[C_8H_8]^{18}$ (1). This geometrical factor, which was not mentioned
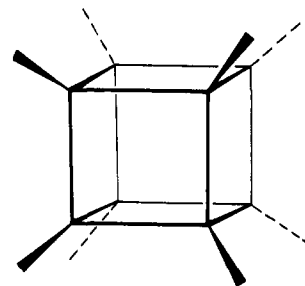
1

by Strel'nitskii, has previously been noted by Stankevich et al.[13a] and Biswas et al.[19] In fact such a structure (dubbed "super-cubane") has been considered as a hypothetical allotrope of carbon and its energy compared with that of the diamond structure for a number of electron counts in an elegant moments analysis by Burdett and Lee,[20] though they were unaware at the time of the report of the C_8 phase. Burdett and Lee found the supercubane structure less stable than diamond for 4 (i.e. C) or fewer e/atom but more stable for electron-rich (more than 4 e/atom) systems.[20]

Inspection of the supercubane structure shown in Figure 1 reveals a discrepancy in the reported crystal structure of the C_8 phase. The structure has higher symmetry than reported, due to the existence of additional mirror planes and 4-fold rotation axes. In fact the 16f sites in $Im\bar{3}$ (on their own) define a solid belonging to the space group $Im\bar{3}m$ (O_h^9, No. 229), where the sites (still labeled 16f) now have C_{3v} symmetry, as can be seen from Figure 1. Since the systematic absences are identical for the two space groups, there is no problem in ascending symmetry to $Im\bar{3}m$. The pyramidally distorted tetrahedral environment of the carbon atoms (with bond angles of 90° and 125.26°) can be seen in 2.
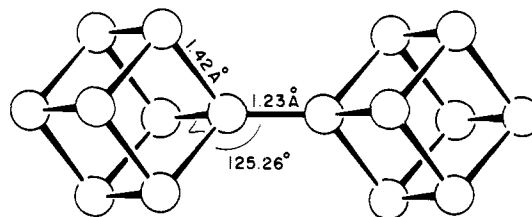
2

There is another factor that leads us to doubt whether the C_8 phase has the reported (supercubane) structure at all. Strel'nitskii

(13) (a) Stankevich, I. V.; Nikerov, M. V.; Bochvar, D. A. *Usp. Khim.* **1984**, *53*, 110 (*Russ. Chem. Rev.* **1984**, *53*, 640), and references therein. (b) Stankevich, I. V.; Nikerov, M. V.; Gal'pern, E. G.; Bochvar, D. A. *Zh. Strukt. Khim.* **1987**, *28*, 96 (*J. Struct. Chem.* **1987**, *28*, 542).

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(16) (a) Vereshchagin, L. F.; Yakovlev, E. N.; Stepanov, G. N.; Vinogradov, B. V. *Pis'ma Zh. Eksp. Teor. Fiz.* **1972**, *16*, 382 (*JETP Lett.* **1972**, *16*, 270). (b) Vereshchagin, L. F.; Yakovlev, E. N.; Vinogradov, B. V.; Sakun, V. P.; Stepanov, G. N. *Pis'ma Zh. Eksp. Teor. Fiz.* **1973**, *17*, 422 (*JETP Lett.* **1973**, *17*, 301). (c) A more recent claim of an fcc metallic phase ("γ-carbon") can be found in: Palatnik, L. S.; Guseva, M. B.; Babaev, V. G.; Savchenko, N. F.; Fal'ko, I. I. *Zh. Eksp. Teor. Fiz.* **1984**, *87*, 914 (*Sov. Phys. JETP* **1984**, *60*, 520). (d) For a theoretical study of the pressure-induced metallization of carbon, see: Yin, M. T.; Cohen, M. L. *Phys. Rev. Lett.* **1983**, *50*, 2006.

(17) (a) Angus, J. C. *Am. Sci.* **1988**, *76*, 123. (b) Angus, J. C., private communication.

(18) Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

(19) (a) Biswas, R.; Martin, R. M.; Needs, R. J.; Nielson, O. H. *Phys. Rev. B* **1984**, *30*, 3210. (b) Biswas, R.; Martin, R. M.; Needs, R. J.; Nielsen, O. H. *Phys. Rev. B* **1987**, *35*, 9559.

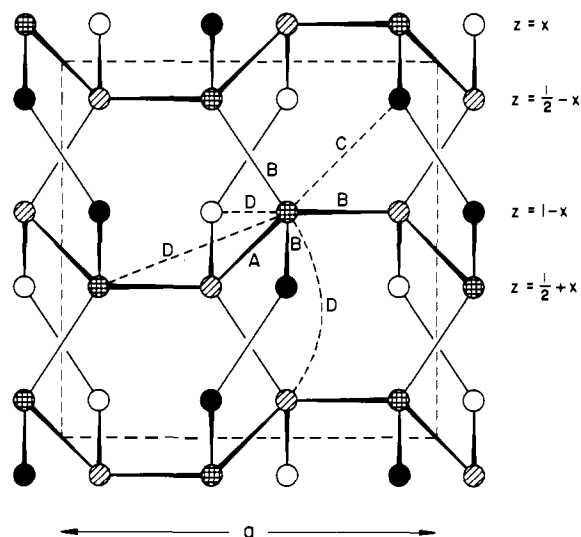(20) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1985**, *107*, 3063.

Figure 2. Two-dimensional projection of the BC-8 structure, including the cubic unit cell (length a). Contacts with the two sets of nearest neighbors (bonds A and B) and next nearest neighbors (nonbonded contacts C and D) of one of the 16 equivalent atoms in the cell are indicated. The distance of an atom above the plane is given by z, which can take one of four values (indicated at right in terms of the structure parameter x, with $x \approx 0.1$).

reports that the C–C bond lengths in the C_8 phase are 1.23 Å (intercube, along the 3-fold axes of the solid) and 1.42 Å (intracube), with each carbon atom associated with one intercube and three intracube bonds (see **2**).[15b] As noted by Stankevich et al.,[13a] these bonds, which are all considerably shorter than a normal C–C single bond (1.54 Å for ethane; 1.55 Å for cubane;[18] 1.5445 Å in cubic diamond[21]), are at odds with our knowledge of carbon bonding. In particular, since the C_8 phase is formed by plasma deposition in vacuo, there would appear to be no reason why the supercubane structure should not simply expand (probably involving a simultaneous increase of the lattice period (a) and a decrease in the x parameter, resulting in a smaller percentage difference in the inter- and intracube C–C bond lengths) to yield a more chemically reasonable distribution of bond lengths.

Is C_8 Really Carbon with the γ-Si(BC-8) Structure? While considering possible structural alternatives for superdense C_8 that might be more chemically reasonable in terms of the C–C bond lengths, we came across the structure of γ-Si. This is a high-pressure allotrope (metastable at atmospheric pressure) of silicon.[21,22] The γ-Si structure (which has been named "BC-8"[10] and "B-8",[9] as it is bcc with 8 atoms in the primitive unit cell) belongs to the space group $Ia\bar{3}$ (T_h^7, No. 206). Like supercubane, the BC-8 structure has 16 equivalent atoms in the bcc (nonprimitive) cell, though the atom distribution, as shown in Figure 2 is quite different. The atoms occupy the 16c sites $(x, x, x; {}^1/_2{-}x, \bar{x}, {}^1/_2 + x, ...,$ etc.), with site symmetry C_3. As in the supercubane structure there are two nonequivalent types of bonds (labeled A and B in Figure 2), with the A bonds lying along the 3-fold axes of the solid and each atom associated with one type A and three type B bonds.[21–23]

For γ-Si at atmospheric pressure (i.e. quenched) the structural parameter x is 0.1003 and the cell constant a is 6.636 Å. This results in Si–Si distances of 2.306 Å (type A) and 2.392 Å (type B). The atomic volume (18.26 Å^3) is 8.8% less than that in the diamond form (20.02 Å^3) (i.e. the γ-Si structure is 8.8% more dense) despite the fact that the average Si–Si bond length (2.371 Å) is slightly longer than that in the diamond form (2.352 Å).

The higher density is manifested in the closeness of the nonbonded next nearest neighbors in γ-Si (one at 3.441 Å and three at 3.575 Å) compared to the diamond form (four at 3.840 Å). These contacts are marked C and D in Figure 2. The high-pressure δ-Ge phase, which is 9.5% denser than the diamond form of germanium, is also believed to have the γ-Si structure.[24]

Wells has noted that the BC-8 structure, in common with the cubic (**3a**) and hexagonal (**3b**) diamond structures,[21] may be described as a 6^6 net, since each atom is associated with six hexagonal rings.[23] In the cubic diamond structure (**3a**) all of

3a   **3b**
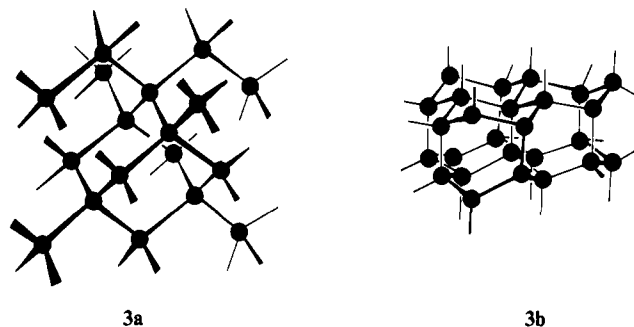
the hexagonal rings are in the chair conformation (**4a**), while in the hexagonal diamond (**3b**) both chair and boat (**4b**) conformations are found. In the BC-8 structure, however, all of the hexagonal rings are in the twist-boat conformation (**4c**).[25] It is this twisting which results in the greater density of the BC-8 structure relative to the cubic and hexagonal diamond structures, even for approximately equal bond lengths.

4a   **4b**   **4c**
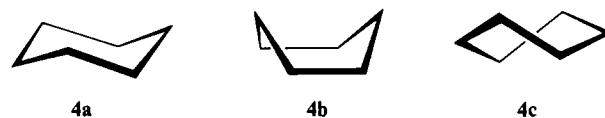
The twist-boat aspect of the hexagonal rings in the BC-8 structure is visible (for some of the rings at least) in the representation of Figure 2. Some of the other features of this remarkable structure, however, need to be emphasized. **5** shows a perspective view of a fragment of the structure that emphasizes the 3-fold axis. In the BC-8 structure such axes run in tetrahedral directions throughout the crystal.

5
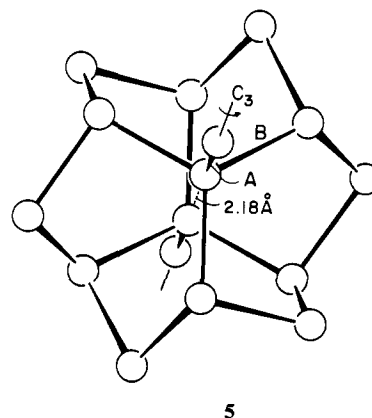
The three-plus-one partitioning of the bonds around a given atom is clearly visible in **5**. Considering a hypothetical BC-8 allotrope of carbon, if we assume a C–C distance of 1.54 Å ("idealized BC-8") for both types of bonds (A and B in Figure 2 and **5**), there arises a next-nearest-neighbor contact of 2.18 Å along the 3-fold axis. This separation (type C in Figure 2) corresponds to a transannular contact in a strained eight-membered ring. There are few nonbonded C–C separations in chem-

(21) (a) Donohue, J. *The Structure of the Elements*, 2nd ed.; Wiley: New York, 1974; Chapter 7, p 250. (b) For a theoretical analysis of bonding in α- and β-Si, see: Biswas, R.; Kertesz, M. *Phys. Rev. B* **1984**, *29*, 1791.
(22) (a) Wentorf, R. H., Jr.; Kasper, J. S. *Science* **1963**, *139*, 338. (b) Kasper, J. S.; Richards, S. M. *Acta Crystallogr.* **1964**, *17*, 752.
(23) Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley: New York, 1977; p 118.

(24) Bates, C. H.; Dachille, F.; Roy, R. *Science* **1965**, *147*, 860.
(25) Johnson, W. S.; Bauer, V. J.; Margrave, J. L.; Frisch, M. A.; Dreger, L. H.; Hubbard, W. N. *J. Am. Chem. Soc.* **1961**, *83*, 606.

Superdense Carbon, C_8

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istry as short as this; one that comes to mind occurs in bicyclo-[1.1.1]pentane (6),[26] where the distance between the bridgehead carbon atoms is 1.87 Å.[27] The contact C will figure prominently in the electronic structure of the BC-8 carbon allotrope.

6
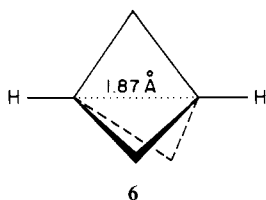
The BC-8 structure, in either the representation of Figure 2 or **5**, appears innocuous. We urge the reader to try to build a model of the saturated analogue of **5**, the D_{3d} star-shaped $C_{14}H_{20}$ hydrocarbon **7**, to gain an appreciation of the strain hidden in this structure.

7
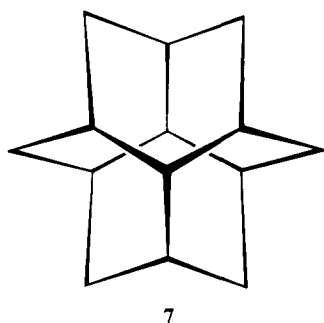
We note in passing that a hydrocarbon with all twist-boat rings has been made, the aptly named twistane (8).[28] Maybe someone should try to synthesize **7**, for which we propose the name star-twistane.[29]

8
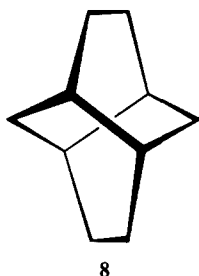
As in supercubane, the local environment of the atoms in the BC-8 structure is a pyramidally (trigonally) distorted tetrahedron. These distortions are in the opposite sense for the two structure types. As **9** shows, in supercubane the tetrahedron is elongated (see also **2**), while in the BC-8 structure it is flattened. In γ-Si $\theta_1 = 99.2°$ and $\theta_2 = 117.9°$ and in the idealized carbon BC-8 allotrope $\theta_1 = 97.94°$ and $\theta_2 = 118.12°$.

The idealized BC-8 carbon structure has a structural parameter $x = (\sqrt{2} - 1)/4 = 0.1036$ and bcc lattice period $a = 4.293$ Å. On this basis, we calculate a density of 4.03 g/cm^3 ($\rho_n = 0.336$

BC-8   DIAMOND   SUPERCUBANE

FLATTENED   REGULAR   ELONGATED
TETRAHEDRON   TETRAHEDRON   TETRAHEDRON

9
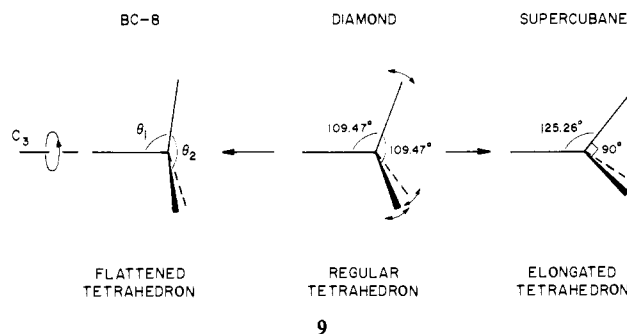
mol·atoms/cm^3) for this allotrope of carbon. This density is very close to that reported by Strel'nitskii et al. for C_8.[15b] It appears, therefore, that there is room for doubt whether the structure of C_8 is really the (supercubane) one proposed by Strel'nitskii. Could it be, instead, the BC-8 structure found for γ-Si, which yields almost the exact same density for more chemically reasonable C–C bond lengths? A slight distortion of the idealized BC-8 structure could account for the experimental density. This possibility has also been mentioned in a recent paper by Biswas et al.[19b]

Though the systematic absences for the space groups $Im\bar{3}m$ and $Ia\bar{3}$ are similar, there is an important difference, which a reviewer of this paper has pointed out to us. For $Im\bar{3}m$ the reflections (0kl) with $k + l$ even are observed, whereas in $Ia\bar{3}$ both k and l must be even for the reflection to be observed. Strel'nitskii et al. have stated that two of the strongest peaks in the electron diffraction pattern correspond to the (011) and (013) reflections.[15b] Though this is at odds with our suggestion that C_8 has the BC-8 ($Ia\bar{3}$) structure, it is still possible that a misassignment of the space group has been made in view of the fairly poor quality of the diffraction data.[15b] It will be interesting to see whether the C_8 phase can be reproduced and whether the space group is indeed $Im\bar{3}m$ or $Ia\bar{3}$.

Joannopolous and Cohen have published a density of states analysis of silicon and germanium with the BC-8 structure.[10] In addition, Biswas et al. have compared the total energies (as a function of pressure) of the Strel'nitskii C_8 structure and a BC-8 form of carbon and have commented on the band structures of these allotropes, as well as γ-Si.[19] Burdett and Lee have also considered (in terms of its energy relative to diamond) the supercubane structure.[20] We believe, however, that there is a need for a systematic comparison of the bonding in the supercubane and BC-8 structures of carbon.

In this paper we will analyze the electronic band structures of carbon in the supercubane and BC-8 forms, with both idealized (all C–C bond lengths 1.54 Å) and distorted geometries, in an attempt to determine which of the two structures mostly likely pertains to the C_8 phase. We will also look at an interesting relationship between the BC-8 carbon structure and a recently synthesized polymer of a [1.1.1]propellane derivative.[30] The calculations that were performed were of the extended Hückel type,[31] using the tight-binding method.[32] Further details are given in the Appendix.

Electronic Structure of Supercubane-C_8. To idealize the supercubane structure (Figure 1), such that all the C–C bond lengths are 1.54 Å, it is necessary to choose an x value of 0.1585 (cf. $x = 0.1667$ in the Strel'nitskii paper)[15b] and for the bcc cell constant (a) to be 4.858 Å. This results in a structure with a density ($\rho_n = 0.231$ mol·atoms/cm^3), which is lower than that of diamond (0.295). Although the nonprimitive ($Z = 16$) bcc cell can be used to calculate the average properties of supercubane (see Appendix for details), in order to simplify the analysis of the band structure,

(26) (a) Wiberg, K. B.; Connor, D. S.; Lampman, G. M. *Tetrahedron Lett.* **1964**, 531. (b) Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437. (c) Meinwald, J.; Szkrybalo, W.; Dimmel, D. R. *Tetrahedron Lett.* **1967**, 731.

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(28) (a) Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3412. (b) Whitlock, H. W., Jr.; Siefken, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929.

(29) (a) For an entertaining and informative account of nonsystematic nomenclature in organic chemistry, see: Nickon, A.; Silversmith, E. F. *Organic Chemistry: The Name Game* (*Modern Coined Terms and Their Origins*); Pergamon Press: Oxford, England, 1987. (b) Star-twistane is an isomer of the less strained [2.2.2]triblattane. That system has been synthesized: Müller, H.; Melder, J.-P.; Fessner, W.-D.; Hunkler, D.; Fritz, H.; Prinzbach, H. *Angew. Chem.* **1988**, *100*, 1140. Naemura, K.; Hokura, Y.; Nakazaki, M. *Tetrahedron* **1986**, *42*, 1763. Nakazaki, M. *Top. Stereochem.* **1984**, *15*, 199.

(30) Schlüter, A.-D. *Angew. Chem.* **1988**, *100*, 283 (*Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 296).

(31) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872.

(32) (a) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. (b) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London* **1979**, *A366*, 23.
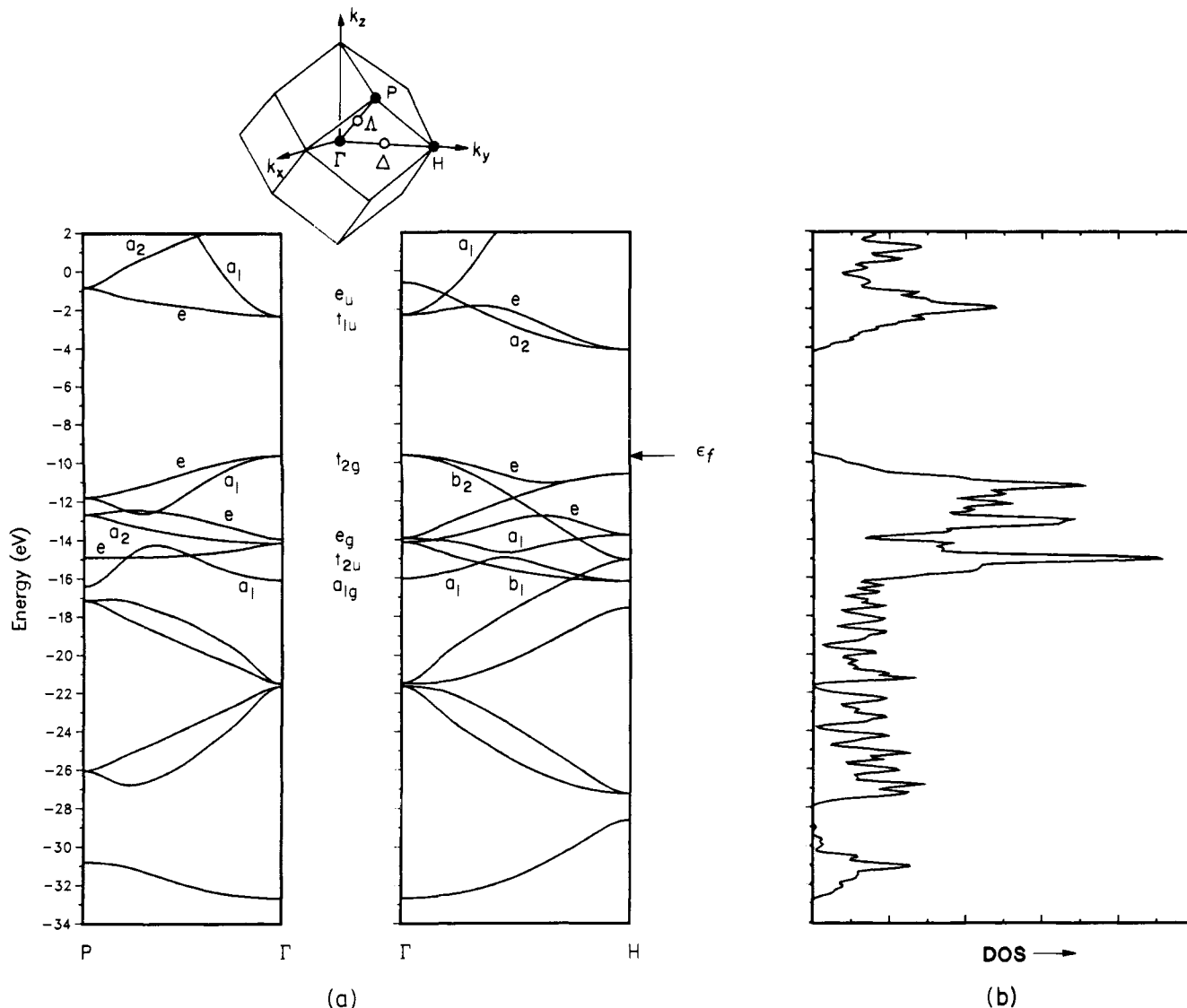
Figure 3. (a) Band structure of idealized supercubane (C–C = 1.54 Å) along lines Λ and Δ of the BZ (shown at top center). Only those bands in the vicinity of the Fermi energy (ϵ_f) are labeled. (b) Total DOS for idealized supercubane.

the rhombohedral primitive cell was chosen. The primitive cell has the following cell constants:

$$a_r = \left(\sqrt{3}/2\right)a_c = 4.207 \text{ Å} \qquad \alpha_r = 109.47°$$

with eight atoms defining a single C_8 cube per cell.

The band structure of idealized supercubane, plotted along the lines $P\Gamma(\Lambda)$ and $\Gamma H(\Delta)$ of the Brillouin zone (BZ),[33] is presented in Figure 3a. As expected for a structure composed of tetravalent carbon in a slightly distorted tetrahedral environment, supercubane is an insulator, with direct band gaps ranging from approximately 6.5 eV at H to 11 eV at P. The smallest indirect band gap is approximately 5.5 eV, as can be seen from the density of states (DOS) shown in Figure 3b.

The Fermi energy calculated for supercubane is –9.68 eV. A calculation on cubic diamond (fcc, C–C = 1.54 Å) gives a smaller band gap (4.5 eV) and higher Fermi energy (–9.54 eV). However, if the total energies are compared (see Figure 4), supercubane is less stable than cubic diamond by approximately 10 kcal/mol·atoms. For comparison, the corresponding stability of cubic over hexagonal diamond is only 1.5 kcal/mol·atoms. The destabilization of supercubane relative to cubic diamond can be attributed largely to repulsive interactions on the faces of the cube (where there are eclipsed C–C bonds only 1.54 Å apart and

(33) Bradley, C. J.; Cracknell, A. P. *The Mathematical Theory of Symmetry in Solids*; Clarendon Press: Oxford, England, 1972.
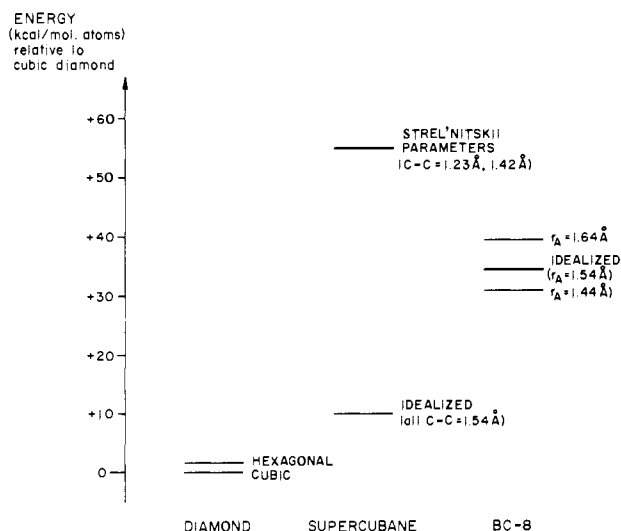

Figure 4. Calculated relative energies (per mole of atoms) of the real and hypothetical allotropes of carbon discussed in this paper.

nonbonded C---C contacts of 2.18 Å across the face diagonal). The local distortion of carbon's tetrahedral environment also contributes to the destabilization (see the paper of Burdett and Lee for a moments analysis).[20]
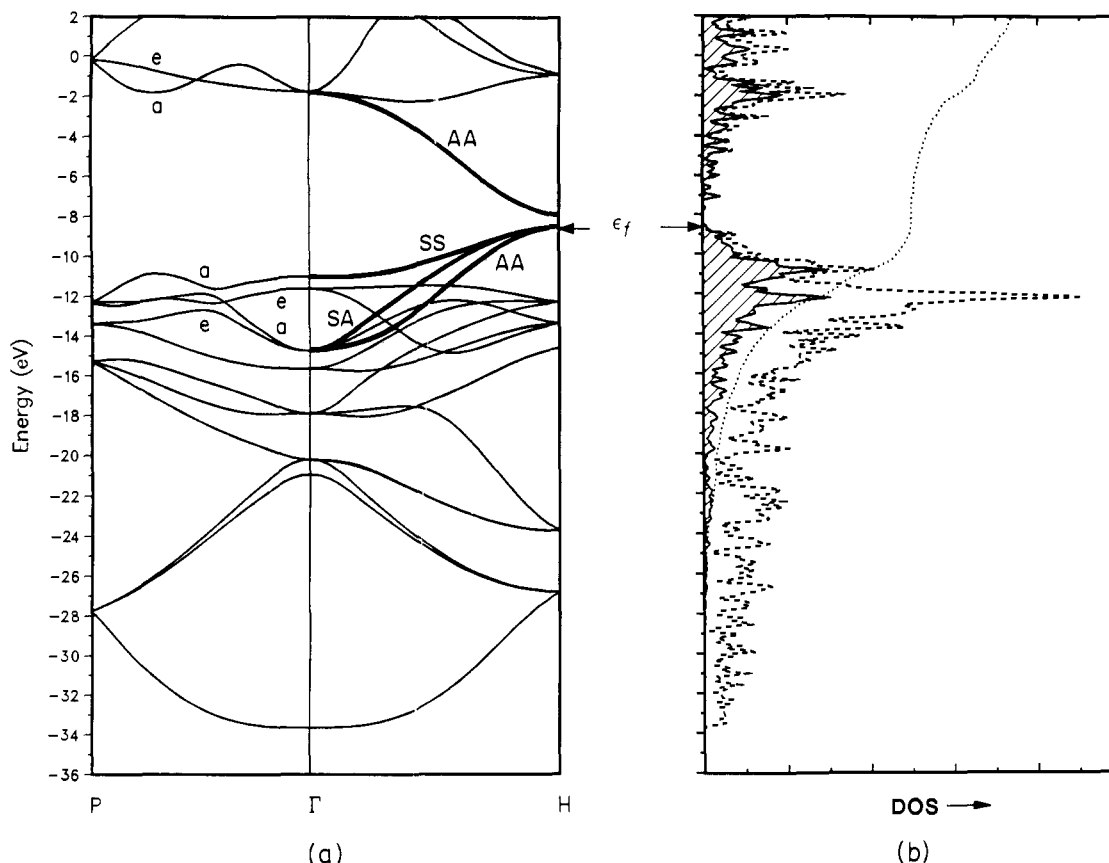
Figure 5. (a) Band structure of idealized BC-8 carbon (C–C = 1.54 Å) along lines Λ and Δ of the BZ (see Figure 3a). Only those bands in the vicinity of the Fermi energy are labeled. Along Δ (which is parallel to the y axis of the BC-8 structure in real space) the bands are labeled according to whether they are symmetric (S) or antisymmetric (A) with respect to the following operations: (i) 2-fold rotation about an axis parallel to y; (ii) a glide in the xy plane parallel to x.[33] (b) Total DOS (dashed line), projected p_A orbital DOS (shaded) and integration of the projected DOS (dotted line) for idealized BC-8 carbon.

The calculated reduced Mulliken overlap populations for the C–C bonds in supercubane are the following: C–C intercube, 0.794; C–C intracube, 0.656 (the corresponding value for cubic diamond is 0.785). These populations indicate that, all other factors being equal, the idealized supercubane structure should distort so that the intercube bonds become shorter than the intracube bonds (i.e. x should increase), in qualitative agreement with the Strel'nitskii structure. They also indicate, however, that the former should be shorter and the latter longer than the C–C bonds in cubic diamond, in marked contrast to Strel'nitskii's proposed structure.[15b]

Note Added in Proof: Recently the crystal structure of cubylcubane has become available.[44] The short intercube bond is 1.458 Å and the average intracube bond 1.553 Å, the same trend that we calculate.

Calculations were also performed on supercubane with the Strel'nitskii parameters, that is on superdense supercubane (a = 4.28 Å, x = 0.1667; a_r = 3.71 Å, α_r = 109.47°). As expected, from the simple valence arguments presented earlier, this "compressed" supercubane structure lies at higher energy than the idealized structure (by as much as 45 kcal/mol·atoms, as shown in Figure 4).

Electronic Structure of BC-8 Carbon. The idealized BC-8 carbon structure, with all C–C bonds equal to 1.54 Å (see Figure 2), requires structural parameters (for the bcc cell) a = 4.293 Å and x = 0.1036. The bond angles in the pyramidally distorted carbon coordination tetrahedron are 97.94° (between axial and basal atoms, i.e. θ_1) and 118.12° (θ_2), as indicated in **9**. Again, the bcc cell (Z = 16) was used for the calculation of average properties and the primitive rhombohedral cell (a_r = 3.718 Å, α_r = 109.47°) was used for the band structure calculation.

Figure 5a shows the band structure of idealized BC-8 carbon, again plotted along the lines PΓ(Λ) and ΓH(Δ) of the BZ (which has the same shape as that for supercubane though the symmetries

of the special k points and lines are different).[33] Along Λ the situation is not too different from that of supercubane (see Figure 3a) though the direct band gaps (around 12 eV at P and 9 eV at Γ) are somewhat larger for the BC-8 structure.

The major difference between the supercubane and BC-8 structures can be seen by comparing their band structures along the line Δ. In the BC-8 case the band gap narrows dramatically on going from Γ to H, where it is only 0.6 eV. This is consistent with the calculations of Joannopolous and Cohen who obtained a small band gap for BC-8 Si at H,[10] while Biswas et al. suggested that this form of silicon should be a semimetal as they calculated that the valence and conduction bands touched at H. In agreement with these calculations, the resistivity of BC-8 silicon (γ-Si) is found to be several orders of magnitude less than diamond–silicon. For carbon, Biswas et al. optimized the BC-8 structure at reduced volumes (V/V_0, with V_0 being the volume per C atom of diamond at 1 atm) of 0.85 (x = 0.0955) and 0.45 (x = 0.1030) and again reported touching of the valence and conduction bands at H.[19]

In our calculations, the BC-8 structure turns out to be less stable than cubic diamond by about 34 kcal/mol·atoms, as shown in Figure 4. It is also less stable than idealized supercubane by 25 kcal/mol·atoms), though it is lower in energy by 21 kcal/mol· atoms than the Strel'nitskii structure.

The most interesting feature of the electronic structure of BC-8 carbon is the small band gap at H. This is somewhat unexpected in what is essentially a distorted four-connected net. Insight into the reason for the narrow band gap at H can be obtained by looking at the DOS shown in Figure 5b. As well as the total DOS, Figure 5b depicts the projected DOS of the carbon p orbitals, which are oriented along the C_3 axes of the crystal (i.e. along the Λ bond vectors). The projection indicates that the states near the Fermi level (top of the valence band and bottom of the conduction band) are predominantly composed of these "p_A" orbitals. The LUMO and one of the (triply degenerate) HOMOs at H are

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shown in **10**, where it can be seen that they do indeed have a considerable amount of (in the case of the LUMO it is exclusively) p_A character. These bands are marked with thick lines in Figure 5a.

The low energy of the LUMO at H (**10a**) is due to the fact that although this orbital is σ-antibonding along all of the 1.54 Å long C–C bonds (type A) that lie on the 3-fold crystal axes,
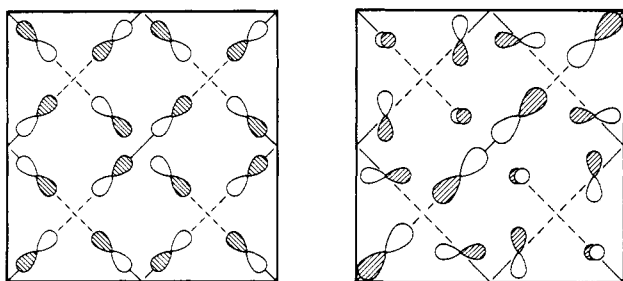

10a   **10b**

it is σ-bonding with respect to all of the short next-nearest-neighbor contacts (type C in Figure 2) along the C_3 axis. As mentioned above, for the idealized carbon BC-8 structure this distance is 2.18 Å (which is identical with the distance across the cube faces in supercubane). The stability of the LUMO is enhanced by a small amount of sp hybridization (not shown in **10a** as the s character is less than 5%), which increases the in-phase overlap at 2.18 Å and decreases the out-of-phase overlap at 1.54 Å.

In an analogous manner, the destabilization of the HOMOs at H (**10b**) can be attributed to σ-type antibonding interactions along some (though not all) of the C-type contacts. Thus the destabilization (by C-type interactions) of the HOMOs (which is reinforced by a small amount of sp hybridization, which increases the antibonding interaction at 2.18 Å) is less than the stabilization of the LUMO at H. Figure 5 shows that the nondegenerate HOMO at Γ is lower in energy than the HOMOs at H. As can be seen from **11**, this is due to the bonding nature of this orbital with respect to both the shorter (A) and longer (C) contacts along all of the 3-fold axes.
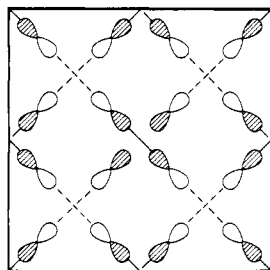
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The calculated reduced Mulliken overlap populations for the BC-8 structure as follows: C–C (type A, r_A = 1.54 Å), 0.721; C–C (type B, r_B = 1.54 Å), 0.809; C---C (type C, r_C = 2.18 Å), −0.010. As for supercubane, when only the immediate coordination environment of the carbon atoms is considered, there is a predicted contraction of one set of bonds (here the three B-type bonds) relative to the other, with the B set being shorter and the A type longer than the C–C bonds in diamond.

In order to determine whether the idealized BC-8 structure is unstable to such a distortion, calculations were performed on the BC-8 structure in two distorted arrangements obtained by changing the x parameter, while leaving the cell constant (a) constant, so that the density is unaltered. This distortion, which leaves the symmetry unchanged, corresponds to sliding the atoms along the C_3 axis, i.e. varying the x parameter. The two distorted forms are characterized by the following structural parameters: x = 0.1103 ($r_A > r_B$); x = 0.0968 ($r_A < r_B$). The partial band structures (plotted along Δ) and DOS (with p_A projection) of these distorted variants, together with those of idealized BC-8 carbon (x = 0.1036, $r_A = r_B$) are plotted in Figure 6.

When x = 0.1103, the A-type C–C bond length is 1.64 Å while the C-type C---C distance is only 2.08 Å. This results in a sharper descent of the LUMO (from Γ to H; see Figure 6a) due to an increase in the bonding interaction (type C) and a decrease in the antibonding interaction (type A) shown in **10a**. The HOMOs are less affected since they are not exclusively oriented along the C_3 axes (see **10b**), and the Fermi energy rises slightly (to −8.11 eV). The important effect of the distortion is that the structure becomes semimetallic, with the valence and conduction bands touching at H (zero band gap). The inversion of the frontier band pattern at H, i.e. 3 below 1 for the idealized BC-8 structure (see Figure 6b) going to 1 below 3 for the distorted BC-8 structure, occurs because one of the components of the triply degenerate HOMOs at H (for the undistorted structure) has the same symmetry (AA; see the caption to Figure 5 for the definition of the symmetry terms) along the line Δ as the LUMO. The rapidly descending LUMO therefore experiences an avoided crossing[34] with this component and correlates with the triply degenerate set instead. The semimetallic nature of this variant can be seen in the DOS shown in Figure 6a. The low density of states near the Fermi energy is a consequence of the fact that there is a large band gap in most regions of the BZ. It should be noted that the calculated overlap populations for idealized BC-8 carbon indicate that this type of distortion may occur. As indicated in Figure 4, however, this distortion destabilizes the structure by 5 kcal/mol·atoms, so the (semi)metalization is unfavorable.

When x = 0.0968, r_A is 1.44 Å, while the C-type C--C distance increases to 2.28 Å. As shown in Figure 4, the distortion to this structure from idealized BC-8 carbon results in a net stabilization of roughly 3 kcal/mol·atoms, which is reflected in the greatly increased band gap at H (2.6 eV, an increase of almost 2 eV over idealized BC-8), as shown in Figure 6c. This increase is due mainly to decreased C-type in-phase overlap and increased A-type antibonding overlap in the LUMO (**10a**).

Our calculations reveal that the favored distortion of the idealized BC-8 carbon (a semiconductor) is to generate a structure with a larger band gap (more insulating). The BC-8 structure should therefore have a C–C bond length distribution (A type shorter than B type as in the experimentally determined γ-Si structure),[21,22] which is contrary to that predicted on the basis of the Mulliken overlap populations of the idealized structure. In general, computed overlap populations correlate well with observed bond length changes. Thus, a calculated overlap population differential (in a structure with assumed equal bond lengths) can usually be taken as an indication of the bond length changes to be expected. As this study has shown, however this is not invariably so. Another example of such a discrepancy was observed by Burdett et al. in their study of the distortion of the TiO_6 octahedra in the rutile form of TiO_2.[35]

The geometry optimization of Biswas et al. for BC-8 carbon at a reduced volume of 0.85 (our reduced volume is $\{(4.293)^3/16\}/5.673 = 0.87$) resulted in an x value of 0.0955 (coupled with the reduced volume, this results in r_A = 1.41 Å, r_B = 1.546 Å, and C---C (type C) = 2.28 Å).[19] A reduced volume of 0.85 corresponds to a structure that is 15% more dense than cubic diamond, which is exactly the density of the reported C_8 phase. The optimized x value is not very different from the unoptimized one (0.0968) that we chose for the second (stabilizing) distortion of the idealized BC-8 structure. In contrast to our results, however, Biswas et al. calculated that there should be no band gap at H for this distorted structure.[19]

In concluding the discussion of the BC-8 structure we want to return to the small band gap and note the relationship to a localized distortion at carbon. Thus, if the tetrahedral methane molecule is elongated or flattened, the (C–H bonding) t_2 HOMOs split into e and a_1 components under the lower, C_{3v}, symmetry.[36,37]

(34) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1969.

(35) Burdett, J. K.; Hughbanks, T.; Miller, G. J.; Richardson, J. W., Jr.; Smith, J. V. *J. Am. Chem. Soc.* **1987**, *109*, 3639.

(36) Zheng, C.; Hoffmann, R.; Nesper, R.; von Schnering, H.-G. *J. Am. Chem. Soc.* **1986**, *108*, 1876.
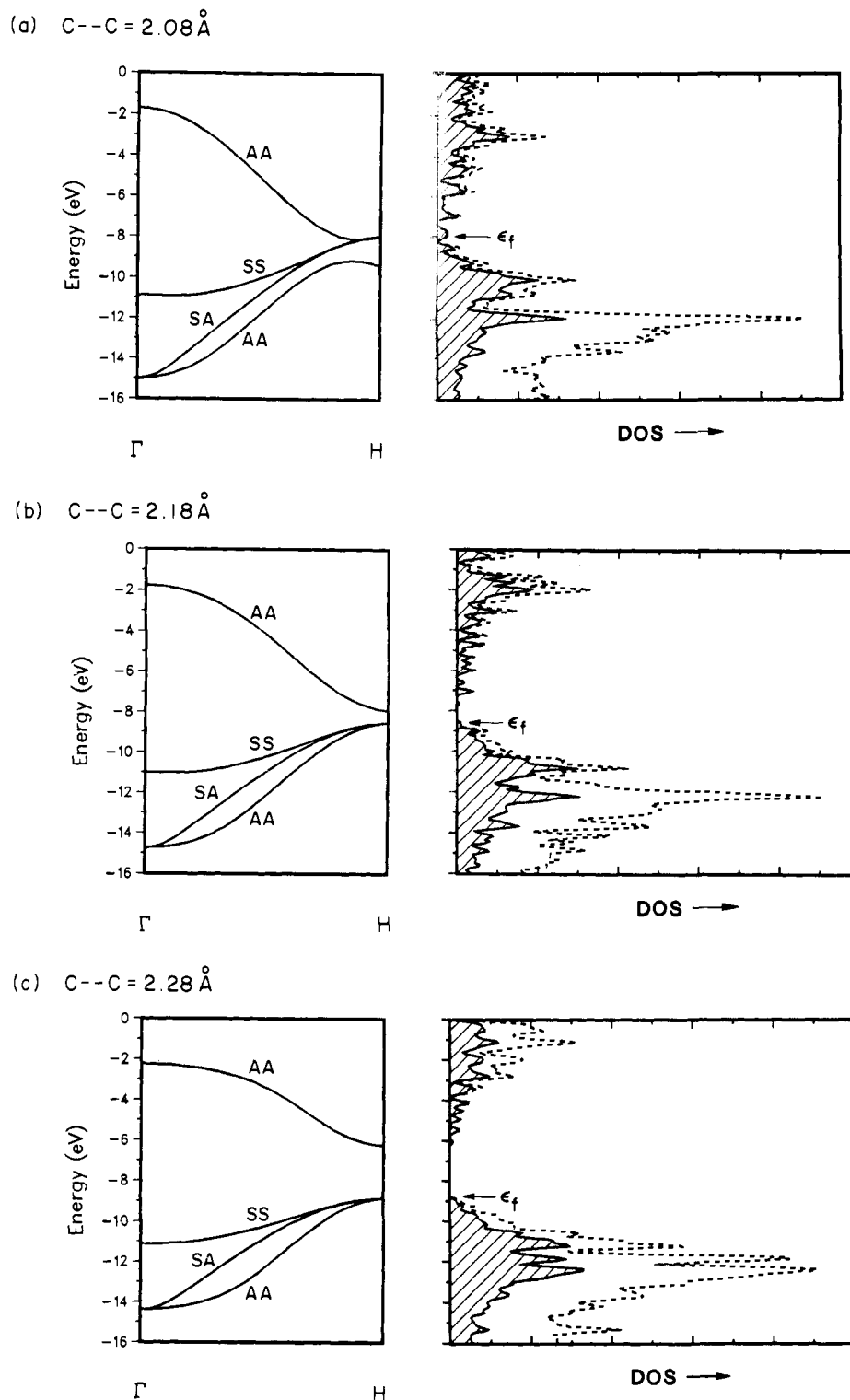
Figure 6. Partial band structure and DOS (total and p_A projection), in the vicinity of the Fermi energy, for idealized and distorted BC-8 carbon. Distortion is indicated by the changing C---C contacts (of type C). The corresponding A-type C–C bond lengths (r_A) are as follows: (a) 1.64 Å; (b) 1.54 Å (idealized structure); (c) 1.44 Å.

Figure 7 shows that the a_1 component is stabilized by elongation (supercubane-type distortion) and destabilized by the flattening (BC-8-type distortion). The reverse situation applies to the (C–H antibonding) LUMOs (also of t_2 symmetry) where the splitting is larger. In addition to these splittings, a small amount of s–p

mixing occurs (all of this can be understood with the aid of perturbation theoretic arguments),[38] which again is larger for the antibonding orbitals than the bonding ones. As indicated in Figure 7, this mixing leads in one case (the elongated tetrahedron) to hybridization along the axial bond and in the other (the flattened tetrahedron) to outward hybridization.[36,37]

In the BC-8 carbon allotrope, an analogous splitting and s–p hybridization occurs to that observed for flattened methane.

(37) (a) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1212. (b) Wiberg, K. B.; Ellison, G. B. *Tetrahedron* **1974**, *30*, 1573. (c) Minkin, V. I.; Minyaev, R. M.; Zhadanov, Yu. A. *Nonclassical Structures of Organic Compounds* (*Advances in Science and Technology in the USSR*); MIR Publications: Moscow, Russia, 1987, and references cited therein.

(38) See, for example: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
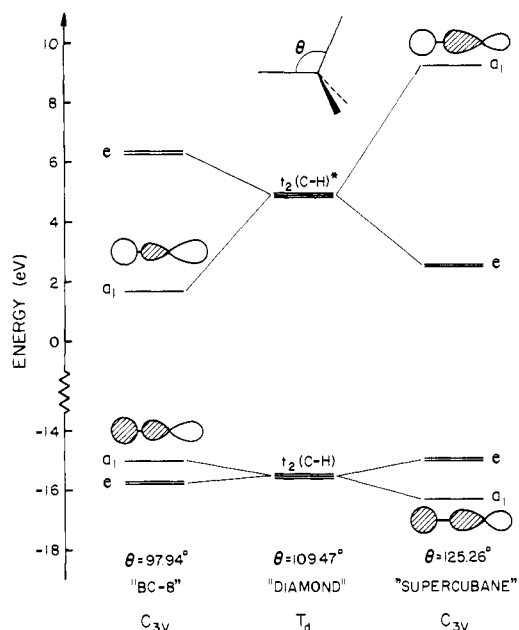
Figure 7. Effect of pyramidal distortion on the frontier orbitals of methane. The sp hybridization of the a_1 components is included (only the axial hydrogen atom is shown). The relationship between these distorted forms and the local environments in BC-8 and supercubane carbon is indicated.

Combined with the short C-type contact in the structure, this makes for larger C---C overlap and a subsequent increase in the widths of the valence and conduction bands, thereby resulting in a narrow band gap (at the point H, where the phases of the orbitals in the LUMOs are such that the C--C interaction stabilizes the LUMO considerably).

Comparison of the Electronic Structures of BC-8 Carbon and Poly[1,1,1]propellane. The remarkable polymerization of tricyclo[4.2.0.0^{2,7}]octane has recently been reported by Schlüter (**12**).[30]

12
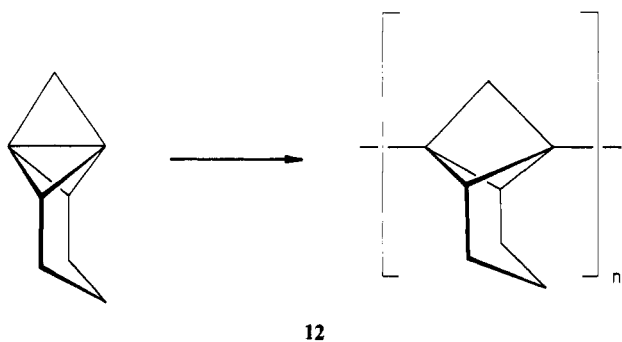
The monomeric unit is a derivative of tricyclo[1.1.1.0^{1,4}]pentane (**13**),[39] which is also known as [1.1.1]propellane. The bonding in **13** has been a source of controversy for a number of years, with the nature of the central "σ-bond" arousing most discussion.[40]

13

(39) (a) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982,** *104,* 5239. (b) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985,** *107,* 7257.

(40) (a) Stohrer, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1972,** *94,* 779. (b) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972,** *94,* 773. (c) Wiberg, K. B. *J. Am. Chem. Soc.* **1983,** *105,* 1227. (d) Honnerger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Soc. Chem.* **1985,** *107,* 7172. (e) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987,** *109,* 4133.
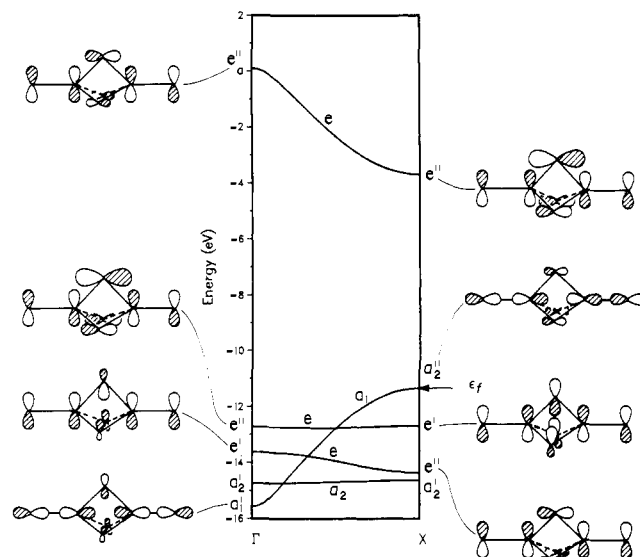
Figure 8. Partial band structure of poly[1.1.1]propellane (**14**, geometry a), with an indication of the nature of the bands at Γ and X.

As indicated in **12**, polymerization involves the formal breaking of the central propellane bond (though as yet there is no crystal structure available for this polymer).[30] Very recently, however, the synthesis of telomers and polymers of the parent [1.1.1]propellane was reported by Michl (who has proposed the trivial name [n]staffanes for these molecules).[41] From the crystal structure of a substituted dimer, the C---C nonbonded distance is found to be 1.87 Å,[41] which is identical with that in bicyclo[1.1.1]pentane (**6**).[27] Since this distance is less than the C-type contact in BC-8 carbon, it was decided to calculate the band structure of poly-[1.1.1]propellane (**4**) with (a) C---C = 1.87 Å and (b) C---C = 2.18 Å (i.e. the same as in idealized BC-8) to see if such a material is also characterized by a small band gap. Only the results for the shorter C---C contact are shown below, since the alternative choice gave quite similar results. The C–C bonds between propellane units were set equal to 1.54 Å for consistency with our previous calculations. Michl's work indicates, however, that these bonds are actually quite short (1.48 Å).[41,42] We repeated the calculations with this distance, but making this change led to a negligible difference in the calculated band structure of polymer **14**.

(a) d = 1.87 Å, θ_1 = 129.52°, θ_2 = 79.04°

(b) d = 2.18 Å, θ_1 = 135°, θ_2 = 90°

(C–H = 1.09 Å, HĈH = 109.47°)

14
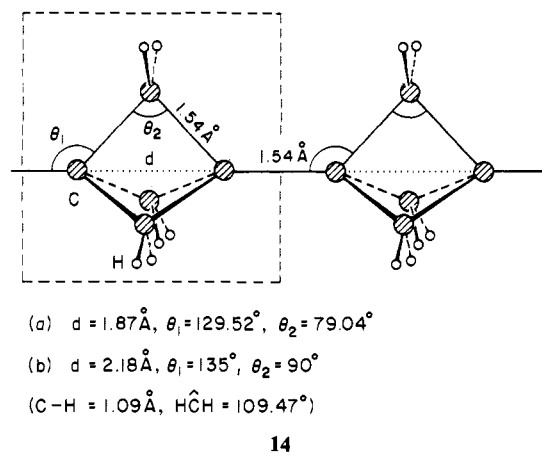
The band diagram for **14**, with C---C = 1.87 Å (geometry a) is shown in Figure 8. The bands near the Fermi energy at k points Γ and X are also depicted in Figure 8. There is indeed a narrowing

(41) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988,** *110,* 5225. The polymer of the parent propellane has also been prepared by: Schlüter, A.-D., private communication.

(42) For a discussion of the reasons for the short inter-ring C–C bond lengths in such molecules, see: Ermer, O.; Lex, J. *Angew. Chem.* **1987,** *99,* 455 (*Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 447).

of the band gap on going from Γ to X at the edge of the BZ. The band gap at X is, however, much larger than the gap for the BC-8 structure at H. At Γ the HOMOs and LUMOs are both doubly degenerate. The short (1.87 Å) C---C distance results in a significant destabilization of the a_2'' band (which has σ-antibonding character with respect to the C---C contact) at X, so that it becomes the HOMO. The LUMO's (e'') however, are not significantly affected, so the band gap at X remains quite large (≈ 8 eV). In the alternative geometry (b; C--C = 2.18 Å), the destabilization of the a_2'' band at X is smaller so it remains below the e' pair.

The difference between the propellane and BC-8 band patterns can be rationalized as follows. The pyramidal distortion of the bridgehead carbon atoms in polypropylene takes the form of an elongation of the tetrahedron. This results in a local orbital splitting pattern and hybridization similar to that of supercubane (see Figure 7).

Appendix

All calculations were of the extended Hückel type,[30] within the tight-binding approach,[31] with standard atomic parameters for carbon and hydrogen.[30]

The following bond lengths were used (unless otherwise stated in the text): C–C = 1.54 Å; C–H = 1.09 Å.

For the calculation of average properties, cubic unit cells (Z = 16) were taken for the supercubane and BC-8 allotropes. The irreducible wedges for supercubane and BC-8 are $1/48$ and $1/24$ of the cubic BZ, respectively. The k point sets were chosen according to the geometrical method of Ramirez and Böhm.[43]

Registry No. C, 7440-44-0.

(43) Ramirez, R.; Böhm, M. C. *Int. J. Quantum. Chem.* **1986**, *30*, 391.
(44) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

# Ab Initio Investigations of the β-Silicon Effect on Alkyl and Cyclopropyl Carbenium Ions and Radicals

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received July 5, 1988

Abstract: Ab initio molecular orbital calculations have been applied to study the effects of β-silicon and β-carbon substitution vs β-hydrogen on the stabilities of secondary and tertiary alkyl carbenium ions, primary, secondary, and tertiary alkyl radicals, and secondary cyclopropyl carbenium ions and radicals. The computations consisted of geometry optimizations with the 6-31G(d) basis set followed by single-point calculations for the correlation energy with second-order Møller–Plesset theory [MP2/6-31G(d)]. The influence of a β-SiH_3 group is pronounced for the cations providing 22.1 and 15.9 kcal/mol stabilization for the secondary and tertiary alkyl species relative to hydrogen, while the corresponding stabilization energies for a β-methyl substituent are 6.6 and 5.0 kcal/mol. A SiH_3-bridged form for the secondary cation, $H_3SiCH_2CHCH_3^+$, was considered, but appears to be ca. 4 kcal/mol higher in energy than the bisected, open form. For the secondary cyclopropyl cations, the hyperconjugative component of the β-silicon effect is diminished by the less optimal orbital alignment. The results for the β effects on the radical stabilities are in sharp contrast with those for the carbenium ions. The influences of β-SiH_3 and β-CH_3 are now nearly identical and yield only 1–4 kcal/mol of stabilization relative to β-hydrogen. The findings are compared with recent experimental results for β-silyl carbenium ions and radicals and provide a quantitative guide to directing effects for synthetic transformations.

The utility of silicon in organic synthesis is much enhanced by the directing effects of silyl groups.[1-3] Some well-known generalizations have emerged, such as silicon stabilizes an adjacent negative charge and a β positive charge relative to hydrogen, though quantification of the corresponding energetic effects has been limited from a physical organic perspective. However, progress is being made along both experimental and theoretical lines. The recent solvolysis work of several groups is particularly notable. Apeloig and Stanger established that in 2-adamantyl derivatives an α-Si(CH₃)₃ group stabilizes the carbenium ion center by 12–14 kcal/mol more than hydrogen and by several kilocalories per mole less than α-CH₃. They also reported results of ab initio calculations that α-SiH₃-substituted carbenium ions are less stable than their CH₃-substituted counterparts in the gas phase by ca. 18, 14, and 9 kcal/mol for the parent primary, secondary, and tertiary cations.[4] Furthermore, the recent studies of Lambert et al. have yielded important data on the magnitude of the β-silicon effect.[5,6] Specifically, they solvolyzed the conformationally constrained **1** and **2** (X = OCOCF₃) and found rate
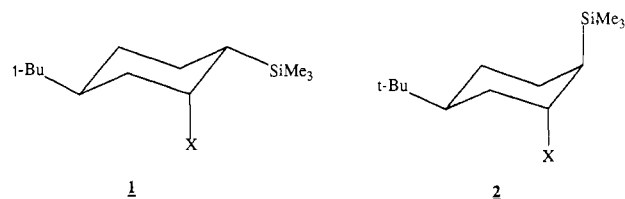
(1) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.
(2) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83.
(3) Birkofer, L.; Stuhol, O. *Top. Curr. Chem.* **1980**, *88*, 33.

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