

Force Field Calculations (MM2) of Carbon Lattices

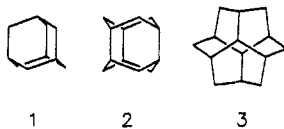
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In 1978, Strel'nitskii reported a novel superdense allotrope of carbon which was obtained by deposition of a high-speed flow of carbon plasma onto a cooled substrate in vacuo.¹ The electron-diffraction pattern of the faceted microcrystals was interpreted in terms of a "supercubane" structure having C-C single bond lengths of 1.42 and 1.23 Å.² These unusual bond lengths gave reason for discussion, and in a critical paper Johnston and Hoffmann (JH)³ recently proposed an alternative γ -silicone structure (BC-8) for this carbon modification. Based on an assumed, idealized C-C bond length of 1.54 Å, calculations for the geometry and the electronic properties of the new carbon phase were approached by extended Hückel methods. As a matter of fact, the hypothetical BC-8 carbon lattice matches the crystallographic and physical parameters, but its strain energy is 85 kJ/mol lower than that of the originally proposed supercubane structure.

To reduce the uncertainty of assumed bond parameters, we now report a general approach to optimized geometries and C-C bond lengths for the two diamond lattices and the BC-8 carbon using Allinger's force field (MM2).⁴ The optimized bond lengths and angles may serve as a more reliable basis for future applications.

The calculation starts with the carbon frameworks⁵ of adamantane (1) (cubic diamond), iceane (2) (hexagonal diamond), and pentacyclo[3.3.3.1^{2,11}.1^{4,8}.1^{6,9}]tetradecane (3) (BC-8 carbon) as the smallest representatives of each carbon lattice. Additional



units are successively added, and the resulting models are calculated by MM2.⁶ As may be seen in Figure 1, the strain energy (SE) of the growing models increases continuously and gradually converges to a limiting value for an infinite crystal C_{∞} . Although the largest calculated model for the BC-8 carbon contains 430 carbon atoms, an accurate estimation of SE is clearly not possible (cf. Figure 1). On the other hand, since the error caused by the surface atoms is proportional to the quotient of surface and volume, an extrapolation to $(SE/C)_{\infty}$ is readily achieved according to relation 1. This expression takes into account that the volume of a crystal grows with the number of carbon atoms (n), while its surface is only proportional to $n^{2/3}$:

$$\begin{aligned} (SE/C)_{\infty} - (SE/C) &\sim A/V \\ &\sim n^{2/3}/n \\ &\sim n^{-1/3} \\ \rightarrow (SE/C) &\cong (SE/C)_{\infty} - \alpha \cdot n^{-1/3} \end{aligned} \quad (1)$$

The graph $SE/C = f(n^{-1/3})$ is a straight line (Figure 2) and enables a reliable estimation of $(SE/C)_{\infty}$. The relative strain energies with cubic diamond as reference (SE/C set equal to 0) are as follows:

hexagonal diamond: 2 kJ/mol
BC-8 carbon: 47 kJ/mol

(1) (a) Strel'nitskii, V. E.; Padalka, V. G.; Vakula, S. I. *Zh. Tekh. Fiz.* 1978, 48, 377; *Sov. Phys.—Tech. Phys. (Engl. Transl.)* 1978, 23, 222. (b) Bakai, A. S.; Strel'nitskii, V. E. *Zh. Tekh. Fiz.* 1981, 51, 2414; *Sov. Phys.—Tech. Phys. (Engl. Transl.)* 1981, 26, 1425.

(2) Matyushenko, N. N.; Strel'nitskii, V. E.; Gusev, V. A. *Pis'ma Zh. Eksp. Teor. Fiz.* 1979, 30, 218; *JETP Lett. (Engl. Transl.)* 1979, 30, 199.

(3) Johnston, R. L.; Hoffmann, R. *J. Am. Chem. Soc.* 1989, 111, 810.

(4) Allinger, N. L. *J. Am. Chem. Soc.* 1977, 99, 8127.

(5) Only carbon lattices were calculated. Dangling bonds were not saturated since MM2 has well-known shortcomings in treating close H-H contacts.

(6) The capacity of the program was enlarged so that models up to 465 atoms could be calculated. The parameter set (1982) was not changed.

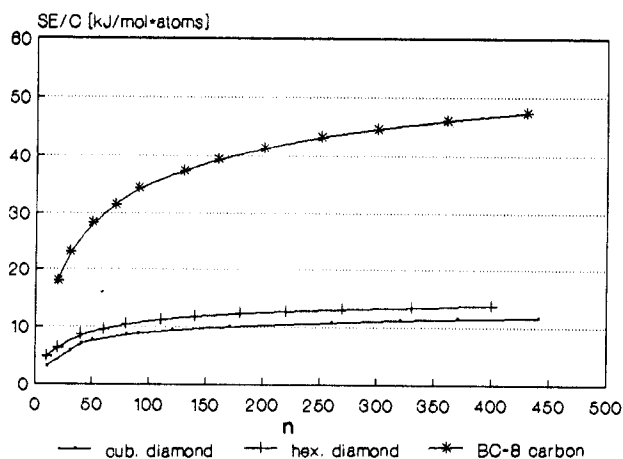


Figure 1. Computed strain energy (SE/C) for diamond and BC-8 models of C_n .

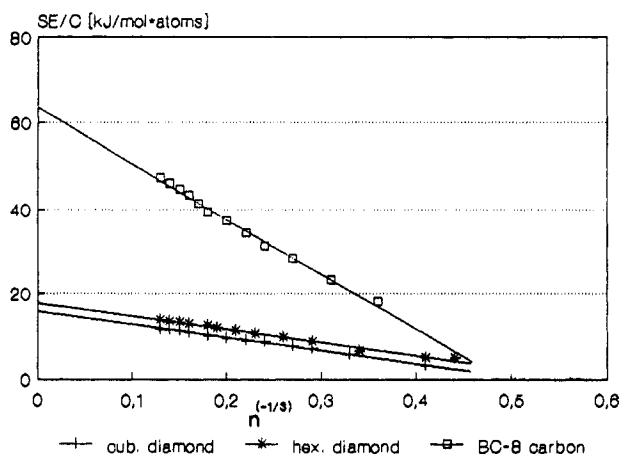


Figure 2. $n^{-1/3}$ plot of strain energies given in Figure 1.

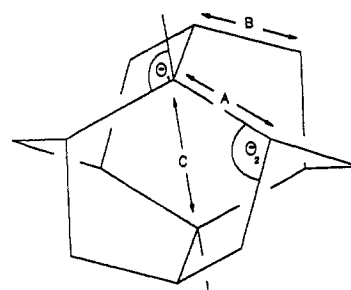


Figure 3. Definitions of structure parameters of BC-8 carbon.

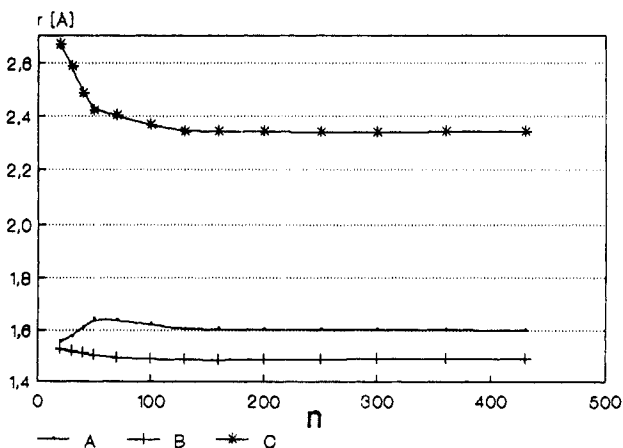


Figure 4. Dependence of the structure parameters A , B , and C , as defined in Figure 3, on n .

Optimized geometries and bond lengths are accessible from the inner shells of the models without appreciable distortion by the

Table I. Comparison of the Newly Calculated MM2 Data of BC-8 Carbon with Previous Work^a

	ref 2	JH ^b	MM2
unit cell, Å	4.28	4.293	4.42
density, g/cm ³	4.1 (calcd)	4.03	3.68
number density, mol-atoms/cm ³	0.338	0.336	0.306
energy, kJ/mol	230 ^c	142	47
A, Å	1.42	1.54 (def)	1.60
B, Å	1.23	1.54 (def)	1.49
C, Å	—	2.18	2.34
θ_1 , deg	99.8	97.94	100.0
θ_2 , deg	116.8	118.12	117.2

^aSee also Figure 3. ^bReferenece 3. ^cCalculated by Hoffmann.

surface atoms. The bond length for both diamond lattices is found to be 1.537 Å (experimental, 1.544 Å) and leads to a cell constant $a = 3.549$ Å of the unit cell of cubic diamond. The calculated density is 3.57 g/cm³.

To ensure that the geometry of BC-8 carbon obtained from the central cage (Figure 3) is independent of surface effects, the distances A, B, and C, are calculated for each model. As can be seen in Figure 4, the corresponding values are constant in models larger than about 200 atoms.

Most important is the nonequivalence of the bond lengths A and B, which were arbitrarily assumed to be identical in the approach of Johnston and Hoffmann. According to our data, every carbon atom has one nearest neighbor at a distance of 1.49 Å and three others at 1.60 Å. The bond angles amount to $\theta_1 = 100.0^\circ$ and $\theta_2 = 117.2^\circ$, respectively. This results in a larger unit cell, with $a = 4.42$ Å and a density of 3.68 g/cm³. Further calculated values are compared with those of Strel'nitskii² and JH³ in Table I.

The geometry of BC-8 obtained from MM2 calculations is more than 90 kJ/mol lower in energy than the idealized lattice assumed previously³ and may be helpful for a more exact calculation of electronic properties.

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Registry No. Carbon, 7440-44-0; diamond, 7782-40-3.

In Situ Chemisorption-Induced Reordering of Oxidatively Disordered Pd(111) Electrode Surfaces

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The preparation and preservation of ordered, well-defined electrode surfaces outside an ultrahigh-vacuum environment are two of the major concerns in electrochemical surface science. We suggest a new, perhaps more general, procedure for generating an ordered surface *under electrochemical conditions*. This method is based upon our observation that a stable, highly ordered superlattice is formed when a Pd(111) single-crystal electrode previously disordered by electrochemical oxidation is exposed, at room temperature and at potentials within the double-layer region, to an alkaline solution of NaI. Four methods have been suggested previously.¹⁻⁵ Three¹⁻³ require high-temperature treatments

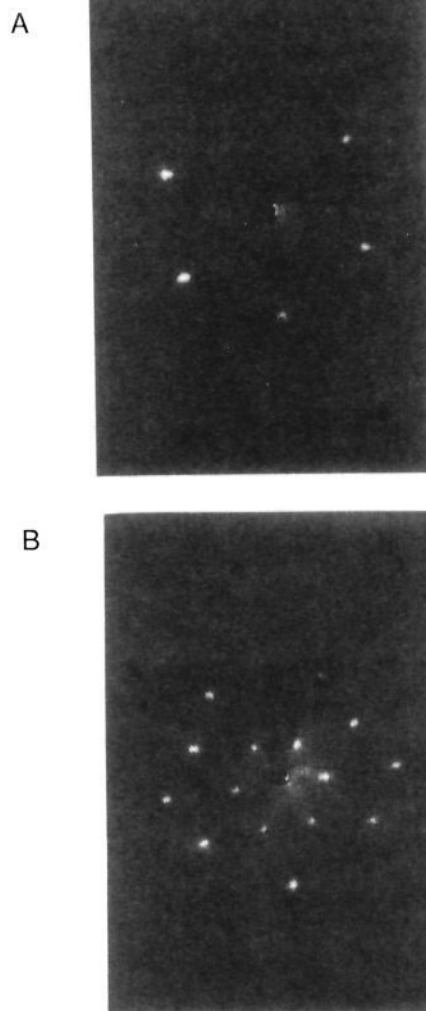


Figure 1. Low-energy electron diffraction (LEED) pattern for a clean and ordered Pd(111) single-crystal electrode before (A) and after (B) exposure to 0.2 mM NaI at pH 10. Beam energy = 60 eV; beam current = 2 μ A.

outside the electrochemical cell. The fourth method,⁵ based upon microscopic electropolishing, may be limited only to reactive metals.

Our experiments were performed in an ultrahigh-vacuum chamber equipped with low-energy electron diffraction (LEED) optics, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and an isolatable compartment for electrochemical experiments.⁶ Preparation of a clean and atomically smooth Pd(111) surface was as described elsewhere.⁶ Electrolytic solutions (pyrolytically triply distilled water⁷) contained 0.1 M NaF adjusted to pH 10 with NaOH. Iodine chemisorption was from 0.2 mM NaI.

Figure 1A shows the LEED pattern for a clean and ordered Pd(111) single crystal. The presence of the sharp (1×1) integral-index spots demonstrate the long-range order of the surface. The LEED pattern that results when the Pd(111) surface is exposed to dilute NaI at pH 10 is shown in Figure 1B. The distinct diffraction spots indicate the existence of a highly ordered layer

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