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Non-superaromatic reference for carbon nanotube as a quasi-one-dimensional π-bonding model for graphite

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A non-superaromatic reference defined for an armchair tubule is proposed as a simple model for the graphite π-electron system. This kind of reference structure is easy to deal with because of its quasi-one-dimensional character. We found that even the non-superaromatic reference for a relatively thin armchair tubule has essentially the same π-binding energy per carbon atom as graphite. The accurate π-binding energy per carbon atom of graphite turned out to be $1.57459724|\beta|$.

1. Introduction

Graphite is a kind of polycyclic benzenoid hydrocarbon with innumerable benzene rings. Many carbonaceous substances, such as soot, charcoal and carbon fiber, consist primarily of microcrystalline forms of graphite. Physical and chemical properties of graphite are primarily determined by its π-electron system. However, it is not easy for chemists to analyze the graphite π-electronic system since it is infinite in size [1–9]. One of the key parameters in the chemistry of carbon is the Hückel π-binding energy per carbon atom of graphite (E_G) [2,3,5–9]. Coulson and Taylor gave E_G in the form of a double integral and obtained the value of $1.576 \cdot |\beta|$ for it [2]. This value has long been referred to in the literature [3,5,6]. In 1987 Stein and Brown [5] and Schmalz and coworkers [6] re-evaluated E_G and reported the improved value of $1.57460|\beta|$.

It is very difficult to estimate an accurate value for E_G from the π-binding energies of planar polycyclic benzenoid hydrocarbons because π-electron properties are very sensitive to the edge structure in the molecule [5,7]. Experiment suggests that planar benzenoid systems with more than 10^5 carbon atoms exhibit a full graphite character [7]. Hosoya and coworkers devised hypothetical edgeless carbon molecules, such as C_{54} in Fig. 1, as π-bonding models for graphite [7–11]. All short straight and long curved lines in the structural formula of C_{54} represent equivalent

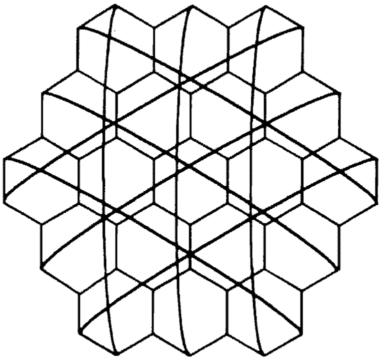

Fig. 1. Structural formula of C_{54}, one of the bezenoid tori.

carbon–carbon π bonds. They noted that the π-binding energy per carbon atom of this type of carbon molecule converges faster to the graphite limit on going to larger members.

We previously found that the π-binding energy per carbon atom of a graphitic tubule is very close to that of graphite [8,11]. It is a novel form of carbon, which is formally obtainable by wrapping a single graphite sheet onto a tubule [12–18]. Carbon nanotubes consist of one or more concentric tubules like this [19]. Many types and thicknesses are conceivable for graphitic tubules [8,11–18]. One may distinguish between them by using the notation (a, b) where a and b are zero or positive integers [13]. Thus, tubule(a, b) is an infinitely long graphitic tubule constructed as shown in Fig. 2.

All graphitic tubules of realistic thickness are as highly aromatic as a graphite sheet [8,11]. Part of the aromatically in graphitic tubules may be attributable to the cylindrical structure of the π-electron system [11]. The aromatic character associated with circumferential π-electron circuits, if any, may be called superaromaticity. However, all graphitic tubules turned out to be essentially non-superaromatic [11]. In this paper, we want to show that the π-binding energy per carbon atom of the superaromaticity-free or non-superaromatic reference structure for graphitic tubules can be formulated analytically. A simple method is also presented for estimating E_G very accurately, which utilizes the π-band energy of the non-superaromatic reference defined for graphitic tubules.

2. Theory

We use the Hückel molecular orbital model in its simplest form, which is identical with a tight-binding approximation in solid-state physics. The mixing of π and σ orbitals due to the curvature of the tubule can be neglected in the first approxima-

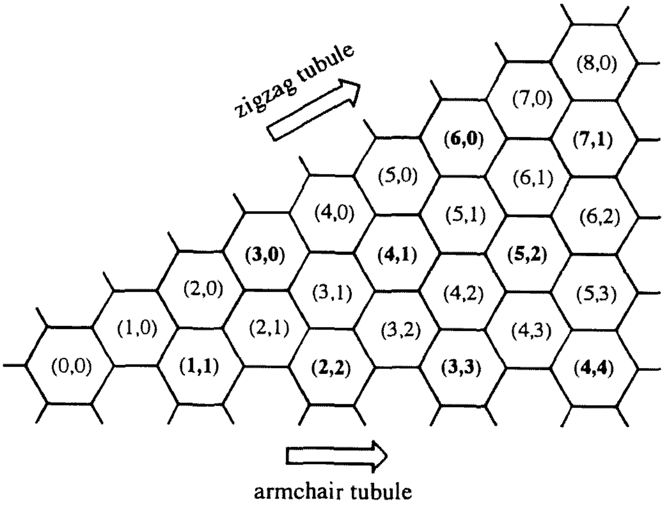

Fig. 2. A single graphite sheet. Tubule(a, b) is formed by rolling the graphite sheet into a cylinder with the hexagon at (a, b) folding onto the hexagon at $(0, 0)$. Bold figures correspond to metallic tubules.

tion [16,20], and thus we consider only π bands. This approximation suffices for the present purpose.

The π-orbital energy of a single graphite sheet can be expressed as a function of a two-dimensional wavenumber vector (k_x, k_y), in which two unit vectors are perpendicular to each other. It is given in the form [1,2,16]

$$\epsilon(k_x, k_y) = \alpha \pm \beta \left[1 + 4\cos\left(\frac{\sqrt{3}k_x c}{2}\right)\cos\left(\frac{k_y c}{2}\right) + 4\cos^2\left(\frac{k_y c}{2}\right) \right]^{1/2} . \tag{1}$$

Here, α and β are the Coulomb integral for sp^2 carbon atoms and the resonance integral between bonded carbon atoms, respectively, and c is $\sqrt{3}$ times the carbon–carbon bond length. In this connection, the Coulson–Taylor formula for E_G is [2]

$$E_G = \frac{|\beta|}{4\pi^2} \int\int [3 + 2\cos x + 2\cos y + 2\cos(x - y)]^{1/2} dx\, dy\,, \tag{2}$$

where the range of integration is $-\pi < x, y < \pi$.

The π-band energy of tubule(a, a) is derived by limiting the values for k_x in eq. (1) to those given by [16]

$$k_x = \frac{2m\pi}{\sqrt{3}ca} \quad (m = 1, \ldots, a) \tag{3}$$

with k_y being taken to be continuous. We then obtain the formula for the π-binding energy per carbon atom of tubule(a, a) in the form

$$E_{\mathrm{T}}(a,a) = \frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1+4\cos\left(\frac{m}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{x}{2}\right)\right]^{1/2}dx$$
$$+\frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1-4\cos\left(\frac{m}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{x}{2}\right)\right]^{1/2}dx. \quad (4)$$

On the other hand, the π-band energy of tubule$(a,0)$ is derived by limiting the values for k_y in eq. (1) to those given by [16]

$$k_y = \frac{2m\pi}{ca} \quad (m=1,\ldots,a) \quad (5)$$

with k_x being taken to be continuous. We then obtain the formula for the π-binding energy per carbon atom of tubule$(a,0)$ in the form

$$E_{\mathrm{T}}(a,0) = \frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1+4\cos\left(\frac{m}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{m}{a}\pi\right)\right]^{1/2}dx$$
$$+\frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1-4\cos\left(\frac{m}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{m}{a}\pi\right)\right]^{1/2}dx. \quad (6)$$

Eqs. (3) and (5) arise from the periodic boundary conditions applied to the circumferences of tubule(a,a) and tubule$(a,0)$, respectively.

Next, a hypothetical isomer of a graphitic tubule is obtained by rolling a long graphitic ribbon into a tubule in such a manner that all carbon–carbon bonds formed at the seam have the resonance integral of $\pm i\beta$, where i is the square root of -1 [21–23]. Every π electron in this structure attains a phase shift of $2n\pi$ rad if it moves around the circumference of the tubule four times. Here and hereafter, n is an arbitrary integer. This isomer is nothing other than a non-superaromatic reference for an actual tubule because circumferential π-electron circuits (i.e., π-electron circuits surrounding the cylinder) do not contribute to aromaticity in this structure [23].

A formula for the π-band energy of the non-superaromatic reference for tubule(a,a) is derived by limiting the values for k_x in eq. (1) to those given by

$$k_x = \frac{(2m+1/2)\pi}{\sqrt{3}ca} \quad (m=1,\ldots,a) \quad (7)$$

with k_y still being taken to be continuous. The π-binding energy per carbon atom of this non-superaromatic reference is obtained in the form

$$E_{\mathrm{ref}}(a,a) = \frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1+4\cos\left(\frac{m+1/4}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{x}{2}\right)\right]^{1/2}dx$$
$$+\frac{|\beta|}{4a\pi}\sum_{m=1}^{a}\int_{-\pi}^{\pi}\left[1-4\cos\left(\frac{m+1/4}{a}\pi\right)\cos\left(\frac{x}{2}\right)+4\cos^2\left(\frac{x}{2}\right)\right]^{1/2}dx. \quad (8)$$

A formula for the π-band energy of the non-superaromatic reference for tubule$(a, 0)$ likewise is derived by limiting the values for k_y in eq. (1) to those given by

$$k_y = \frac{(2m + 1/2)\pi}{ca} \quad (m = 1, \ldots, a) \tag{9}$$

with k_x still being continuous. The π-binding energy per carbon atom of this non-superaromatic reference is obtained in the form

$$\begin{aligned} E_{\mathrm{ref}}(a, 0) = & \frac{|\beta|}{4a\pi} \sum_{m=1}^{a} \int_{-\pi}^{\pi} \left[1 + 4\cos\left(\frac{m + 1/4}{a}\pi\right) \cos\left(\frac{x}{2}\right) \right. \\ & \left. + 4\cos^2\left(\frac{m + 1/4}{a}\pi\right) \right]^{1/2} dx + \frac{|\beta|}{4a\pi} \sum_{m=1}^{a} \int_{-\pi}^{\pi} \\ & \times \left[1 - 4\cos\left(\frac{m + 1/4}{a}\pi\right) \cos\left(\frac{x}{2}\right) + 4\cos^2\left(\frac{m + 1/4}{a}\pi\right) \right]^{1/2} dx \,. \end{aligned} \tag{10}$$

Eqs. (7) and (9) are related to unrealistic boundary conditions that lead to non-superaromatic references of tubule(a, a) and tubule$(a, 0)$, respectively.

3. Results and discussion

Saito and coworkers classified graphitic tubules into armchair, zigzag, and other chiral ones [16]. Tubule$(a, 0)$ and tubule(a, a) represent zigzag and armchair tubules, respectively. Table 1 lists the π-binding energies per carbon atom for six zigzag and armchair tubules and their non-superaromatic references. In general, the π-binding energy per carbon atom of tubule(a, b), $E_{\mathrm{T}}(a, b)$, is slightly dependent on the values of a and b [8]. It is still true that all realistic graphitic tubules are essentially non-superaromatic because their π-binding energies per carbon atom are

Table 1
π-binding energies per carbon atom of graphitic tubules and their non-superaromatic references in units of $|\beta|$.

a	Zigzag tubule		Armchair tubule		Approximate value for E_{G}
	$E_{\mathrm{T}}(a, 0)$	$E_{\mathrm{ref}}(a, 0)$	$E_{\mathrm{T}}(a, a)$	$E_{\mathrm{ref}}(a, a)$	
3	1.55785597	1.57639035	1.56970139	1.57500498	1.575
6	1.57215639	1.57483862	1.57406026	1.57464583	1.5746
12	1.57427337	1.57462812	1.57453262	1.57460325	1.57460
35	1.57460261	1.57459664	1.57459466	1.57459748	1.574597
95	1.57459752	1.57459721	1.57459711	1.57459725	1.5745972
112	1.57459742	1.57459722	1.57459716	1.57459724	1.57459724

close to E_G [11]. This implies that circumferential π-electron pathways in tubule(a, b) are not very important in determining $E_{\mathrm{T}}(a, b)$ [11]. Note that there are no such π-electron circuits in graphite.

The π-binding energy per carbon atom of the non-superaromatic reference, $E_{\mathrm{ref}}(a, b)$, again depends slightly on a and b. For all types of tubules, both $E_{\mathrm{T}}(a, b)$ and $E_{\mathrm{ref}}(a, b)$ converge to the graphite limit E_{G} as we go to thicker ones. In principle, $E_{\mathrm{ref}}(\infty, \infty)$ and $E_{\mathrm{T}}(\infty, \infty)$ are identical with E_{G}. However, the rate of approach to this limit varies among different types of tubules. $E_{\mathrm{ref}}(a, b)$ converges faster than $E_{\mathrm{T}}(a, b)$. It is of interest to note that $E_{\mathrm{ref}}(a, a)$ converges very fast to the limit. The convergence of $E_{\mathrm{ref}}(a, 0)$ is slower, which is partly due to the fact that tubule(a, a) is larger in diameter than tubule$(a, 0)$. It follows that even if a is fairly small, $E_{\mathrm{ref}}(a, a)$ is nearly equal to E_{G}. The convergence of $E_{\mathrm{T}}(a, a)$ is much slower than that of $E_{\mathrm{ref}}(a, a)$.

Approximate values of E_{G} derived from $E_{\mathrm{ref}}(a, a)$ are presented in the sixth column of Table 1. Every number for a given in the first column indicates the smallest one with which $E_{\mathrm{ref}}(a, a)$ represents the approximate E_{G} value given in the sixth column. As can be seen from this table, even $E_{\mathrm{ref}}(3, 3)$ is better as an estimate for E_{G} than the Coulson–Taylor value [2]. $E_{\mathrm{ref}}(6, 6)$ can be used instead of a sufficiently accurate value of $1.5746|\beta|$ for E_{G}. $E_{\mathrm{ref}}(12, 12)$ is comparable to a more accurate value of $1.57460|\beta|$. Thus, even the non-superaromatic reference for a relatively thin armchair tubule, say, tubule(12, 12), appears to be very similar in the π-electronic structure to the infinite graphite sheet. A very accurate value of $1.57459724|\beta|$ for E_{G} is obtainable not only by our so-called triangle method [9] but also from $E_{\mathrm{ref}}(112, 112)$. We found that $E_{\mathrm{ref}}(200, 200)$ and $E_{\mathrm{ref}}(1000, 1000)$ are almost equal to $E_{\mathrm{ref}}(112, 112)$.

Thus, the non-superaromatic references of relatively thin tubules have essentially the same π-binding energy per carbon atom as graphite. However, since large round π-electron circuits are missing in it, it is clear that large round π-electron circuits are not very important in determining the magnitude of $E_{\mathrm{ref}}(\infty, \infty)$ or E_{G} [11]. Non-superaromatic references of all tubules were found to be more or less semiconductive with band gaps. Therefore, the metallic character of tubules with $a + 2b = 3n$ [13,14,16,17] must be related to circumferential π-electron circuits.

As shown in Fig. 3, the densities of states in a two-dimensional graphite sheet and the non-superaromatic reference for tubule(12, 12) are fairly similar to each other although the latter has many singular points. Singular points in the density-of-states curves for tubule(a, a) and its non-superaromatic reference are located at

$$\left|\frac{\epsilon - \alpha}{\beta}\right| = \left|\sin\left(\frac{m+\theta}{a}\pi\right)\right| \quad \text{and} \quad \sqrt{5 \pm 4\cos\left(\frac{m+\theta}{a}\pi\right)} \quad (m = 1, \ldots, a)\,. \tag{11}$$

Here, θ is a constant to be set equal to 0 and 1/4 for tubule(a, a) and its non-superaromatic reference, respectively. The non-superaromatic reference of tubule(a, a) has about twice as many isolated singular points as tubule(a, a) itself. Therefore,

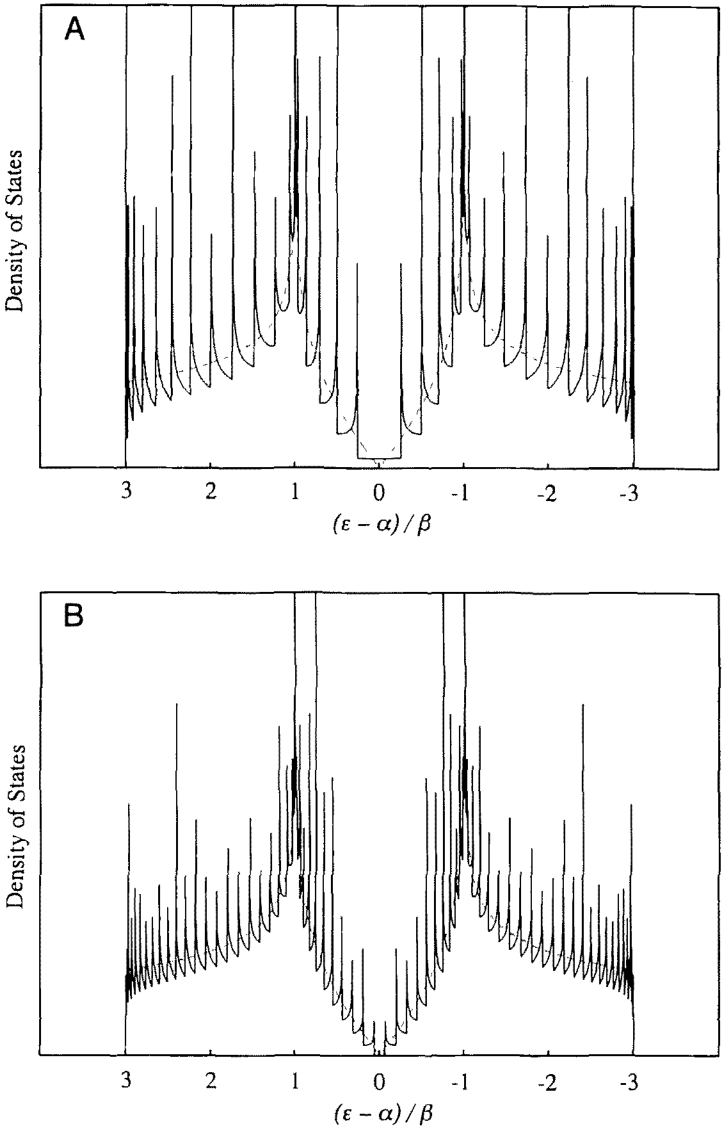

Fig. 3. Densities of states in tubule(12, 12) (A) and its non-superaromatic reference (B). Dashed lines indicate the density of states in graphite.

the density-of-state curve for the former structure oscillates about that for a graphite sheet more frequently and with a smaller effective amplitude. This is the primary reason why the π-binding energy per carbon atom of the hypothetical reference structure is very close to that of graphite.

Stein and Brown attempted to estimate π-electron properties of graphite by utilizing some homologous series of hexagonally symmetric polycyclic benzenoid hydrocarbons [5]. They found that for the fully benzenoid series [24] with benzene and hexabenzeno[*bc,ef,hi,kl,no,qr*]coronene as the first two members, the Hess–Schaad resonance energy per carbon atom [25] converges fairly rapidly to the graphite limit as the molecular size increases. This reminds us that the graphite sheet is an infinite fully benzenoid hydrocarbon [8]. Its hexagonal network can be covered completely with aromatic sextets [24]. Every carbon atom in graphite belongs to any of the aromatic sextets. All metallic tubules can also be viewed as fully benzenoid hydrocarbons. Such a structural similarity may explain why the non-superaromatic reference for an armchair tubule has a strong resemblance to graphite.

4. Concluding remarks

As has been seen above, the non-superaromatic reference for an armchair tubule of fairly small thickness can be used as a quasi-one-dimensional π-bonding model for a two-dimensional graphite sheet. It might be the best π-electron system conceivable for estimating E_G using a small personal computer. It is obvious that eq. (8) is much easier to deal with than the Coulson–Taylor formulation or eq. (2) because the former is given as a sum of simpler integrals. It is still a very mysterious thing that the non-superaromatic references of relatively thin tubules with non-zero band gaps have essentially the same π-binding energies per carbon atom as graphite with no band gap. Since the former structures are semiconductive in nature, they cannot be used to estimate the π-binding energy per carbon atom of charged graphite [9].

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References

[1] P.R. Wallace, Phys. Rev. 71 (1947) 622.
[2] C.A. Coulson and R. Taylor, Proc. Phys. Soc. London A65 (1952) 815.
[3] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic Press, London, 1973) ch. 3.
[4] I. Gutman, Z. Naturforsch. (a) 36 (1981) 128.
[5] S.E. Stein and R.L. Brown, J. Am. Chem. Soc. 109 (1987) 3721.
[6] T.G. Schmalz, W.A. Seitz, D.J. Klein and G.E. Hite, J. Am. Chem. Soc. 110 (1988) 1113.
[7] H. Hosoya, Y. Tsukano, M. Ohuchi and K. Nakada, in: *Computer Aided Innovation of New Materials II*, eds. M. Doyama, J. Kihara, M. Tanaka and R. Yamamoto (Elsevier, Amsterdam, 1993) pp. 155–158.

[8] J. Aihara, T. Yamabe and H. Hosoya, Synth. Met. 64 (1994) 309.
[9] J. Aihara and T. Tamaribuchi, J. Chem. Soc. Faraday Trans. 90 (1994) 3513.
[10] M. Randić, Y. Tsukano and H. Hosoya, Nat. Sci. Rep. Ochanomizu Univ. 45 (1994) 101.
[11] J. Aihara, J. Phys. Chem. 98 (1994) 9773.
[12] J.W. Mintmire, B.I. Dunlap and C.T. White, Phys. Rev. Lett. 68 (1992) 631.
[13] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.
[14] K. Tanaka, K. Okahara, M. Okada and T. Yamabe, Chem. Phys. Lett. 191 (1992) 469.
[15] K. Harigaya, Phys. Rev. B45 (1992) 12071.
[16] R. Saito, M. Fujita, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. B46 (1992) 1804.
[17] D.J. Klein, W.A. Seitz and T.G. Schmalz, J. Phys. Chem. 97 (1993) 1231.
[18] K. Okahara, T. Satoh, H. Aoki, K. Tanaka and T. Yamabe, Chem. Phys. Lett. 219 (1994) 462.
[19] S. Iijima, Nature 354 (1991) 56.
[20] R.C. Haddon, Acc. Chem. Res. 21 (1988) 243.
[21] L.J. Schaad, B.A. Hess, Jr., J.B. Nation and N. Trinajstić, Croat. Chem. Acta 51 (1979) 233.
[22] J. Aihara, Bull. Chem. Soc. Jpn. 52 (1979) 1529.
[23] J. Aihara, J. Chem. Soc. Faraday Trans. 91 (1995) 237.
[24] E. Clar, *The Aromatic Sextet* (Wiley, London, 1972).
[25] B.A. Hess, Jr. and L.J. Schaad, J. Am. Chem. Soc. 93 (1971) 305.