

residue. The mixture was acidified to pH 6 at 0 °C with 2% hydrochloric acid. The ethyl acetate layer was separated and treated with ethereal CH₂N₂ until a yellow color persisted. The solvent was rotoevaporated off and the residue stirred for 18 h at 20 °C in dihydropyran (10 mL) containing toluene-*p*-sulfonic acid (5 mg). Saturated aqueous Na₂CO₃ (10 mL) was then added and the mixture extracted with EtOAc (3 × 10 mL). The EtOAc extracts were dried (K₂CO₃) and evaporated, and the oily residue was chromatographed on silica gel (50 g). EtOAc-hexane (1:20) elution yielded methyl (+)-(2*S*,3*R*)-*cis*-3-[(tetrahydropyranyloxy)methyl]bicyclo[2.2.2]octane-2-carboxylate (489 mg, 38% yield), IR ν 1736 cm⁻¹.

This material (300 mg, 1.06 mmol) was refluxed for 18 h in MeOH (5 mL) containing Na (24 mg, 1.06 mmol). The MeOH was removed by rotoevaporation and the residue dissolved in water (10 mL) and extracted with EtOAc (4 × 10 mL). The EtOAc extracts were washed with saturated aqueous NaCl (2 × 5 mL), dried (MgSO₄), and evaporated. The residue was purified by TLC on silica (EtOAc-hexane (1:3) development) to give methyl (+)-(2*S*,3*R*)-*trans*-3-[(tetrahydropyranyloxy)methyl]bicyclo[2.2.2]octane-2-carboxylate (269 mg, 88%): $[\alpha]_D^{25} +33.8^\circ$ (*c* 1, CHCl₃); IR ν 1736 cm⁻¹; ¹H NMR δ 1.0-2.70 (m, 18 H), 3.22-4.36 (m, 4 H), 3.72 (s, 3 H), 4.82 (br d, 1 H, *J* = 21 Hz).

This (+)-*trans*-THP ester (260 mg, 0.92 mmol) in THF (2 mL) was added with stirring to LiAlH₄ (53 mg, 1.3 mmol) in THF (1 mL) at 20 °C, and stirring was continued for 16 h. The reaction was then quenched by the careful sequential addition of water (0.05 mL), 15% aqueous NaOH (0.05 mL), and water (0.15 mL). The mixture was filtered and the filtrate rotoevaporated. The residue obtained was stirred for 4 h with acetic acid-H₂O-THF (3:1:1, 2 mL). Aqueous NaOH, 15%, was then added until the mixture was basic. It was then extracted with EtOAc (3 × 5 mL). The EtOAc extracts were washed with saturated aqueous NaCl (1 × 5 mL), dried (MgSO₄), and evaporated. Kugelrohr distillation of the residue afforded (+)-(2*R*,3*R*)-*trans*-bis(hydroxymethyl)bicyclo[2.2.2]octane ((+)-**27**, 88 mg, 56% yield): bp 130 °C (0.25 mmHg), mp 90-94 °C (lit.^{10a} mp 108-110 °C), $[\alpha]_D^{25} +50.9^\circ$ (*c* 1, MeOH), lit.^{10b} $[\alpha]_D^{25} +53.4^\circ$ (*c* 1, MeOH); IR ν 3390 cm⁻¹; ¹H NMR δ 1.70 (s, 12 H), 3.30-3.72 (m, 2 H), 4.40 (br s, 2 H).

(+)-(2*S*,3*R*)-*cis*-*endo*-3-(Hydroxymethyl)bicyclo[2.2.2]oct-5-ene-2-carboxylic Acid Lactone ((+)-**14**). The absolute configuration of the saturated [2.2.2] lactone (+)-**14** (100 mg, 0.61 mmol) was established as for (+)-**12** → (+)-**13** by its hydrogenation to (+)-(2*S*,3*R*)-*cis*-3-(hydroxymethyl)bicyclo[2.2.2]octane-2-carboxylic acid lactone ((+)-**15**, 93 mg, 95% yield), $[\alpha]_D^{25} +114.7^\circ$ (*c* 0.74, CHCl₃).

Conversion of Lactone (+)-10 to the Prostaglandin Precursor 28. The [2.2.1] lactone (+)-**10** (1.0 g, 6.7 mmol) was refluxed for 1 h in MeOH (5 mL) containing KOH (560 mg, 10 mmol). The solvent was then rotoevaporated and EtOAc (50 mL) added to the residual white solid.

The mixture was cooled to 0 °C, acidified to pH 4 with 2 M hydrochloric acid, and extracted with EtOAc. The EtOAc extracts were treated with ethereal CH₂N₂ until faintly yellow. Excess CH₂N₂ was removed by bubbling N₂ into the solution, which was then dried (MgSO₄) and rotoevaporated. The residual oil was dissolved in CH₂Cl₂ (10 mL) at 20 °C and pyridinium chlorochromate (2.02 g, 10 mmol) added with stirring. After 1 h, the mixture was filtered and the solid washed with ether (10 × 5 mL). The combined organic solutions were filtered through a Celite plug and rotoevaporated. The residual oil was diluted with MeOH (20 mL) containing concentrated H₂SO₄ (2 drops) and the mixture refluxed for 36 h and then cooled. Saturated aqueous Na₂CO₃ (50 mL) was added cautiously and the aqueous layer extracted with EtOAc (5 × 15 mL). The dried (MgSO₄) EtOAc solution was evaporated and the residue purified by TLC on silica gel with EtOAc-hexane (1:10) development to give methyl (+)-(2*S*,3*R*)-*trans*-3-(dimethoxymethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate (**28**, 630 mg, 42% yield): bp 80 °C (0.25 mmHg) (lit.¹¹ bp 114-115 °C (6 mmHg)), $[\alpha]_D^{25} +95.7^\circ$ (*c* 0.28, CHCl₃); IR ν 1736 cm⁻¹; ¹H NMR δ 1.40-1.64 (m, 2 H), 2.02-2.36 (m, 1 H), 3.06-3.24 (m, 1 H), 3.32 (d, 6 H, *J* = 6 Hz), 4.24 (d, 1 H, *J* = 7.5 Hz), 5.94 (d of d, 1 H, *J* = 3 Hz), 6.26 (d of d, 1 H, *J* = 3 Hz).

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Registry No. **1**, 699-97-8; **2**, 5062-98-6; **3**, 699-95-6; **4**, 5062-97-5; **5**, 57427-48-2; **6**, 65942-08-7; (+)-**10**, 95340-88-8; (±)-**10**, 95340-89-9; (+)-**11**, 95340-90-2; (±)-**11**, 95340-91-3; (+)-**12**, 95340-92-4; (±)-**12**, 95340-93-5; (+)-**13**, 95340-94-6; (±)-**13**, 95340-95-7; (+)-**14**, 95340-96-8; (±)-**14**, 95403-17-1; (+)-**15**, 95340-97-9; (±)-**15**, 95218-40-9; **16**, 95218-41-0; **17**, 15216-53-2; **18**, 95340-98-0; **19**, 95218-42-1; **20**, 95340-99-1; **21**, 95341-00-7; **22**, 95218-43-2; **23**, 95218-44-3; **24**, 95341-01-8; **25**, 95341-02-9; **26**, 95341-03-0; **27**, 57222-02-3; **28**, 95341-04-1; *cis*-*endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride, 129-64-6; *cis*-*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride, 24327-08-0; methyl (+)-(2*S*,3*R*)-*cis*-*exo*-3[(phenylselenyl)methyl]bicyclo[2.2.1]heptane-2-carboxylate, 95218-45-4; methyl (+)-(2*S*)-*exo*-bicyclo[2.2.1]heptane-3-one-2-carboxylate, 95341-05-2; methyl (+)-(2*R*)-*endo*-3-methylenebicyclo[2.2.1]heptane-2-carboxylate, 95341-06-3; methyl (+)-(2*S*,3*R*)-*cis*-3-[(tetrahydropyranyloxy)methyl]bicyclo[2.2.2]octane-2-carboxylate, 95218-46-5; methyl (+)-(2*R*,3*R*)-*trans*-3-[(tetrahydropyranyloxy)methyl]bicyclo[2.2.2]octane-2-carboxylate, 95341-07-4; alcohol dehydrogenase, 9031-72-5.

Exact Hückel Molecular Orbitals of the Finite, Square-Cut, FCC Crystal

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Abstract: The exact Hückel molecular orbitals of the finite, square-cut, FCC crystal are derived from the molecular orbitals of a "master", finite, cubic crystal by constructing the former from the latter by crossing out a series of atoms analogous to the starred atoms of an alternant hydrocarbon.

Although Bloch waves have been used for more than a generation to describe the tight-binding in infinite crystals,^{1,2} little

interest has focused on the wave functions for finite crystals. It was only in 1977 and 1979 that first Messmer,³ in his "analytical

(1) See, for example: (a) Peierls, R. E. "Quantum Theory of Solids"; Oxford University Press; London, 1955. (b) Reitz, J. R. *Solid State Phys.* **1955**, *1*, 1.

(2) Slater, J. C.; Koster, G. F. *J. Chem. Phys.* **1954**, *94*, 1498. The matrix elements between plane waves in the infinite FCC crystal are given in Table III, terms with subscript 2.

(3) (a) Messmer, R. P. *Phys. Rev. B* **1977**, *15*, 1811. (b) Messmer, R. P. In "The Nature of the Surface Chemical Bond"; Rhodin, T. N., Ertl, G., Ed.; North Holland: Amsterdam, 1979; Chapter 2, pp 65-67. A much earlier reference is actually the following: Baldock, G. R. *Proc. Phys. Soc. London, Ser. A* **1953**, *66*, 2. Baldock gives the wave functions (1) for the simple cubic lattice and also for a BCC lattice bound by one (100) and two (110) type faces.

cluster model⁷, and then we⁴ showed that the Hückel molecular orbitals, for the finite cubic crystal, have extremely simple analytical expressions. This is true whether each atom carries an s orbital, a p orbital, or a d orbital.⁵ For a cube with N atoms along each edge, these Hückel orbitals are given in terms of the atomic orbitals Φ_{rst} as

$$\psi_{jkl} = \left(\frac{2}{N+1} \right)^{3/2} \sum_{rst} (\sin r\theta \sin s\phi \sin t\chi) \Phi_{rst} \quad (1)$$

$$\theta = \frac{j\pi}{N+1}, \phi = \frac{k\pi}{N+1}, \chi = \frac{l\pi}{N+1} \quad 1 \leq j, k, l \leq N \quad (2)$$

The integers j , k , and l characterize the wave vector associated with the molecular orbital ψ .⁴ The matrix element between two different molecular orbitals is easily evaluated by taking a central atom r , s , and t surrounded by its six nearest neighbors, as shown in Figure 1 for an s orbital surrounded by six d_{z^2} orbitals. The s orbital is assumed to belong to a wave ψ_{jkl} while the z^2 orbitals belong to a wave $\psi_{j'k'l'}$. The off-diagonal matrix element is then

$$\begin{aligned} \langle \psi_{jkl} / \psi_{j'k'l'} \rangle = & \sum_{rst} [\beta_x (\sin(r-1)\theta' + \\ & \sin(r+1)\theta') \sin s\phi' \sin t\chi' + \beta_y (\sin(s-1)\phi' + \\ & \sin(s+1)\phi') \sin r\theta' \sin t\chi' + \beta_z (\sin(t-1)\chi' + \\ & \sin(t+1)\chi') \sin r\theta' \sin s\phi'] \\ & \sin r\theta \sin s\phi \sin t\chi = \\ & \delta_{j'j} \delta_{k'k} \delta_{l'l} (2\beta_x \cos \theta + 2\beta_y \cos \phi + 2\beta_z \cos \chi) \quad (3) \end{aligned}$$

which is nonzero only for identical wave vectors. It is easily verified that (3) holds also if atom rst is an edge atom or a corner atom. The matrix element (3) is identical with that found by Slater and Koster for the infinite crystal,² thus, replacing the plane waves of an infinite cubic crystal by the sine waves of a finite cubic crystal has no consequence on the mixing between the waves.

If instead of two different types of AO's in Figure 1 we had used a single type, the parentheses in (3) would give the corresponding diagonal Hückel energy for the molecular orbital of that type

$$\epsilon_{jkl} = 2\beta_x \cos \theta + 2\beta_y \cos \phi + 2\beta_z \cos \chi \quad (4)$$

Let us now turn to a finite face-centered cubic (FCC) crystal, assumed to be cut along square, (001)-type faces. It is convenient to consider this crystal as deriving from a "master" cubic crystal in which one atom out of two (the "starred" atoms in Figure 2) has been crossed out. We keep the same principle for atom numbering as in the matter cube: the indexes r , s , and t increase, respectively, by 1 for each unitary translation along the x , y , and z directions marked by the edges of the cube. The FCC atoms then have the numberings shown in Figure 2 for a "3 × 3" cube. When going from one of the FCC crystal to its nearest neighbor, the sum of the atomic indexes varies by 0 or 2, instead of 1, in the cubic crystal.

Let us now first assume that each atom carries a single (s, p, or d) orbital. We then take a central atom rst surrounded by its 12 nearest neighbors, as shown in Figure 3A for s atomic orbitals. If we try again a sine solution of the form of (1), we find in a straightforward manner

$$\epsilon_{jkl} = 4\beta_{xy} \cos \theta \cos \phi + 4\beta_{zx} \cos \theta \cos \chi + 4\beta_{zy} \cos \phi \cos \chi \quad (5)$$

which is exactly the Slater-Koster diagonal energy for s orbitals in the infinite FCC crystal. The same result holds if rst is a face, an edge atom, or a corner atom. Thus, sine waves seem to be

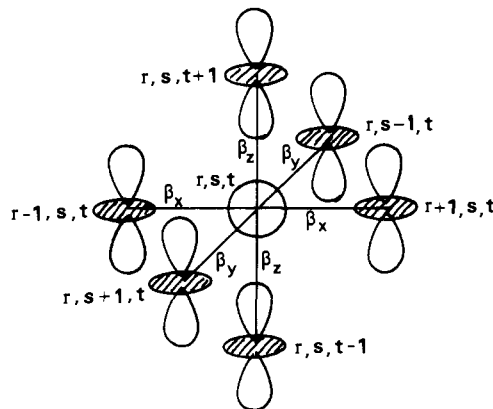


Figure 1. Nearest-neighbor atomic interactions in a cubic crystal.

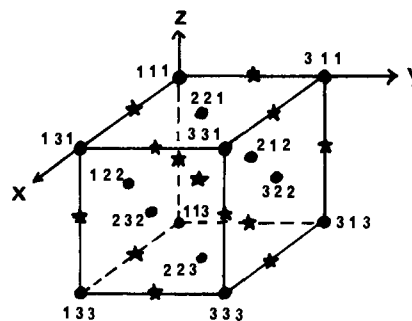


Figure 2. Numbering of the atoms in a finite FCC crystal. Starred atoms belong to the master cubic crystal from which the FCC crystal is derived by deleting one atom out of two.

potential analytical solutions for the MO's of the finite FCC crystal.

However, we cannot choose any arbitrary ensemble of sine waves. The FCC crystal has half as many atoms as the master cubic crystal from which it derives (Figure 2). We must therefore choose combinations of the "master"-cube functions which vanish on the extra starred atoms. Now it is a remarkable fact that the extra atoms of the master cube and the true atoms of the FCC crystal are like the starred and unstarred atoms of an alternant hydrocarbon.⁶ To cancel the atomic orbital coefficients on one set of atoms, it suffices to remember that the MO's of alternant hydrocarbons occur in pairs, with energies ϵ and $-\epsilon$ and with a changed sign on one set of atoms.⁶ Hence, in terms of the solutions ψ_{jkl} of the cube given in (1), the exact solutions for the finite FCC crystal are

$$\psi_{jkl}^{\text{FCC}} = \frac{1}{(2)^{1/2}} (\psi_{jkl}^{\text{master cube}} + \psi_{N+1-j, N+1-k, N+1-l}^{\text{master cube}}) \quad (6)$$

$$3 \leq j + k + l \leq \frac{3(N+1)}{2}$$

Equation 6 can also be written

$$\psi_{jkl}^{\text{FCC}} = \frac{1}{(2)^{1/2}} \left(\frac{2}{2N+1} \right)^{3/2} \sum_{rst} [1 - (-1)^{r+s+t}] (\sin r\theta \sin s\phi \sin t\chi) \Phi_{rst} \quad (7)$$

$$\frac{3\pi}{N+1} \leq \theta + \phi + \chi \leq \frac{3\pi}{2}$$

(4) Salem, L.; Leforestier, C. *Surf. Sci.* 1979, 82, 390. In this paper, ξ should replace ξ on p 398, while the (2,4) and (4,2) elements of matrix A.2 should have a negative sign. On p 392 a is defined as the lattice spacing in the cubic crystal ($2^{1/2}a$ for the FCC crystal, $3^{1/2}a$ for the BCC crystal).

(5) Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* 1983, 105, 1079. For another recent treatment see: Montella, N.; Barone, V.; Del Re, G. *Int. J. Quantum Chem.* 1984, 26, 869.

(6) (a) Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Phil. Soc.* 1940, 36, 193. (b) Longuet-Higgins, H. C. *J. Chem. Phys.* 1950, 18, 265. (c) Hall, G. G. *Proc. R. Soc. London, Ser. A* 1955, 229, 251. (d) Salem, L. In "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966; Section 1-9.

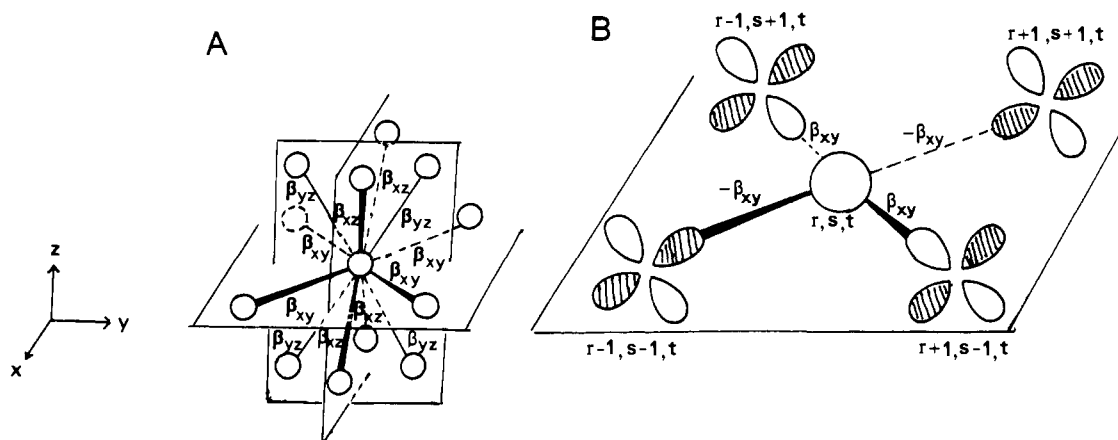


Figure 3. Nearest-neighbor atomic interactions in a FCC crystal: (A) identical atomic orbitals; (B) different atomic orbitals with matrix element of variable sign.

These solutions have nonvanishing amplitudes only on those atoms for whom the sum of the indexes r , s , and t is odd—as required by the numbering of Figure 2. Their energy, which would vanish in the parent cubic network, is given by (5) in the FCC network.

If we now allow for several different types of atomic orbitals on each center, the problem becomes more complex. Two cases arise.

(1) If the matrix elements between a central orbital (s , say) and its 12 neighbors (z^2 , say) have a constant sign in each of the three planes (xy , xz , and yz) of interaction, the two corresponding molecular orbitals ($\psi_{jkl}^s, \psi_{j'k'l'}^{z^2}$) mix only if they correspond to the same wave vector (jkl). The mixings are then again identical with the Slater–Koster mixings² for the infinite FCC crystal. The situation for the finite FCC crystal in this case is similar to that for the finite cubic crystal.

(2) If the matrix elements between a central orbital (s , say) and its nearest neighbors in a plane (xy , say) change sign as a Figure 3B,⁷ then a complicating factor arises: *molecular orbitals corresponding to different wave vectors jkl and $j'k'l'$ mix together.*

This complication is the “price” which we must pay for having a lower translational symmetry in the finite FCC crystal than in the finite cubic crystal.⁸

Nevertheless, it is a great advantage to know the analytical form of the Hückel MO's in the FCC crystal. In the study of the catalytic dissociative interaction between an adsorbate and a finite crystal, we may now calculate the contributions to the interaction energy of distinct families of functions, each characterized by its wave vector. Such studies are now in progress for the nickel, H_2 system.

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(7) The presence of β 's of opposite signs in the same plane coincides with the fact that the Slater–Koster matrix element for the infinite crystal is a product of two sine functions,² instead of a product of two cosine functions.

(8) Other types of faceting of the FCC crystal will not give as simple results as eq 6 and 7.

Design, Synthesis, and DNA Binding Properties of Bifunctional Intercalators. Comparison of Polymethylene and Diphenyl Ether Chains Connecting Phenanthridine

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Abstract: A bifunctional DNA intercalating agent N,N' -(4,4'-oxydibenzyl)bis(phenanthridinium chloride) (**9**) has been synthesized. Interaction of this compound with DNA has been compared to an analogous bifunctional intercalator, N,N' -decamethylenebis(phenanthridinium bromide) (**10**) and to analogous monofunctional intercalators. Viscometric titrations with sonicated calf thymus DNA show compound **9** to be a bifunctional intercalator. Thermal denaturation of calf thymus DNA and Scatchard analysis of the DNA binding of these mono- and bifunctional intercalators show that the relatively rigid compound **9** has a significantly higher affinity for DNA. X-ray crystallographic studies of **9** indicate that the phenanthridine rings are parallel and properly spaced for bifunctional intercalation. This conformation is consistent with a neighbor exclusion model. Crystallographic studies of **10** indicate that the phenanthridine rings are coplanar in contrast to the solution DNA binding properties.

The suggestion that planar organic compounds can bind to DNA by an intercalation mechanism was first stated explicitly

by Lerman¹ in his classic studies of the binding of acridines to DNA. Since that pivotal work, interference with nucleic acid

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(1) Lerman, L. S. *J. Mol. Biol.* **1961**, *3*, 18.