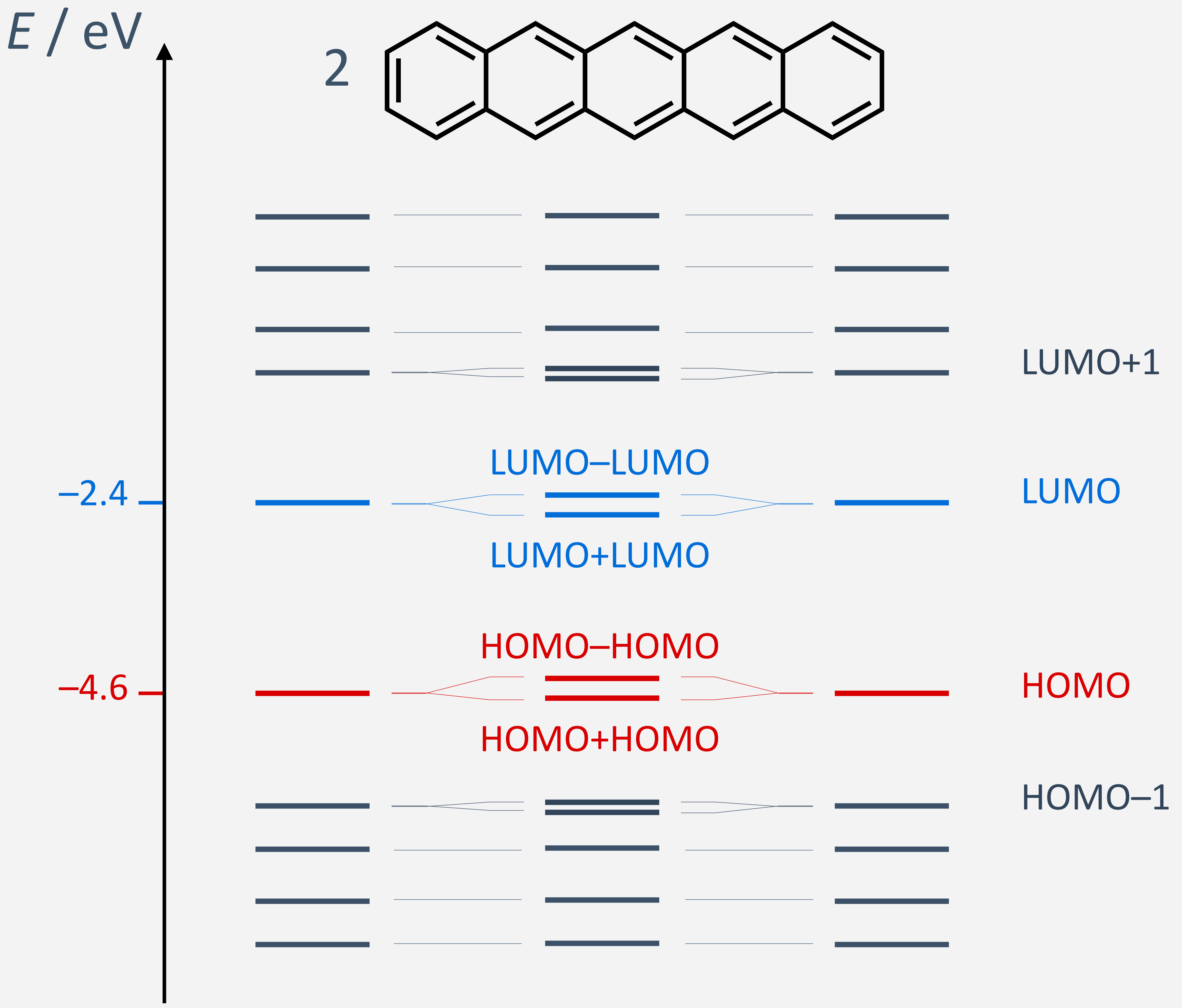
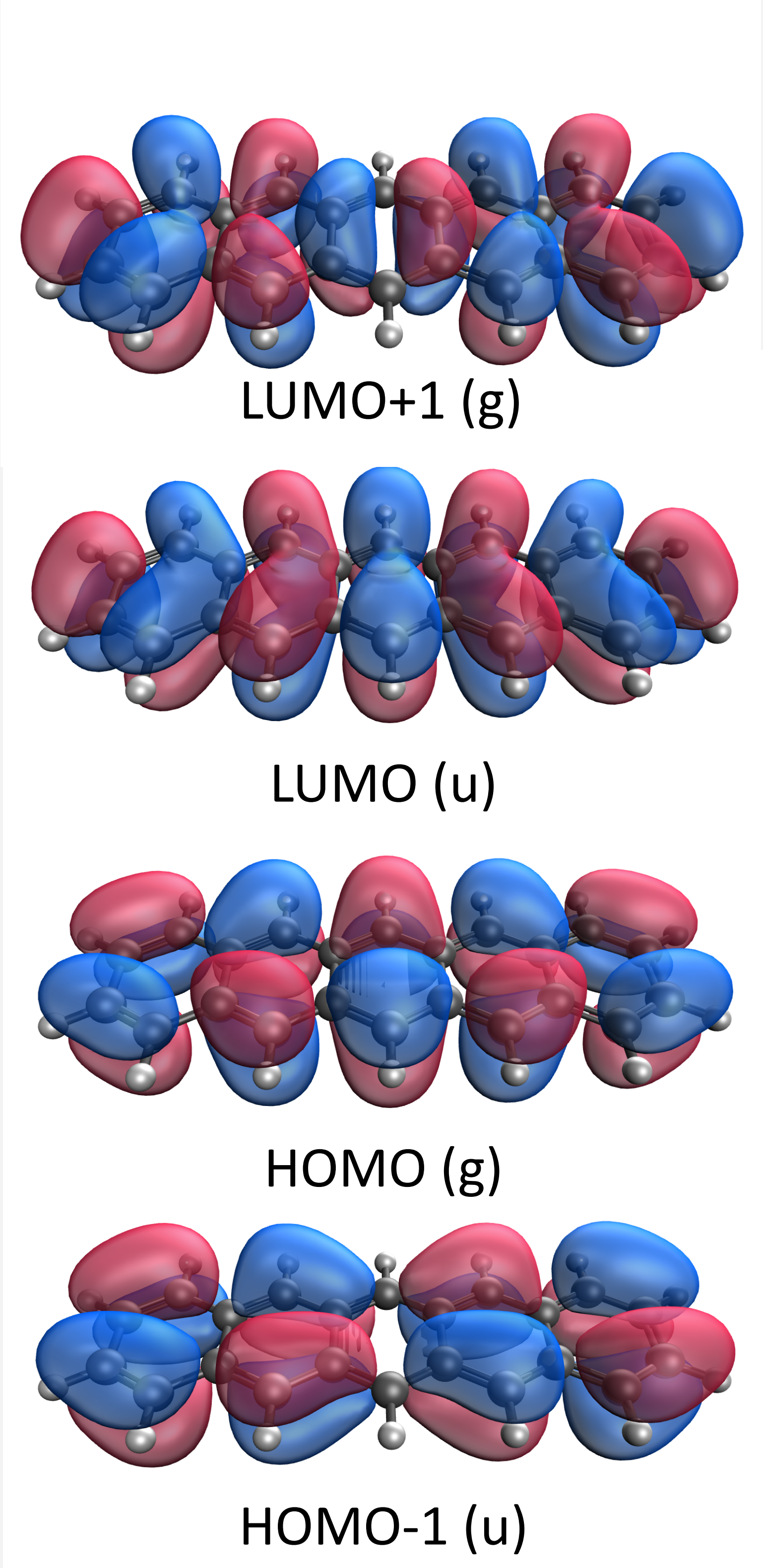
3.3 Intermolecular Electron Delocalization

Intermolecular MO Interactions in the Solid State

- close packing results in (weak) electronic coupling between π MO of matching symmetry
- interaction of π MO can be expressed in linear combination, resulting in (small) splitting





- **HOMO interacts with HOMO, LUMO interacts with LUMO, because of same parities**
- **no interaction between HOMO and LUMO, because of opposite parity & energy difference**
- **MO interactions are not the reason but the consequence of other π interactions !**

Model for Band Structure in Organic Crystals

- band structure computed using a basis set $\psi_{k,i}$ built from localized molecular orbitals ϕ_i of the isolated molecule i, which have been adapted for translational symmetry (Bloch states):

$$\psi_{k,i} = \frac{1}{\sqrt{N}} \sum_{R} \phi_i(\vec{r} - \vec{R})\ e^{ik\vec{R}}$$

where $\vec{r}$ is the position within the unit cell and $\vec{R}$ is a translational element of crystal lattice in direct space (Bravais lattice), in terms of its unit vectors:

$$\vec{R} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

and the wave vector k is a lattice vector in reciprocal space (by Fourier transform of direct space) in terms of its unit vectors:

$$\vec{k} = m_1\vec{a'} + m_2\vec{b'} + m_3\vec{c'}$$

- **“tight binding model” based on “linear combination of molecular orbitals” (analogous to LCAO for covalent bond) under periodic boundary conditions**

Homework: Troisi, Orlandi, *J. Phys. Chem. B*, 2005, *109*, 1849.

Model for Band Structure in Organic Crystals

- the effective one-electron Hamiltonian matrix elements are a sum over non-zero couplings between pairs of molecular orbitals originating from neighboring molecules i and j):

$$H_{kij} = \langle \psi_{ki} | H | \psi_{kj} \rangle = \sum_{R} e^{ik\vec{R}} \langle \phi_i(\vec{r}) | H | \phi_j(\vec{r} - \vec{R}) \rangle$$

- given that the basis elements are non-orthogonal, the spatial overlap of molecular orbitals are given by the matrix elements:

$$S_{ij} = \langle \phi_i(\vec{r}) | \phi_j(\vec{r} - \vec{R}) \rangle$$

- band energies are obtained by solving the matrix eigenvalue equation for each value of $\vec{k}$ (which is continuous but needs to be discretized):

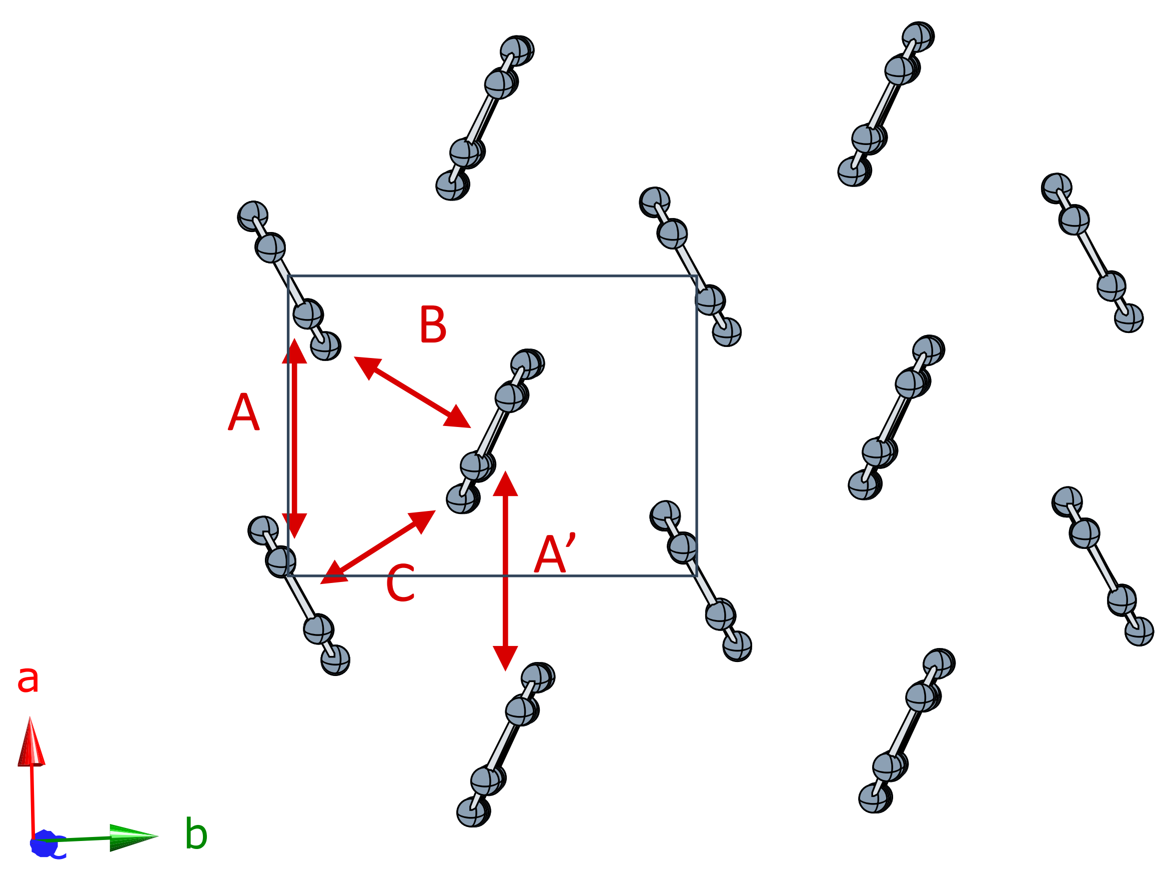
$$H_k C_k = \epsilon_k S_k C_k$$

where ϵ_k is the energy and C^k is the matrix of expansion coefficients (both depending on $\vec{k}$)

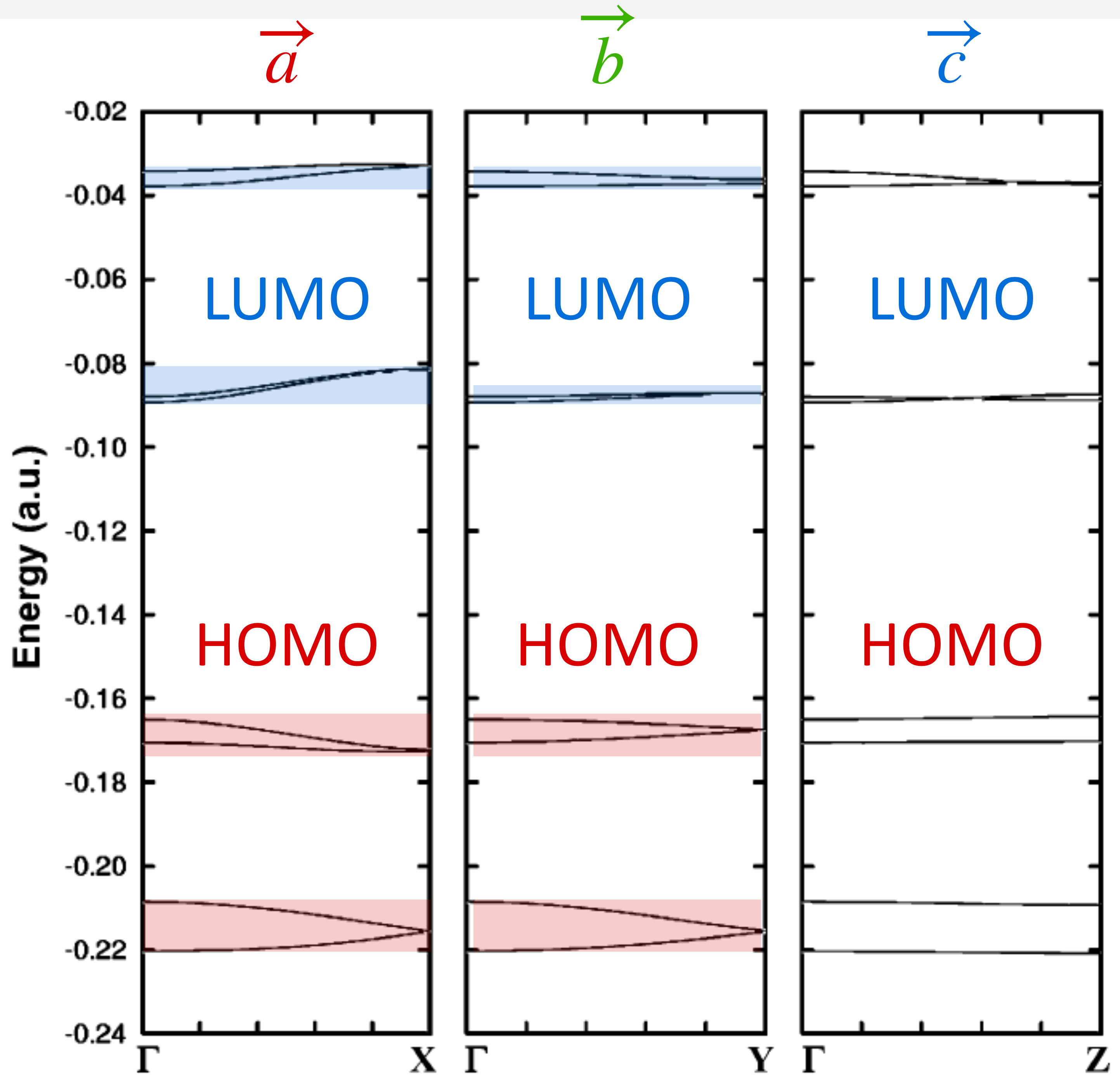
Homework: Troisi, Orlandi, *J. Phys. Chem. B*, 2005, *109*, 1849.

Band Structure of Pentacene

intemolecular couplings



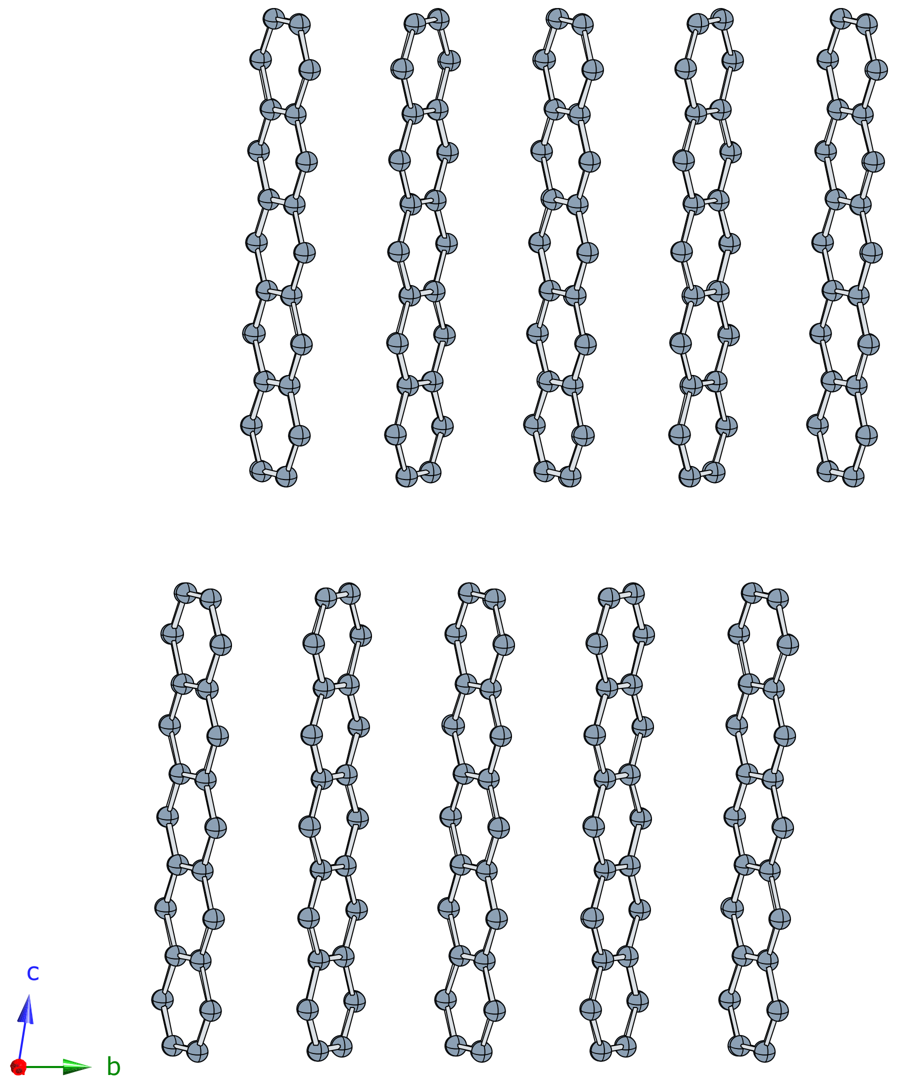
two inequivalent moleculesin unit cell

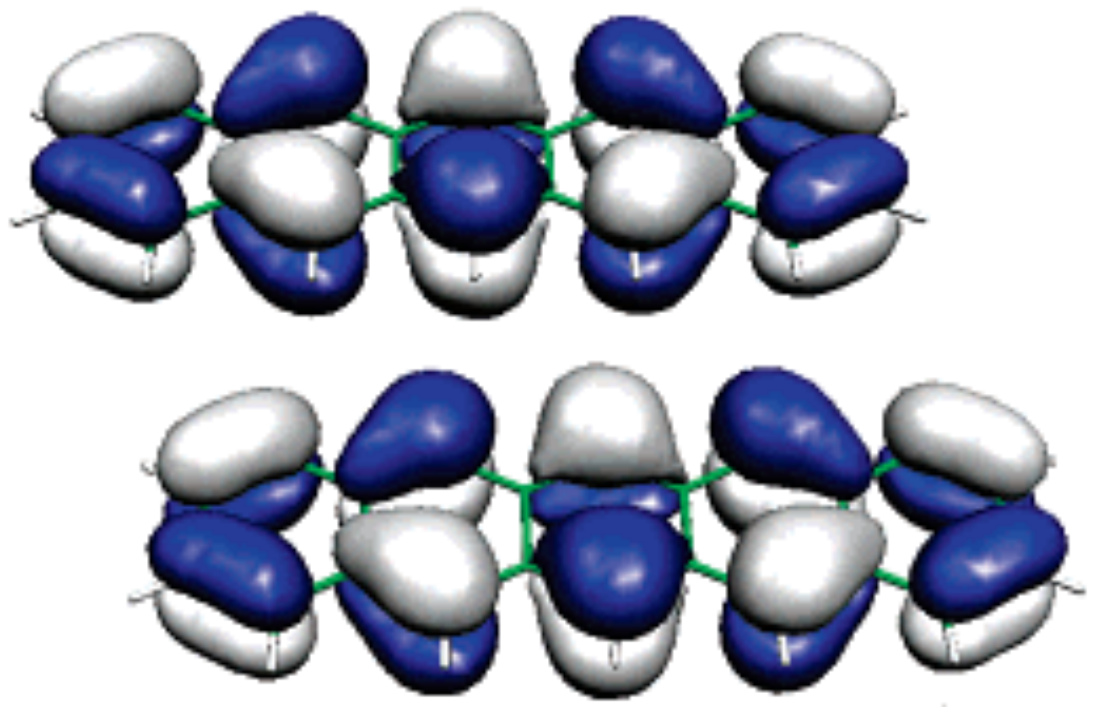


band widths 70–200 meV

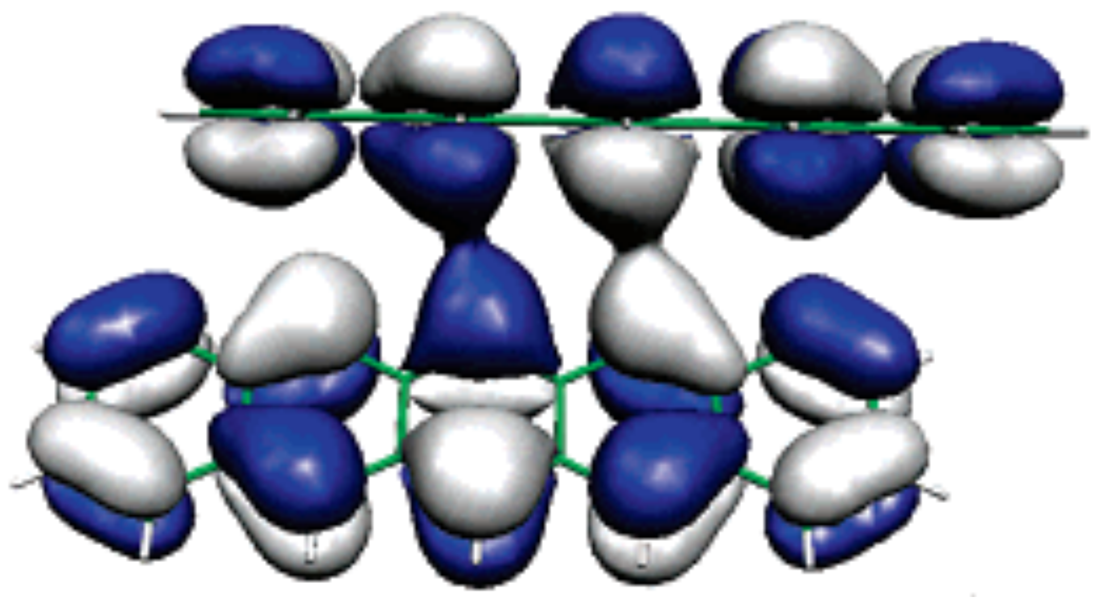
sharp energy levels

no interlayer coupling

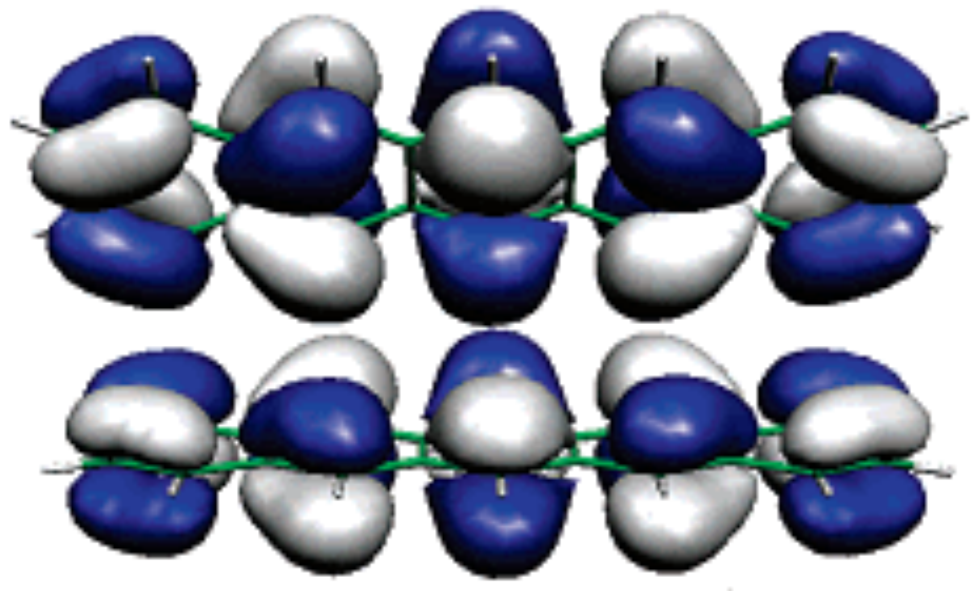




A



B



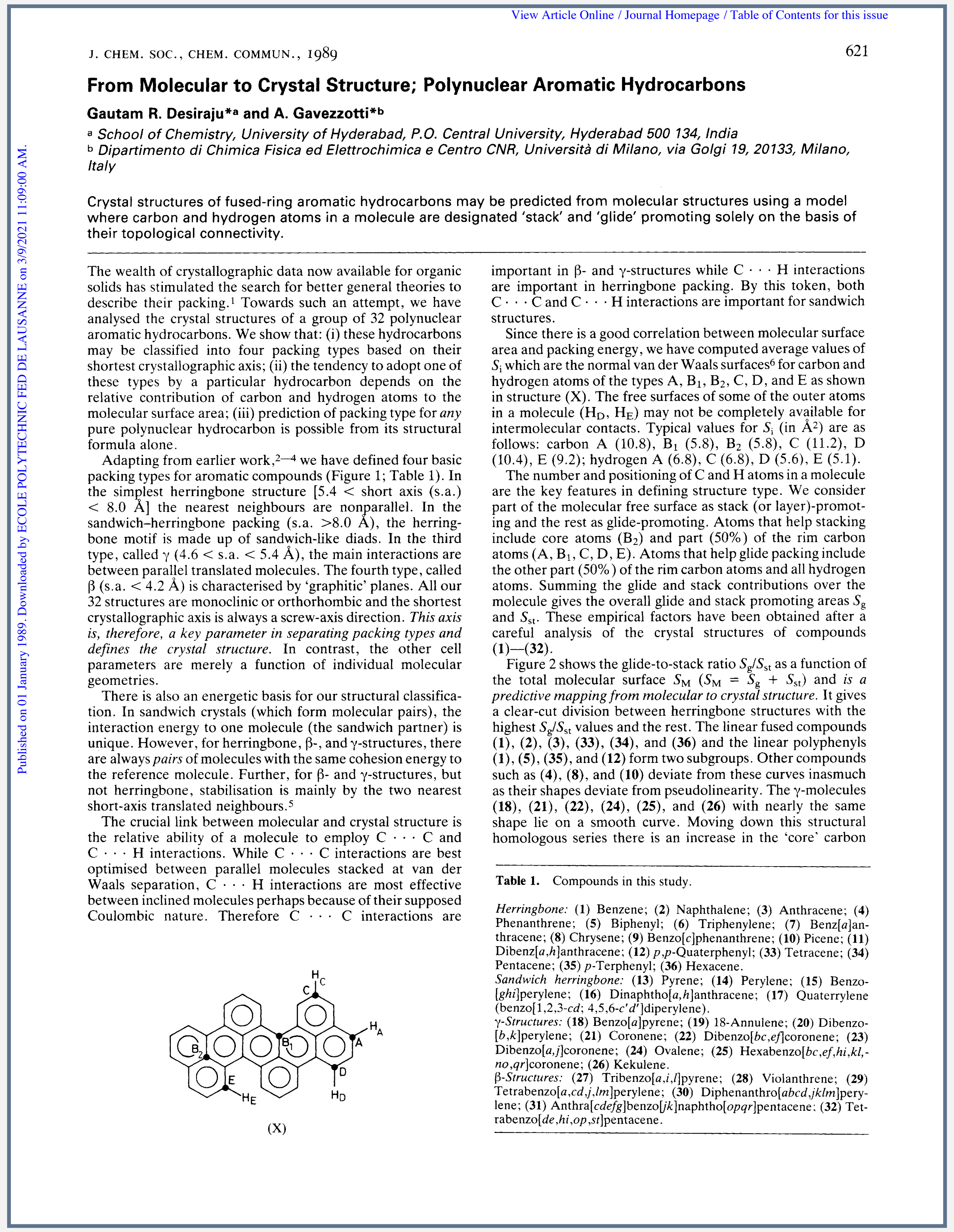
C

Troisi, Orlandi, *J. Phys. Chem. B*, 2005, *109*, 1849.

Learning Outcome

- **Dispersive and quadrupolar π interactions drive the packing of π-conjugated molecules in the solid state**
- **MO interactions are the consequence of dispersive and quadrupolar π interactions !**
- **π molecular orbitals interact because of the resulting parallel-displaced or edge-to-face interactions**
  - π-overlap small but energetically disfavorable in terms of electronic energy
  - overall increase in electron density
- **nevertheless, resulting π-interactions result in narrow, anisotropic intermolecular bands**

Homework and Reading Assignments



J. CHEM. SOC., CHEM. COMMUN., 1989 621

From Molecular to Crystal Structure; Polynuclear Aromatic Hydrocarbons

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Crystal structures of fused-ring aromatic hydrocarbons may be predicted from molecular structures using a model where carbon and hydrogen atoms in a molecule are designated 'stack' and 'glide' promoting solely on the basis of their topological connectivity.

The wealth of crystallographic data now available for organic solids has stimulated the search for better general theories to describe their packing.[1] Towards such an attempt, we have analysed the crystal structures of a group of 32 polynuclear aromatic hydrocarbons. We show that: (i) these hydrocarbons may be classified into four packing types based on their shortest crystallographic axis; (ii) the tendency to adopt one of these types by a particular hydrocarbon depends on the relative contribution of carbon and hydrogen atoms to the molecular surface area; (iii) prediction of packing type for *any* pure polynuclear hydrocarbon is possible from its structural formula alone.

Adapting from earlier work,[2—4] we have defined four basic packing types for aromatic compounds (Figure 1; Table 1). In the simplest herringbone structure [5.4 < short axis (s.a.) < 8.0 Å] the nearest neighbours are nonparallel. In the sandwich–herringbone packing (s.a. >8.0 Å), the herringbone motif is made up of sandwich-like diads. In the third type, called γ (4.6 < s.a. < 5.4 Å), the main interactions are between parallel translated molecules. The fourth type, called β (s.a. < 4.2 Å) is characterised by 'graphitic' planes. All our 32 structures are monoclinic or orthorhombic and the shortest crystallographic axis is always a screw-axis direction. *This axis is, therefore, a key parameter in separating packing types and defines the crystal structure.* In contrast, the other cell parameters are merely a function of individual molecular geometries.

There is also an energetic basis for our structural classification. In sandwich crystals (which form molecular pairs), the interaction energy to one molecule (the sandwich partner) is unique. However, for herringbone, β-, and γ-structures, there are always *pairs* of molecules with the same cohesion energy to the reference molecule. Further, for β- and γ-structures, but not herringbone, stabilisation is mainly by the two nearest short-axis translated neighbours.[5]

The crucial link between molecular and crystal structure is the relative ability of a molecule to employ $C \cdots C$ and $C \cdots H$ interactions. While $C \cdots C$ interactions are best optimised between parallel molecules stacked at van der Waals separation, $C \cdots H$ interactions are most effective between inclined molecules perhaps because of their supposed Coulombic nature. Therefore $C \cdots C$ interactions are important in β- and γ-structures while $C \cdots H$ interactions are important in herringbone packing. By this token, both $C \cdots C$ and $C \cdots H$ interactions are important for sandwich structures.

(X)

Since there is a good correlation between molecular surface area and packing energy, we have computed average values of S_i which are the normal van der Waals surfaces[6] for carbon and hydrogen atoms of the types A, B_1, B_2, C, D, and E as shown in structure (X). The free surfaces of some of the outer atoms in a molecule (H_D, H_E) may not be completely available for intermolecular contacts. Typical values for S_i (in Å^2) are as follows: carbon A (10.8), B_1 (5.8), B_2 (5.8), C (11.2), D (10.4), E (9.2); hydrogen A (6.8), C (6.8), D (5.6), E (5.1).

The number and positioning of C and H atoms in a molecule are the key features in defining structure type. We consider part of the molecular free surface as stack (or layer)-promoting and the rest as glide-promoting. Atoms that help stacking include core atoms (B_2) and part (50%) of the rim carbon atoms (A, B_1, C, D, E). Atoms that help glide packing include the other part (50%) of the rim carbon atoms and all hydrogen atoms. Summing the glide and stack contributions over the molecule gives the overall glide and stack promoting areas S_g and S_{st}. These empirical factors have been obtained after a careful analysis of the crystal structures of compounds **(1)**—**(32)**.

Figure 2 shows the glide-to-stack ratio S_g/S_{st} as a function of the total molecular surface S_M ($S_M = S_g + S_{st}$) and *is a predictive mapping from molecular to crystal structure.* It gives a clear-cut division between herringbone structures with the highest S_g/S_{st} values and the rest. The linear fused compounds **(1)**, **(2)**, **(3)**, **(33)**, **(34)**, and **(36)** and the linear polyphenyls **(1)**, **(5)**, **(35)**, and **(12)** form two subgroups. Other compounds such as **(4)**, **(8)**, and **(10)** deviate from these curves inasmuch as their shapes deviate from pseudolinearity. The γ-molecules **(18)**, **(21)**, **(22)**, **(24)**, **(25)**, and **(26)** with nearly the same shape lie on a smooth curve. Moving down this structural homologous series there is an increase in the 'core' carbon

Table 1. Compounds in this study.

Herringbone: **(1)** Benzene; **(2)** Naphthalene; **(3)** Anthracene; **(4)** Phenanthrene; **(5)** Biphenyl; **(6)** Triphenylene; **(7)** Benz[*a*]anthracene; **(8)** Chrysene; **(9)** Benzo[*c*]phenanthrene; **(10)** Picene; **(11)** Dibenz[*a,h*]anthracene; **(12)** *p,p*-Quaterphenyl; **(33)** Tetracene; **(34)** Pentacene; **(35)** *p*-Terphenyl; **(36)** Hexacene.
Sandwich herringbone: **(13)** Pyrene; **(14)** Perylene; **(15)** Benzo[*ghi*]perylene; **(16)** Dinaphtho[*a,h*]anthracene; **(17)** Quaterrylene (benzo[1,2,3-*cd*; 4,5,6-*c′d′*]diperylene).
γ-Structures: **(18)** Benzo[*a*]pyrene; **(19)** 18-Annulene; **(20)** Dibenzo[*b,k*]perylene; **(21)** Coronene; **(22)** Dibenzo[*bc,ef*]coronene; **(23)** Dibenzo[*a,j*]coronene; **(24)** Ovalene; **(25)** Hexabenzo[*bc,ef,hi,kl,no,qr*]coronene; **(26)** Kekulene.
β-Structures: **(27)** Tribenzo[*a,i,l*]pyrene; **(28)** Violanthrene; **(29)** Tetrabenzo[*a,cd,j,lm*]perylene; **(30)** Diphenanthro[*abcd,jklm*]perylene; **(31)** Anthra[*cdefg*]benzo[*jk*]naphtho[*opqr*]pentacene; **(32)** Tetrabenzo[*de,hi,op,st*]pentacene.

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PERSPECTIVE

Rethinking the term "pi-stacking"

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It has become common to reference "pi-stacking" forces or "pi–pi interactions" when describing the interactions between neighbouring aromatic rings. Here, we review experimental and theoretical literature across several fields and conclude that the terms "pi-stacking" and "pi–pi interactions" do not accurately describe the forces that drive association between aromatic molecules of the types most commonly studied in chemistry or biology laboratories. We therefore propose that these terms are misleading and should no longer be used. Even without these terms, electrostatic considerations relating to polarized pi systems, as described by Hunter and Sanders, have provided a good qualitative starting place for predicting and understanding the interactions between aromatics for almost two decades. More recent work, however, is revealing that direct electrostatic interactions between polarized atoms of substituents as well as solvation/desolvation effects in strongly interacting solvents must also be considered and even dominate in many circumstances.

This review seeks to summarize some of the key theoretical and experimental findings related to the interactions that are observed between aromatic molecules. A more detailed picture of the parameters important for defining the geometry and strength of aromatic–aromatic interactions is now emerging. Dominant notions of complementary electrostatic interactions between polarized pi systems[1,2] are being refined or even supplanted by considering the importance of solvation effects in strongly interacting solvents,[3,4] as well as the direct interactions between ring substituents.[5–7]

Given these new insights, it is both timely and useful to question whether the commonly used terms "pi-stacking" and "pi–pi interactions" are appropriate to describe situations in which two or more aromatic rings are associated in some fashion. In particular, "pi-stacking" or "pi–pi interactions" are often cited as a specific type of intermolecular attraction unique to aromatic molecules, with the tacit understanding of an interaction that is distinct from the non-covalent interactions used to describe all intermolecular complexes. But is this really the case? What is the evidence in support of special effects attributable to the structural features of aromatic pi systems that promote intermolecular stacking? Do such considerations specifically apply to the small one- or two-ring aromatic systems that we synthesize and study most often? In other words, is there any unique attraction between aromatic pi systems that favours stacking and transcends the suite of electrostatic attractions, desolvation/solvent effects and induced-electrostatic (London dispersion) forces that influences the association of *all* molecules? And, if much of what is called "pi-stacking" is not based upon inherent attraction between *pi* cloud electron density, nor involves parallel, face-centred *stacking* that maximizes pi cloud contact, is it still appropriate to deem instances in which aromatic rings are near each other in space as exhibiting "pi-stacking" or "pi–pi interactions"?

Several reviews on the interactions between aromatic molecules, focused on both theoretical[8,9] and experimental studies,[10] have already been written. Here, we summarize the experimental and theoretical evidence and conclude that "pi-stacking" or "pi–pi interactions" are misleading terms because they connote a special type of attraction that is in reality not significant. We therefore propose that these terms should either be reserved for very specific cases yet to be defined or even dropped from common usage altogether when describing the energetics and intermolecular interactions of common aromatic molecules. Note that although they are related, we will not discuss cation-pi,[11] anion-pi,[12,13] pi-hydrogen bonds,[14] or radical-pi interactions, the last of which have gained increased attention lately due to the seminal work of Stoddart and co-workers.[15,16] A recent thorough review by Diederich covers many of these topics, as well as interactions between aromatic molecules in a comprehensive fashion.[17]

We are not the first to suggest that the terms "pi-stacking" and "pi–pi interactions" are widely overused and deserve clarification. Grimme made the same point.[18] In many ways, this review is following his lead by providing our own review of the literature in order to amplify the arguments. In particular, Grimme argued for a more precise definition that reserves the application of the terms to large, multi-ring aromatic systems, a position that we also favour (see below).[18] Marsili *et al.* suggested as much in their work investigating aromatic interactions in over 6,000 solved

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J. Phys. Chem. B **2005,** *109,* 1849−1856 **1849**

Band Structure of the Four Pentacene Polymorphs and Effect on the Hole Mobility at Low Temperature

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The band structure of the four known polymorphs of pentacene is computed from first principles using the accurate molecular orbitals of the isolated molecule as the basis for the calculation of the crystalline orbitals. The computed bands are remarkably different for each polymorph, but their diversity can be easily rationalized using a simple analytical model that employs only three parameters. The effect of the electronic structure on the hole mobility was evaluated using a simple model based on the constant relaxation time approximation. It is found that the mobility tensor is highly anisotropic for three of the four considered polymorphs. The practical implication of this prediction on the technology of thin-film organic transistors is discussed.

1. Introduction

The possibility of practical applications for organic semiconductors, demonstrated in the late 1980s[1] and followed by an impressive improvement of the performance and efficiency of the devices based on such materials,[2] have renewed the interest of many researchers toward this field whose first contributions appeared more than fifty years ago.[3] Organic materials (crystals or polymers) based on polyacenes, polythiophenes, and polyetilene have been used to realize light-emitting diodes (LEDs), thin-film transistors (TFTs), and photovoltaic cells, and an increasingly large set of data on these systems are now available.[4−8]

The most important property of these materials is the charge carrier mobility μ, whose lower limit for practical application is 100 cm^2 V^{-1} s^{-1}. Organic synthesis provides, in principle, the possibility to fine-tune the charge-transport properties, but the mobility of these materials is very difficult to predict, and the available mobility data lack a proper rationalization. Many groups are therefore active in the development of phenomenological theories[9] and computational models[10−13]to provide reliable predictive and interpretative tools.

In ordered organic materials such as pentacene,[2] the low-temperature transport is described as band-like (i.e., delocalized carriers move coherently across the crystal and are scattered by the lattice phonons). This mechanism is characterized by a power law dependence of the mobility upon the temperature ($\mu \approx T^{-n}$).[14−16] At higher temperatures (∼300 K), polaron transport becomes important; that is, the charge carriers (and their associated lattice deformation) move by thermally activated hopping leading to an Arrhenius-type temperature dependence of the mobility ($\mu \approx \exp(-E_a/kT)$).[17,18] The possibility of a unified description of both transport regimes through suitable effective Hamiltonians is discussed by several authors.[9a,19−21]

While phenomenological theories account qualitatively for the observations, they cannot explain the differences observed for similar materials, for which accurate electronic structure calculations are needed. Analogous materials can show dramatic differences in the transport properties,[22] because the interaction between molecules strongly and subtly depends on structural details. We illustrate this point in the present paper, computing the band structure of the four polymorphs of pentacene and discussing the effect of pentacene polymorphism on the low-temperature hole mobility. Since the first reports of high hole mobility for the pentacene single crystal,[23] several groups studied this[24−28] and related materials[29−31] for their potential application in organic electronics. Several pentacene polymorphs were grown as thin films,[33−38] and one of the thin-film structures was shown to coincide[35] with the bulk single-crystal structure reported by two recent studies.[32,35] A classification and a rationalization was proposed by Mattheus et al.[33] that also found the conditions to reproducibly grow thin films of four crystal forms.[34] The possibility of different transport properties for different growth conditions is of great technological interest. In fact, one of the typical experimental setups involves pentacene thin films, grown on a silicon oxide surface between the source and drain electrodes, forming a prototype of organic thin-film transistors (OTFTs).

To compute the band structure, we propose a first-principles method that uses accurate molecular orbitals computed for the isolated molecule as basis functions for the crystal wave function. A simple analytical model will be proposed to interpret all the band structure, and the results will be further justified through the use of simple orbital overlap arguments. We will not consider in this paper the polaronic mechanism of conduction, limiting our discussion to band-like low-temperature conduction. According to recent measurements,[16] the band-like transport is the dominant one in pentacene up to ca. 300 K.

2. Method

The most commonly used packages[39] for the first-principles computation of band structures have been optimized for the calculation of materials with a relatively small number of atoms in the unit cell and with band gaps ranging from several electronvolts to zero (metals). Molecular crystals contain up to hundreds of atoms per unit cell, and they are usually insulators or semiconductors. The appropriate description of molecular orbitals (MOs) for the isolated molecule requires a split-valence atomic basis set with the inclusion of polarization functions. This basis set makes the calculation of the molecular crystal band structure extremely heavy and the convergence of a self-

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