Markus Schwoerer, Hans Christoph Wolf

Organic Molecular Solids

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Organic Molecular Solids

Foreword

The investigation of the physical properties of organic solids, in particular those whose structural elements contain conjugated π-electron systems, has in recent decades become an active and attractive subfield of solid-state physics and this field is now growing rapidly.

There are several reasons for this development. On the one hand, the great variety of phenomena and properties observed in the organic solids greatly exceeds that seen with inorganic materials: an example is energy transport via excitons, i.e. without charge transport, over comparatively long distances. Furthermore, organic chemical methods allow the variation of these interesting properties within wide limits. On the other hand, there are many promising new technological applications of these materials, e.g. in organic colour displays or in a novel molecular electronics which would complement and enlarge upon conventional electronics based on inorganic semiconductor materials. Finally, the organic solids form a link between the physics of inorganic materials and biophysics. The solid-state physics of organic materials has thus already made important contributions to the elucidation of elementary processes in photosynthesis.

In the organic solids, a hierarchy of forces can be observed: there are both strong covalent intramolecular chemical bonds and weak intermolecular van der Waals bonds. Many of the characteristic properties of the organic solids are due to the interplay of these two forces with their differing strengths.

In the usual course of studies, i.e. in the required courses, the student of physics learns nearly nothing about these materials and their properties. In the established textbooks on solid-state physics, there is almost no mention of the organic solids. Only in special-topics lectures and as electives is this topic treated in detail, if these are offered at all.

The present book is intended to fill this gap. It treats in particular the fundamentals of the physics of organic solids and is written for students taking such elective or special-topics courses and those who want to pursue research in the field of organic solids. In addition, it is intended for all physicists, photochemists and perhaps also chemists who want to broaden their knowledge of the solid state. We assume that the reader has a basic knowledge of solid-state physics corresponding to standard introductory courses on the subject. What do we intend to offer

the reader? An initiation into the fundamentals of the subject, links to the more detailed literature and an introduction to topics of current research are our goals.

Organic solid-state physics is a very broad field. In an introductory book such as this, it can be treated only with selected examples; an exhaustive treatment is neither possible nor desirable in an introduction.

We concentrate on π-electron systems. One can learn most of what is interesting in organic solid-state physics from them and they provide an entry to the physics of other materials. We use the term molecular crystals not only in the narrow sense, but also consider thin layers of oriented molecules which are attracting increasing interest.

We authors have been carrying our research in this area for several decades. We wish to thank our numerous students and co-workers with whom we have been able to explore much new territory in this fascinating subfield of solid-state physics. We also wish to thank Ms. Christine Leinberger for processing our texts which underwent numerous revisions, and Mr. Heinz Hereth for preparing a number of drawings. Ms. A. Tschörtner of the Wiley-VCH publishers is due thanks for excellent cooperation in the preparation of this book. It is a great pleasure for us to thank Prof. W. D. Brewer for his excellent translation from the German.

Bayreuth, Stuttgart,   *Markus Schwoerer*
September 2006   *Hans Christoph Wolf*

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Introduction

Solid-state physics became an independent discipline only in the middle of the past century. In the intervening years, it has developed into the largest and in some respects most important branch of physics. Previously, in the first half of the 20th century, metals were at the focus of interest. Parallel to their increasing practical applications, theoretical understanding of metallic materials increased rapidly. In the second half of the century, inorganic semiconductors and superconductors took over the forefront of interest in basic research and applications of materials science. Indications are now strong that in the 21st century, a new group of materials will become similarly important and will be at the focus of interest: the organic solids.

In any case, in recent years the investigation of the physical properties of organic solids has attained greatly increased importance and attention. The wide variety of these compounds and the possibility to modify them in a practically unlimited fashion using the methods of synthetic organic chemistry have aroused high expectations for the development of new materials and their applications. Current interest focuses in particular on solids composed of those organic molecules which contain conjugated systems of π electrons. In this book, we give an introduction to the structure and especially to the dynamic, optical, electrical and electro-optical properties of this group of materials and show using selected examples their importance for practical applications.

This introduction can only attempt to summarise the typical properties and the most important concepts needed to understand organic solids. In the interest of brevity, we must often skip over the details of the experimental methods and of theoretical descriptions. The references given in each chapter can be consulted by the reader to provide a deeper understanding of the individual topics. In particular, we wish to draw attention to the few detailed monographs available in this area, which are relevant to all of the chapters in this book: [M1]–[M3].

1.1
What are Organic Solids?

Molecules or their ions (molecular ions or radical ions) from the area of organic chemistry, i.e. expressed simply, compounds with carbon atoms as their essential

Molecule		Absorption	Molecule		Absorption
Benzene		254 nm	Perylene		434 nm
Naphthalene		311 nm	Fluoranthene		356 nm
Anthracene		375 nm	2,3-Dimethyl-naphthalene	CH$_3$ CH$_3$	315 nm
Tetracene		471 nm	Fluorene		
Pentacene		582 nm			
Pyrene		352 nm			
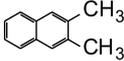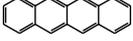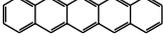
Fig. 1.1 Molecular structures of some polyacene molecules, indicating the wavelengths of their lowest-energy optical absorption regions in solution at room temperature. All of these molecules have a conjugated π-electron system. The regions of absorption shift towards longer wavelengths with increasing length of the conjugated electron chains. Many of these molecules are building blocks of still larger molecules, e.g. of dimers, oligomers, or polymers, or else they are components of the side chains in polymers or ligands to central metal ions.

structural elements, form solids as single crystals, polycrystals, or glasses. These are the organic solids. Polymers in the solid state also belong to this group. When we speak in the following sections of organic solids, then we include a broad category of materials under this generic term, but in particular those organic molecular crystals, radical-ion crystals, charge-transfer crystals, thin films or layered structures and polymers which include conjugated π-electron systems in their skeletal structures. These are in turn primarily constructed of carbon atoms but often contain also N, O, S, or Se atoms. To this class belong in particular the aromatic hydrocarbons and alkenes (olefins) (Fig. 1.1), but also N-, O- or S-containing heterocyclic compounds such as pyrrole, furane, thiophene, quinoxaline and others (Fig. 1.2). Also C$_{60}$ and related molecules such as carbon nanotubes should be included here. The nanotubes, however, do not belong among the materials treated in this book. Only in exceptional cases will we treat the aliphatic hydrocarbons, which of course also form organic solids but contain no π electrons, only σ electrons and still more strongly bound (inner) electrons.

Why are molecules with π-electron systems of particular interest to organic solid-state physics? The electron configuration of the free carbon atom in its ground state is $1s^2 2s^2 2p^2$. Carbon has the valence four due to the fact that the electron configurations in chemically-bonded carbon are derived from the configuration $1s^2 2s 2p^3$. From molecular physics, we know that a so called double bond between two carbon atoms can form due to an sp^2 hybridisation: three degenerate orbitals are constructed out of one s and two p orbitals. They are coplanar and oriented at 120° relative to one another. Chemical bonds formed by these orbitals are called σ bonds; they are localised between the bonding C atoms. The fourth orbital, p_z, remains

Molecule

Pyrrole

Carbazole

Furane

Benzofurane

Thiophene

Benzothiophene

Pyridine

Molecule

Acridine

Pyrazine

Quinoxaline

Pyrazole

3,4-Ethylene-dioxithiophene

Dibenzothiophene
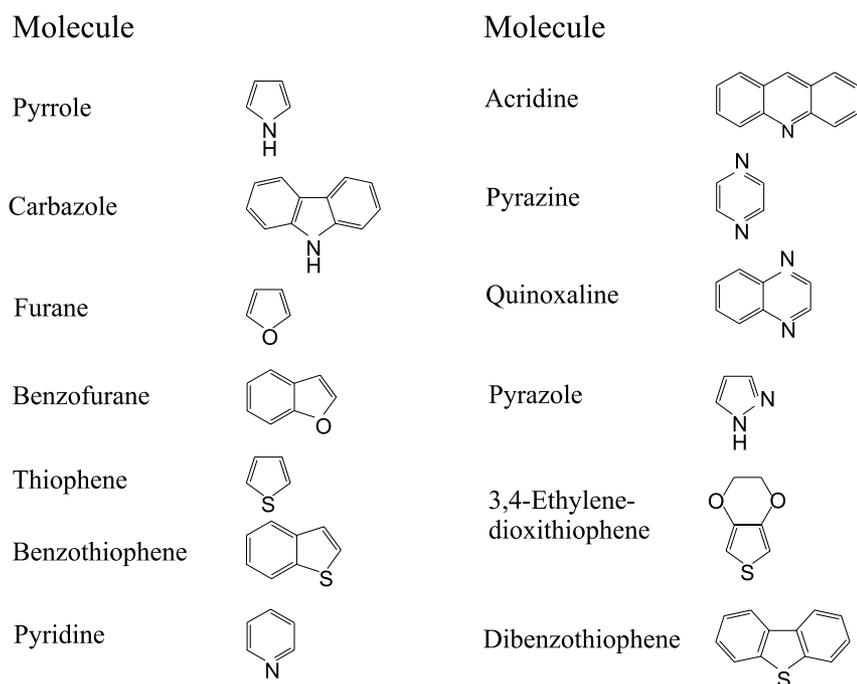
Fig. 1.2 Some typical heterocyclic molecules.

unchanged and is directed perpendicular to the plane of the sp^2 orbitals, and thus to the plane of the C atoms.

The p_z orbitals of neighbouring atoms overlap. This leads to an additional bond, the so called π bond, and to a delocalised density of electrons above and below the plane of the molecule. This is the nodal plane for the π-electron density.

Fig. 1.3 shows the overall electron distribution in an aromatic molecule, anthracene. In addition to the total electron density, Fig. 1.3 also shows two π orbitals, the energetically highest which is occupied in the ground state (HOMO) and the energetically lowest which is unoccupied in the ground state (LUMO).

In comparison with the σ electrons, the contribution of the π electrons to bonding of the molecule is thus weak. Organic molecules and molecular crystals with conjugated π-electron systems therefore possess electronic excitation energies in the range of only a few eV and absorb or luminesce in the visible, the near infrared or the near ultraviolet spectral regions. The electronic excitation energies of this absorption shift towards lower energies with increasing length of the conjugated system; cf. Fig. 1.1. The lowest electronic excitation states are excitations of the π electrons. In the organic radical-ion crystals or the charge-transfer crystals, it are likewise the π-electron systems which are ionised. Most of the characteristic physical properties of the organic solids treated in this book are based on these π-electron systems. Above all they determine the intermolecular interactions, the
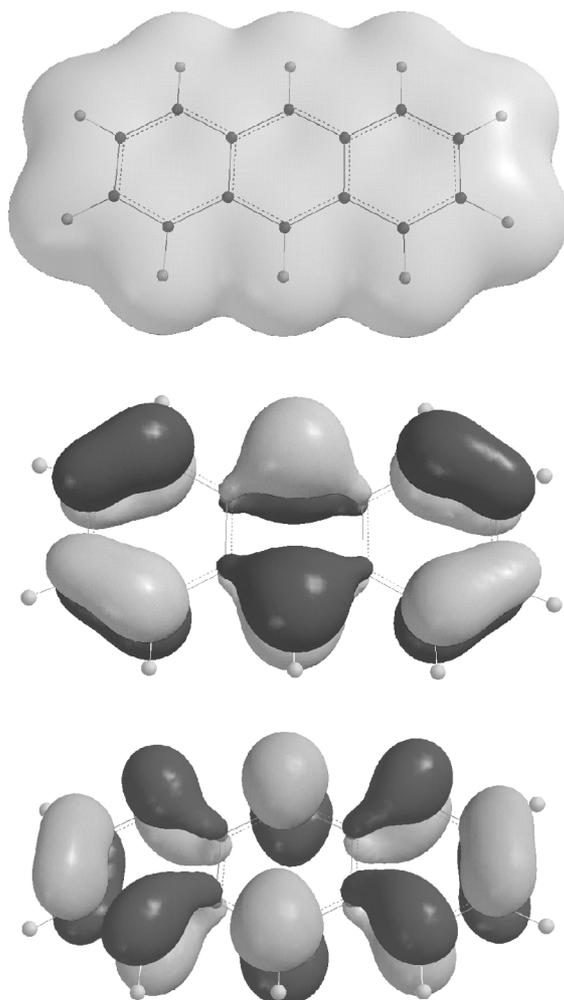
Fig. 1.3 Above: the overall distribution of the π electrons in the electronic ground state of the anthracene molecule, $C_{14}H_{10}$. The boundary was chosen so that ca. 90% of the total electron density was included. Centre: the distribution of a π electron in the highest occupied molecular orbital (HOMO). Below: the distribution of a π electron in the lowest unoccupied molecular orbital (LUMO). The figure was kindly provided by M. Mehring.

van der Waals interactions. They are essentially due to the outer, readily polarisable and readily-excited π electrons.

These intermolecular forces which hold the molecules together in the solid state are in general weak in molecular crystals in comparison to the intramolecular forces. Molecular crystals derive their name from the fact that the molecules as such remain intact within the crystals and thus directly determine the physical
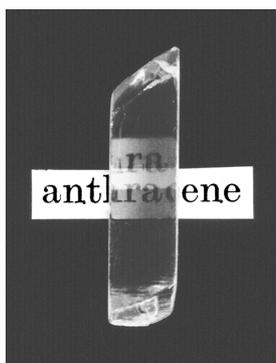
Fig. 1.4 An anthracene single crystal made by the Bridgman crystal-growth method, then cleaved and polished. The length of the crystal is about 2 cm and its thickness 1 cm. Along the direction of sight in this photograph, the c' direction, the strong double refraction is apparent. Image provided by N. Karl [1]. Cf. the coloured plates in the Appendix.

properties of the material. What an organic molecular crystal looks like to the naked eye is illustrated using the example of anthracene in Fig. 1.4.

In solid-state physics, it is a frequent and convenient practice to concentrate basic research on a few model substances. It is then attempted to apply what is learned from these substances to the large number of similar materials, i.e. those belonging to the same class of materials. An overview of the most important classes of materials treated in this book is given in Table 1.1.

Table 1.1 Organic molecular crystals and solids, important classes of materials, and characteristic examples treated in this book.

Class of materials	Examples	Figure
Aliphatic hydrocarbons	*n*-Octane	2.9
Aromatic hydrocarbons	Naphthalene, Anthracene	1.1, 1.3, 1.4, 2.10, 3.8
Weak donor-acceptor complexes, nonpolar in the ground state	Anthracene-Tetracyanobenzene (TCNB)	1.6
Strong donor-acceptor complexes, polar in the ground state	Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)	2.8, 2.17
Radical-ion salts	$Cu^+(DCNQI)_2^-$ $(Fa)_2^+PF_6^-$ $C_{60}^-(TDAE)^+$	1.7, 1.8, 2.18
Polymers Low-molecular-mass layers	Poly(paraphenylene-vinylene) (PPV), CuPc, Alq$_3$, NPB	11.5, 11.4
Polymer single crystals	Poly(diacetylene) (TS6)	1.10, 1.11

a   b   c
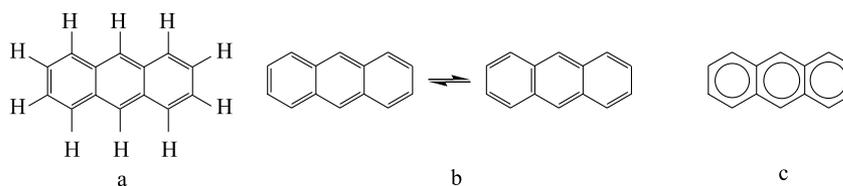
Fig. 1.5 Various typical representations of the structural formula of anthracene ($C_{14}H_{10}$). The C atoms are always left out, the H atoms often. Occasionally, structural formulas are written without indicating the π electrons, i.e. without showing the double valence lines or the circles in cyclic molecules. This, however, does not correspond at all to the usual rules.

The class which has been most intensively investigated in solid-state physics includes the crystals of simple **aromatic hydrocarbons** such as anthracene or naphthalene. Various usual versions of the structural formula of anthracene are given in Fig. 1.5. For the **aliphatic compounds**, we take *n*-octane as model substance. Here, the optically-excitable states lie at considerably higher quantum energies than in the case of the aromatic compounds, since here there are no π electrons. We will not treat them at any length in this book.

A further important class of materials are the **donor-acceptor complex crystals**. They consist of two partner compounds in a stoichiometric ratio, of which one transfers charge to the other. When the charge transfer occurs only in an electron-

c

b   ● N   ○ C
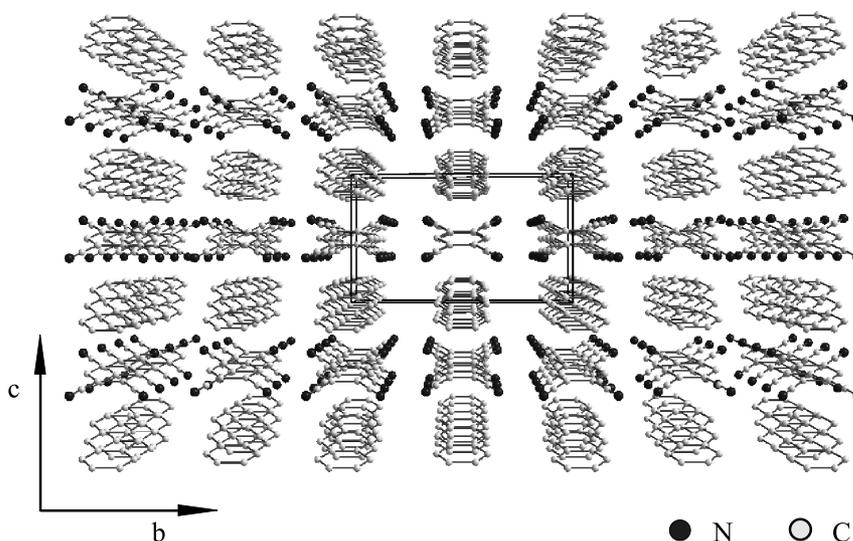
Fig. 1.6 The crystal structure of the weak donor-acceptor crystal anthracene-tetracyanobenzene (TCNB). One can clearly see how the two components alternate in parallel planes. The CN groups are indicated by a darker shade. The crystal structure is monoclinic, with $a = 9.528$ Å, $b = 12.779$ Å, $c = 7.441$ Å, $\beta = 92.39°$.
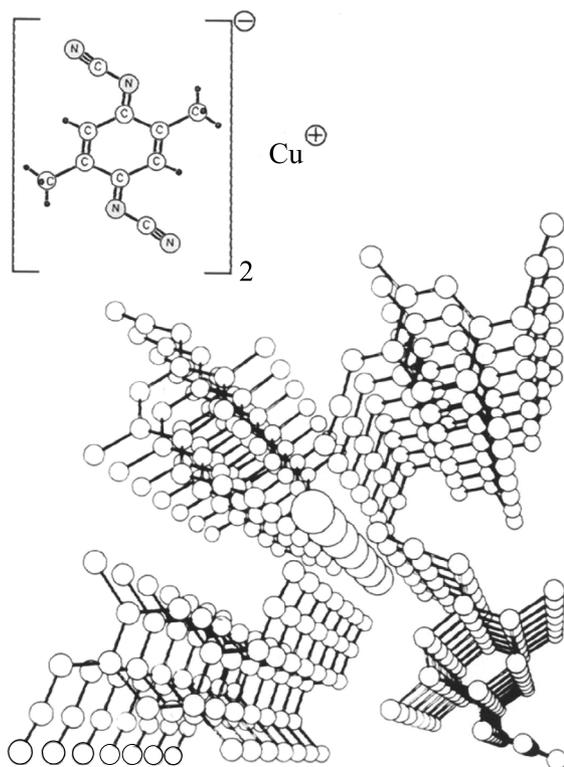
Fig. 1.7 Below: the crystal structure of the radical-anion crystal 2,5-dimethyl-dicyanoquinone-diimine, $Cu^+(DCNQI)_2^-$. In the middle, one can discern a chain of Cu ions which are however not responsible for the metallic conductivity of the compound, as well as four stacks of the organic partner. The electrical conductivity takes place along these stacks. The stacks are connected via the CN groups and the central Cu ions to one another, so that their one-dimensionality is reduced. In the molecular structure scheme (above), the H atoms are indicated as dots. The crystal structure is tetragonal, with $a = 21.613\,\text{Å}$ and $c = 3.883\,\text{Å}$. The DCNQI molecules are inclined with respect to the axis of the stacks, i.e. the c-direction, by $\phi = 33.8°$. The perpendicular spacing of the planes between them is $\alpha = 3.18\,\text{Å}$. This radical-anion salt is grown by electrocrystallisation from an acetonitrile solution containing the DCNQI and CuI ions. After [2].

ically excited state, they are termed weak D-A crystals. A good example of these is anthracene-tetracyanobenzene (TCNB) (Fig. 1.6). The crystal is constructed as a sandwich of planes which alternately contain the donor and the acceptor molecules. In the strong D-A or **charge-transfer complexes**, for example the compound TTF : TCNQ or the **radical-ion salts**, the charge transfer takes place in the electronic ground state. Examples of these are shown in Fig. 1.7, the crystal structure of the radical-anion salt $Cu^+(DCNQI)_2^-$ and in Fig. 1.8, a photograph of crystals of the radical-cation salt $(Fa)_2^+PF_6^-$. These crystals are not transparent like the molecular crystals, but rather they look metallic, since they reflect visible light strongly over a broad bandwidth. An example of organic molecules in the form of an **epitaxial thin**
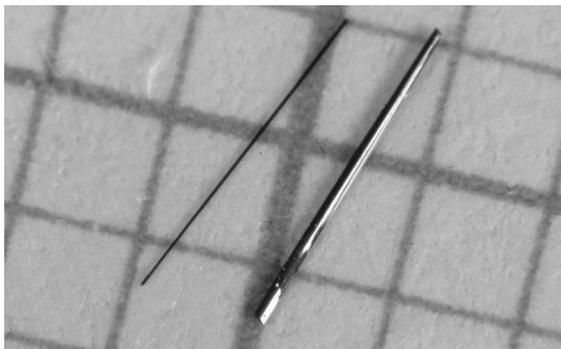
Fig. 1.8 Two crystals of the radical-cation salt (di-fluoranthene) hexafluorphosphate, $(Fa)_2^+PF_6^-$. The right surface of the right-hand crystal is orientated in such a way that it reflects the light coming from the light source on the right. The reflectivity is metallic due to the high conductivity of the crystal along its long axis (*a* axis, see Fig. 2.18). The grid corresponds to 1 mm^2. Cf. the coloured plates in the Appendix.

film is shown in Fig. 1.9. Finally, Fig. 1.10 shows the crystal structure and Fig. 1.11 a photograph of some crystals of a representative of the macroscopic **polymer single crystals** of poly-diacetylene. These two material classes, the non-crystalline polymers and low-molecular-mass evaporated films, are the most important classes which we shall describe as organic solids in the following chapters.
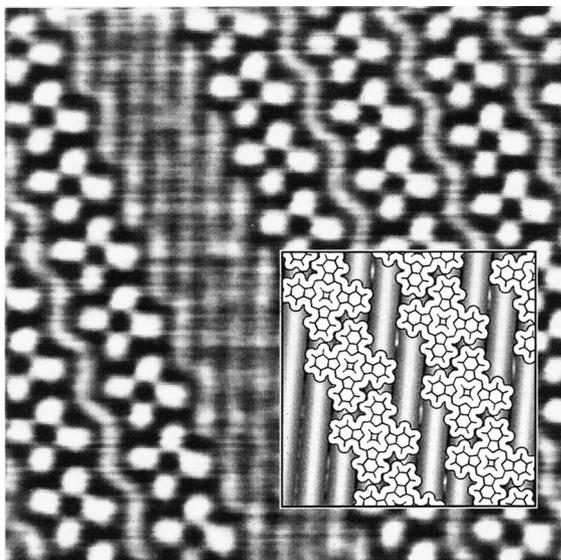
Fig. 1.9 Cu-phthalocyanine molecules on the surface of a MoSe$_2$ crystal; image made with a scanning tunnel microscope. The area shown has the dimensions 10 nm $\times$ 10 nm. The inset shows the molecular structure to the same scale. From [3].
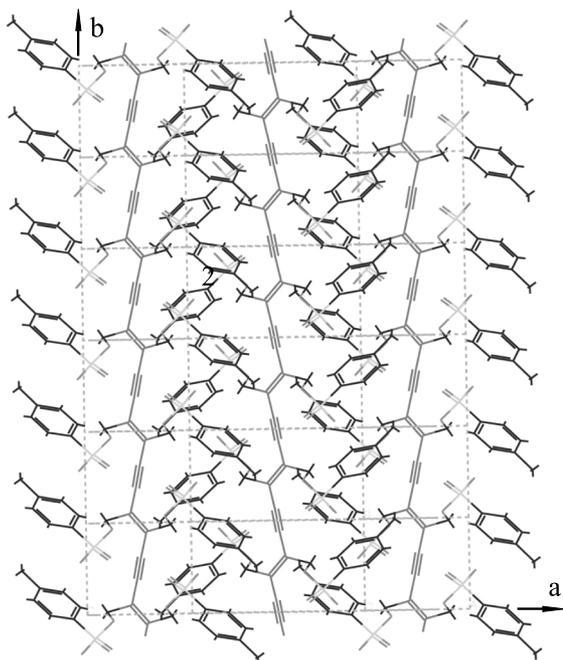
Fig. 1.10 The crystal structure of macroscopic poly-diacetylene paratoluylsulfonyl-oximethylene (p-TS6) single crystals. The picture shows the projection on the crystallographic (ab)-plane of the monoclinic crystal ($a = 14.993$ Å, $b = 4.910$ Å, $c = 14.936$ Å, $\beta = 118.14°$ at $T = 295$ K). The covalently bonded carbon chains with periodic double-single-double bonds are oriented parallel to the twofold b axis. They carry a conjugated π-electron system. The side groups are covalently bonded to the chain. The chains are bonded to each other by van der Waals bonds, The unit cell contains two differently-oriented monomer units. After [4].

1.2
What are the Special Characteristics of Organic Solids?

In solids, one can distinguish four essential types of bonds: ionic bonds, metallic bonds, covalent bonds, and van der Waals bonds. In addition, in rare cases, hydrogen bonding is observed; it is indeed especially important in bio-macromolecules.

Ionic bonding results directly from the long-range Coulomb attraction between oppositely-charged ions. A typical representative of this type of bonding is sodium chloride. Ionically-bonded solids have as a rule a relatively high melting point, are brittle and, at least at lower temperatures, they are poor electronic conductors (insulators). **Metallic bonding** is likewise based mainly on the Coulomb interaction. In this case, a portion of the negative charges, the conduction electrons, are delocalised and more or less freely mobile. Their electrical conductivity, like their reflectivity, is high; the melting point is also relatively high. **Covalent bonding** results from the sharing of electrons between neighbouring atoms in the solid – the bonding electrons. This bonding type includes the inorganic semiconductors such
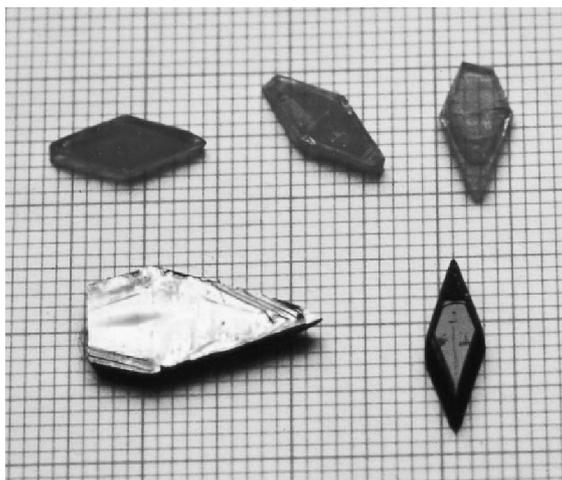
Fig. 1.11 Below: Two single crystals of the polydiacetylene paratoluyl-sulfonyl-oximethylene-diacetylene (TS6). Above: three monomer crystals, illuminated with linearly polarised light. The polarisation direction of the light is horizontal, and the b axis of the polymer chains is oriented parallel to the long axis of the crystals. The polymer crystals strongly reflect light (below left) when the light is polarised parallel, and almost not at all (below right) when the light is polarised perpendicular to the axis of the polymer chains. The monomer crystals contain only a small fraction of polymerised chains and are thus opaque (above left) when the light is oriented parallel, but transparent (above right) when the light is perpendicular to the to the *b* axis. Cf. the coloured plates in the Appendix.

as Si or Ge. These solids are semiconductors and as pure materials typically have a low electronic conductivity and a high melting point. They are hard and brittle. Polymer chains are also held together by the strong covalent bonds between the atoms within the chain. **Van der Waals** bonding is, finally, mainly responsible for the cohesion within molecular solids and is therefore particularly important for the topics in this book. It is based on weak electrical dipole forces between neutral molecules with fully-occupied molecular orbitals, i.e. molecular orbitals which can form neither ionic bonds, nor covalent bonds, nor metallic bonds. Molecular solids which consist of only one type of molecules, e.g. anthracene molecules, exhibit pure van der Waals bonding. They usually have a low electronic conductivity, are relatively soft and have a comparatively low melting point.

Van der Waals bonding is particularly weak in comparison to covalent bonding and has a very short range. Therefore, the properties of the individual molecules in all **nonpolar organic solids** remain intact to a much greater extent than those of the bonding units in the other materials classes. In the simplest approximation, a molecular crystal can be understood in terms of an **oriented gas**. This means that the solid structure simply holds the molecules in fixed positions without changing their (molecular) physical properties. Thus, for example, the molecular dimensions and the characteristic intramolecular vibrational frequencies are only slightly changed relative to those of the free molecules, since the intramolecular forces are dominant. Other properties such as energy and charge transport only become pos-

Table 1.2 Occupation probabilities for the phonons with the highest frequency ν in a typical molecular crystal as compared to Si.

	exp($-h\nu/kT$)	
T/K	$\nu = 3.5$ THz (Naphthalene)	$\nu = 14$ THz (Si)
300	0.57	0.11
100	0.19	1.2×10^{-3}
30	3.7×10^{-3}	1.8×10^{-10}
4.2	2.8×10^{-18}	

sible through the intermolecular forces and are therefore essentially determined by them.

A notable measure of the intermolecular forces is the maximum frequency ν of the lattice vibrations (optical phonons). In a typical organic molecular crystal, it is of the order of 3.5 THz; in Si, in contrast, it is 14 THz. Thus the difference in the Boltzmann factors exp($-h\nu/kT$) for the thermal occupation of phonon states, which plays a decisive role in many solid-state properties, is already great when comparing organic and inorganic solids at room temperature, and it becomes very much greater at low temperatures (Table 1.2).

In Table 1.3, a number of the physical properties of the crystalline solids anthracene and germanium are compared with each other. Especially important are the lower binding energy, the lower melting point, and the higher compressibility of anthracene in comparison to the covalently-bonded inorganic semiconductor. The weak intermolecular interactions furthermore lead to a greater freedom of variation in the crystal structures and in structurally-determined properties as functions of the state variables such as pressure and especially temperature, and of external electromagnetic fields and waves, in particular UV, visible and IR radiation.

Polar organic solids, e.g. the radical-ion salts mentioned in Sect. 1.1, are bonded not only through van der Waals interactions but also through ionic bonds. Since molecules are larger than atoms, the distances between positive and negative charges are larger in the former and therefore, the ionic bonding energy of molecular ionic crystals is as a rule smaller than that of inorganic salts. However, it often determines the crystal structure. Electrically-conducting molecular crystals, e.g. $Cu(DCNQI)_2$ or $(Fa)_2PF_6$, additionally exhibit a metallic-bonding contribution to their crystal bonding.

Precisely those solid-state properties which are due to the relatively weak mutual bonding of the molecules in the crystal are what make the organic solids so interesting. This is the topic of the present book.

There are a whole series of properties and problems which distinguish the organic molecular crystals in characteristic ways from other solids and make them

Table 1.3 Comparison of the physical properties of anthracene and germanium crystals. From Pope and Swenberg, as well as from S. M. Sze, *Physics of Semiconductor Devices*, John Wiley and Sons, New York (**1981**).

Property	Germanium	Anthracene
Atomic weight	72.63	178.22
Melting point / °C	937	217
Density / $(g\,cm^{-3})$	5.3	1.28
Density / molecules per cm^3	4.42×10^{22}	0.42×10^{22}
Crystal structure	Diamond structure	monoclinic
Lattice constant* / Å	5.66	6.04–11.16
Volume compressibility / (cm^2 /dyn)	1.3×10^{-12}	9×10^{-12}
Dielectric constant** (static)	16	3.2
Electronic band gap E_g (at $T = 300\,K$)/eV	0.66	4.0
Vacuum ionisation energy I_e/eV	4.8	5.8
Electron mobility* } (at $T = 300\,K$)/	3800	} ≈ 1
Hole mobility* } (cm^2/Vs)	1800	
Thermal expansion coefficient* / K^{-1}	6.1×10^{-6}	140×10^{-6}
Specific heat (at $T = 300\,K$)/(J/g K)	0.31	1.30
Longitudinal sound velocity*,** /(cm/s)	9.4×10^5	3.4×10^5

* These values are anisotropic in molecular crystals. The values given hold for a particular direction (see the corresponding chapters).

** For each case in the [100] direction.

attractive objects for study in solid-state physics. We shall list a few of these here. More information is to be found in later chapters.

First of all, we consider the **surfaces**: Due to the short range of the interaction forces, one can more readily produce surfaces and interfaces of high quality, with low defect and impurity concentrations, than in other types of crystals.

Then the **transport of electric charge**: among the organic solids there are insulators, semiconductors, metallic conductors and superconductors. To the solid-state physicist, it is a great challenge to understand how this enormous range of conductivity behaviours can be explained from the molecular and the crystal structures. Fig. 1.12 shows as an illustration the electrical conductivity of some radical-anion salts of DCNQI. The measured values are spread over more than 8 orders of magnitude, even though the variations in the molecules are small. Furthermore, the electrical conductivity of organic crystals is in general very anisotropic: many radical-ion salts are highly one-dimensional with respect to their conductivities. Closely connected to this is the Peierls instability. In this phase transition, the metallic conducting crystal becomes a semiconductor on cooling below the phase transition temperature T_p. Fig. 1.13 shows the specific electrical conductivity of the radical-cation salt $(Fa)_2PF_6$, which varies by more than 14 orders of magnitude within a relatively small temperature interval.
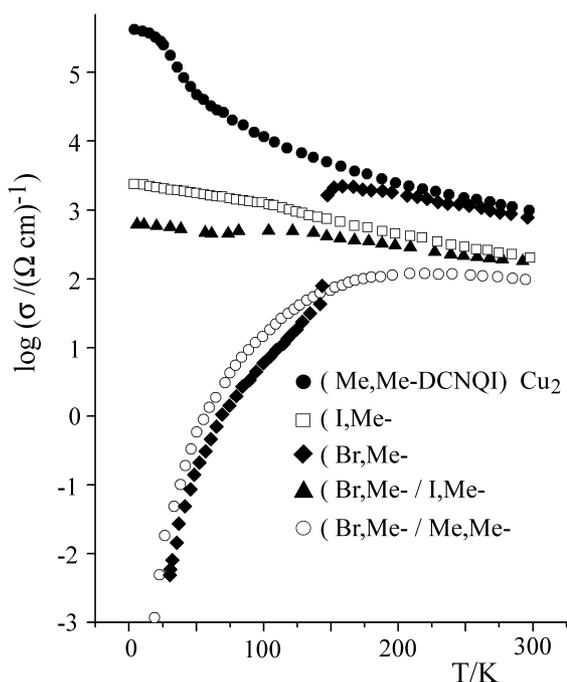
Fig. 1.12 The temperature dependence of the specific electric conductivity σ of some Cu$^+$ (DCNQI)$_2^-$ radical-anion salts with different substituents of the two Me groups on the DCNQI molecules (cf. Fig. 1.7). Me refers to a methyl group, I and Br to an iodine or bromine atom; compare the image of the crystal structure in Fig. 1.7. The crystal structure is very similar in all cases. The conductivity ranges from the organic metals down to the lowest temperatures (upper curve) to semimetallic semiconductors (the two lowest curves; one of them refers to an alloy). For details see Sect. 9.5.

In addition, these materials are particularly interesting owing to their enormous **variability**. Specifically, this means that their physical properties can be modified in often very small steps by comparatively minor chemical changes. The organic chemist can furthermore prepare molecules with a wide variety of properties in almost unlimited variations. Can this offering of the chemist be exploited in physics also, can crystals with the desired properties be so to speak synthetically "tailor-made"? Can one thus tell the chemists which molecule they should synthesize in order to produce a new semiconductor, or how a molecule is to be constructed in order to obtain a new superconductor with a high transition temperature? These are two of the problems which are currently key issues in the solid-state physics of organic molecular crystals. Such problems are often considered with a background of possible technical applications in mind.

An especially important and typical property of molecular crystals is the existence of **excitonic states**, in some cases with long lifetimes. These are neutral electronic excitation states with an excitation energy which is smaller than the energy required to excite an electron from the valence band into the conduction band, i.e. for the excitation of a dissociated electron-hole pair. One can also speak of an
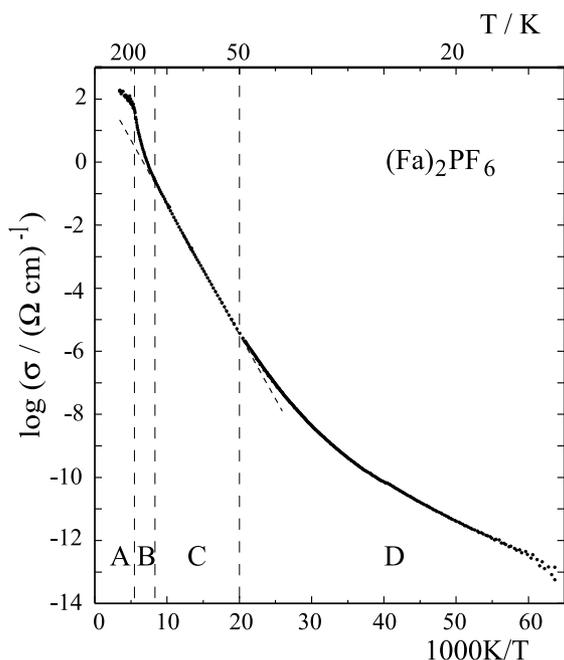
Fig. 1.13 The temperature dependence of the specific electrical conductivity σ of the radical-cation salt $(Fa)_2^+PF_6^-$ (cf. Fig. 1.8). Fa refers to fluoranthene (Fig. 1.1). At $T_p = 182$ K, the crystal undergoes a structural phase transition (Peierls transition). At $T > T_p$ it behaves almost like a metal; at $T < T_p$ it is a semiconductor. In the region between 300 K and 20 K its electrical conductivity varies by 14 orders of magnitude. The temperature ranges A, B, C and D denote four different mechanisms of electrical conductivity. In the range A ($T > T_p$), the conductivity is one-dimensional and metallic with strong fluctuations between metal and semiconductor. In the range B ($T < T_p$), the crystal is a semiconductor with a temperature-dependent activation energy. In the range C, the activation energy is constant. In the range D, the conductivity of the semiconductor is limited by thermal activation of charge carriers from defect states. See Sect. 9.6 for more details.

excitation below the conduction band. As a rule, the excitation energy of excitons in molecular crystals is so much smaller than the energy required to produce a non-bound electron-hole pair, that is a free electron in the conduction band and a free hole in the valence band, that thermal ionisation of the excitons cannot take place even at room temperature. When the quantum energy of the photons is not too great, the photo-excitation in molecular crystals thus does not produce free charge carriers, but rather bound electron-hole pairs, in which the distance between the electron and the hole is small in comparison to that of the so called Wannier excitons, excitations below the conduction band in the inorganic semiconductors. In the first approximation, the excitons in molecular crystals are molecular excitation states which are mobile within the crystal. They are termed Frenkel excitons and can be used to store and transport electronic excitation energy, i.e. for energy transport. Molecular crystals can in this case be used as model substances for the

investigation of energy conduction processes in polymers and in particular also in biological systems. Photosynthesis, the mechanism of sight, and questions of molecular genetics are among these.

The organic solids are also interesting as highly nonlinear optical materials and as highly and nonlinearly polarisable **dielectrics**, as **electrets**, as **ferroelectric materials** and as **photoelectrets**. In electrets, a macroscopic polarisation is present due to a macroscopic orientation of permanent dipole moments of the structural elements: the solid has a positive and a negative end. In photoelectrets, this state is induced by light excitation, and in ferroelectric materials by an external static electric field. These properties of organic materials are made use of in copying machines. In radiation physics, organic crystals such as anthracene are employed due to their high fluorescence quantum yields and their short relaxation times as **scintillator crystals**.

Finally, solid-state physicists make use of molecular crystals when they wish to understand certain aspects of solid-state physics better theoretically and experimentally. Weak intermolecular bonding forces, electrical conductivity with a very narrow bandwidth, large anisotropies in their electrical, optical and magnetic properties, one-dimensional conductivity, linear excitons, and linear magnetic ordering states are best studied in these material classes.

1.3
Goals and Future Outlook

In textbooks on solid-state physics, the organic materials, in particular molecular crystals, are traditionally left out entirely or are treated only in a cursory manner. One learns in detail how atoms or ions can form a crystal and which properties lead to insulators, semiconductors, or metals; but an understanding of the physical properties of solids which are composed of molecules is a neglected chapter in solid-state physics. This book has the goal of awakening or stimulating understanding of this interesting subfield of solid-state physics and in the process to show what these materials can contribute to our knowledge of other classes of materials. Therefore, most attention will be given to:

- the peculiarities of lattice dynamics, which are characterised by the fact that molecules, in contrast to atoms, may be excited not only to translational oscillations but also to rotational oscillations (librations);
- the Frenkel excitons with all the consequences which follow from the energy transport within the crystals which they make possible;
- the strong anisotropies with the possibilities they provide for low-dimensional transport processes;
- the notable delocalisation of electrons within the structural units of organic solids, but not between them, from which e.g. very narrow conduction bands result;

- as well as the great possibilities of variation of phases of the crystal structure and correspondingly of structurally-determined properties on varying the temperature and pressure.

Such specific properties are the reason why the organic molecular crystals and solids assume a special status within the wide field of the chemistry and physics of solid materials. We will thus make an effort to show which new concepts in solid-state physics are necessary or helpful for the understanding of these materials.

Technical applications of organic solids are as yet relatively few. The most important are based on their behaviour as dielectric materials or electrets in electrophotography. Furthermore, electrically-conducting polymers (e.g. poly (3,4-ethylenedioxithiophene) or PEDOT), mixed with polystyrolsulfonate (PSS) and called BAYTRON find application as antistatic or electrically-conducting coatings for photographic and X-ray films and for coating printed-circuit boards. It is becoming apparent that the semiconducting properties of organic solids will soon widen the spectrum of their applications. The **electroluminescence** of polymers and of low-molecular-mass vapour-deposited organic coatings is already being used in technology. In recent years, **transistors** and **integrated circuits** have been fabricated exclusively of organic materials. The "buzzword" **molecular electronics** covers all the efforts to employ molecules as the active components in logic and data-storage elements. The organic compounds can look to an important future role in electronics and optoelectronics as **new materials**. We will take up these topics also in the following chapters, with the intention of contributing to progress in research and applications through an improved understanding of the physical fundamentals.

Problems

Note: the problems for Chap. 1 involve the fundamentals of chemical bonding, electron transfer, electron and energy exchange and the Hückel model of the linear combination of the $2p_z$ atomic orbitals of the C atoms to yield the π orbitals of aromatic molecules (LCAO-MO). Knowledge of these fundamentals of molecular physics is a precondition for using this book. Solutions to the following problems 1–4 can be found in the corresponding chapters of textbooks on molecular physics.

Problem 1.1. Chemical Bonding 1; the hydrogen molecular ion, H_2^+, electron and charge transfer:

The model system H_2^+ is the simplest for chemical bonding and for electron transfer. H_2^+ consists of two protons a and b at a distance R, with one electron. (See e.g. HERMANN HAKEN and HANS CHRISTOPH WOLF, *Molecular Physics and Elements of Quantum Chemistry*, 2nd ed., Springer-Verlag (**2004**), Sect. 4.3, page 58 ff.)

    a. Calculate the mean electronic energy and the energy splitting ΔE of the two eigenstates (bonding and antibonding states) in units of the Coulomb

integral *C*, the exchange or transfer integral *D* and the overlap integral *S* for the case $S \ll 1$.

b. Look in the literature for the calculation of the three integrals *C*, *D* and *S* as a function of the reduced nuclear distance $R' = R/a_0$, where a_0 is the Bohr radius. (See e.g. Max Wagner, *Elemente der theoretischen Physik 1*, Rowohlt Taschenbuch Verlag (**1975**) or P. Gombás, *Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik*, Verlag Birkhäuser, Basel (**1950**).)

c. Calculate the equilibrium distance R_0 of the two protons.

d. Show that for $S \ll 1$, the transfer integral *D* is proportional to the reciprocal of the transfer time t_{trans} of the electron from nucleus a to nucleus b. *Note*: Compute the time-dependent linear combination (sum) of the time-dependent wavefunctions Ψ_+ and Ψ_-.

Problem 1.2. Chemical Bonding 2; the hydrogen molecule, electron exchange and energy transfer:

The Heitler-London model for H_2 is the simplest model both for chemical bonding of two neutral species, here the bonding to two H atoms, as well as for electron exchange and energy transfer. (See e.g.: Hermann Haken and Hans Christoph Wolf, *Molecular Physics and Elements of Quantum Chemistry*, 2nd ed., Springer-Verlag (**2004**), Sect. 4.4.) The two energetically lowest stationary states Ψ_u and Ψ_g of the H_2 molecule and their energies E_u and E_g are given by

$$E_u = 2E_0 + \frac{e^2}{4\pi\varepsilon_0 R} + \frac{C-A}{1-S^2}, \quad \Psi_u = \frac{1}{\sqrt{2}}(\Psi_1 - \Psi_2) \tag{P1.1}$$

and

$$E_g = 2E_0 + \frac{e^2}{4\pi\varepsilon_0 R} + \frac{C+A}{1+S^2}, \quad \Psi_g = \frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2) \tag{P1.2}$$

where

$$\Psi_1(r_1, r_2) = \psi_a(r_{a1})\psi_b(r_{b2}) \tag{P1.3}$$

and

$$\Psi_2(r_1, r_2) = \psi_a(r_{a2})\psi_b(r_{b1}). \tag{P1.4}$$

These are the two mutually-degenerate stationary ground states of the non-interacting H atoms a and b; Ψ_1 describes the state in which electron 1 is around proton a and electron 2 is around proton b. In Ψ_2, the electrons are exchanged. When the two H atoms interact at a proton spacing *R*, the degeneracy is lifted (see Eqns. (P1.1) and (P1.2)). The symbols used there are the overlap integral,

$$S^2 = \int \Psi_1 \Psi_2 \, d\tau_1 \, d\tau_2 \tag{P1.5}$$

the Coulomb integral or the average Coulomb interaction of the two atoms,

$$C = \int \frac{1}{4\pi\varepsilon_0} \left\{ -\frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} \right\} \psi_a^2(r_{a1})\psi_b^2(r_{b2})\,d\tau_1\,d\tau_2 \tag{P1.6}$$

and the exchange integral,

$$A = \int \frac{1}{4\pi\varepsilon_0} \left\{ -\frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} + \frac{e^2}{r_{12}} \right\} \psi_a(r_{a1})\psi_b(r_{b2})\psi_a(r_{a2})\psi_b(r_{b1})\,d\tau_1\,d\tau_2\,. \tag{P1.7}$$

Show that the superposition of the two stationary states Ψ_u and Ψ_g to give a state $\Psi = \frac{1}{\sqrt{2}}(\Psi_u + \Psi_g)$ is no longer a stationary state, but describes the exchange of the two electrons. Determine the exchange frequency in units of A. For simplicity, set $S = 1$.

Problem 1.3. Hückel LCAO-MO theory 1: the allyl radical (See e.g.: Lionel Salem, *The Molecular Orbital Theory of Conjugated Systems*, W. A. Benjamin, Inc. (**1974**), Chap. 1, or Peter W. Atkins, *Physical Chemistry*, Wiley-VCH (**1988**).)

In chemical bonding of the C atoms of a planar unsaturated hydrocarbon molecule, e.g. in benzene (Fig. P1.1), one can distinguish between σ bonds and π bonds or π electrons. The σ bonds are formed from the sp^2 hybrid orbitals of two neighbouring C atoms or from the sp^2 hybrid orbital of one C atom and the $1s$ orbital of an H atom. The sp^2 hybrid orbitals are orthogonal linear combinations of a $2s$ and the two $2p_z$ orbitals in the molecular plane. They make angles of 120° in the plane (Fig. P1.1b). The σ bonds are strongly localised and form the skeleton of the aromatic molecule. The energy levels of the sp^2 electrons bound in the σ bonds are therefore greatly reduced in comparison to the energy of the four valence electrons of the free C atom. Owing to their strong bonding, they can be excited only by high energies and are not considered further in the Hückel theory which follows.

The π bonds are formed by overlap of the $2p_z$ orbitals. Each carbon atom in the aromatic part of the molecule has one $2p_z$ electron (Fig. P1.1c). Their orbitals are orthogonal to the sp^2 orbitals. The spatial extent of the $2p_z$ orbitals is small in all directions within the molecular plane; the π bonds are therefore weak in comparison to the σ bonds. Owing to the equal C–C distances between all the C atoms in benzene (and nearly equal C–C distances in all other aromatic molecules) due to the σ bonds, and owing to the rotational symmetry of
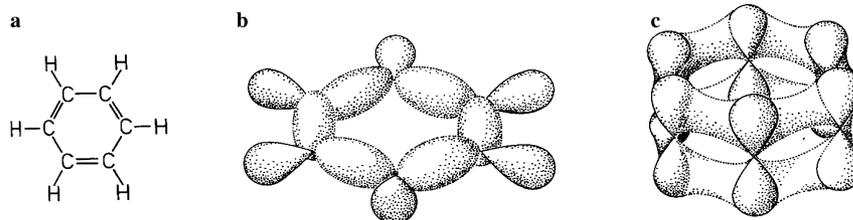
Fig. P1.1 Benzene molecule: a: skeleton, b: σ electrons, c: π electrons.