

COMPUTATIONAL
and
EXPERIMENTAL CHEMISTRY
Developments and Applications

Editors
Tanmoy Chakraborty, PhD
Michael J. Bucknum, PhD
Eduardo A. Castro, PhD



Apple Academic Press



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Edited by

**Tanmoy Chakraborty, PhD, Michael J. Bucknum, PhD,
and Eduardo A. Castro, PhD**



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LIST OF ABBREVIATIONS

AFM	atomic force microscopy
AIM	atoms-in-a-molecule
APGD	atmospheric pressure glow discharge
APPJ	atmospheric pressure plasma jet
CDC	carbide derived carbon
CE	correlation energy
DAC	diamond anvil synthesis cell
DB	discrete breathers
DBD	dielectric barrier discharge
DC	direct current
DCC	dicyclohexylcarbodiimide
DFT	density functional theory
DMF	dimethylformamide
DOS	density of states
EEP	electronegativity equalization principle
FWHM	full width at half maximum
HF	Hartree-Fock
HIPIMS	high power impulse magnetron sputtering
HMDS	Hexamethyldisilane
HMDSO	hexamethyl disiloxane
ILM	intrinsic localized modes
LDA	local density approximation
MF	magnetic field
MFE	magnetic field effect
MO	molecular orbital
MSTO	modified Slater type orbitals
MW	microwave
NPs	nanoparticles
P	pressure
PAA	polyacrylic acid

PDR	percept desizing ratio
PET	photo-induced electron transfer
PVA	polyvinyl alcohol
PVD	physical vapor deposition
QBs	quantum breathers
RF	radio frequency
RIPs	radical ion pairs
ROMP	ring opening metathesis polymerization
S	singlet
SAR	structure activity relationship
SEM	scanning electron microscopy
SPM	scanning probe microscopy
SPR	structure property relationship
SRR	split-ring-resonator
T	temperature
TE	total energy
TEM	transmission electron microscopy
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TPBS	two-phonon bound states
TPc	critical treatment power
TTMSVS	tris(trimethylsilyloxy)vinylsilane
VB	valence bond
VQAS	vinyl quaternary ammonium salt
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

B	bulk modulus
R_c	radius of a sphere
Z	atomic number
\hat{J}_i	Coulomb operators
\hat{K}_i	exchange operators
F	Fock matrix
S	overlap matrix
$Y_{l,m}$	spherical harmonics
w_0	ratio of molar concentration of water to AOT
V	voltage
P_s	saturation polarization in C/m ²
E_c	coercive field
t_c	critical time scale
W_L	domain wall width
E_0, E_1 and E_2	eigen values
k	wave vector
a_n^+ and a_n	creation and annihilation operators
hc	Hermitian conjugate
c	velocity of light
R	lattice parameter
l	measure of the form of the structure
r'	elastic chemical bond deformation
a^2	area of a crystalline plane normal to that elastic chemical bond deformation

Greek Symbols

μ	chemical potential
η	hardness of the system
ϵ_{HOMO}	orbital energies of the highest occupied orbitals
ϵ_{LUMO}	orbital energies of the lowest unoccupied orbitals
ζ	coefficient of hydraulic resistance

ν	dimensionalities of energy
ν	electromagnetic wave frequency
l	interaction term
L	diagonal matrix

PREFACE

Computational and Experimental Chemistry: Developments and Applications provides an eclectic survey of contemporary problems in theoretical chemistry and applied chemistry. The problems addressed in its pages vary from the prediction of a novel spiro quantum chemistry edifice of carbon-based structures to applications of many body perturbation theory in helium-like ions, and also from the elucidation of a novel dynamic elasticity theory applied to carbon, to the description of equalization principles in chemistry. The book is divided into two main parts. Part I entitled “Exotic Carbon Allotropes” is in four chapters and describes the theoretical work of Bucknum et al. applied to the enumeration of novel carbon patterns and their properties. Part II entitled, “New Developments in Computational and Experimental Chemistry” comprises the last eight chapters of the book and provides an interesting survey of contemporary problems in theoretical chemistry and applied chemistry.

In the first part of *Computational and Experimental Chemistry: Developments and Applications*, the book provides a popular as well as technical presentation of the ideas surrounding the emergence of a synthetic, analytical, and theoretical spiro quantum chemistry edifice of carbon-based structures, as well as a chemical topology scheme that successfully describes molecules and patterns, including the hydrocarbons and allotropes of carbon. Thus the purpose of Part I of this book is to describe the generalization and realization of the organic chemistry concept of spiroconjugation into 1-, 2- and 3-dimensions. Chapter 1 covers the theory of spiroconjugation and a lattice is described, the so-called “glitter” lattice, that exhibits the spiroconjugation phenomena in fully 3-dimensions. Also described is the corresponding 1-dimensional substructures of this lattice that exhibit spiroconjugation delocalized in 1-D.

In Chapter 2, experimental evidence is provided and assessed for the prediction of the synthetic realization of the “glitter” allotrope of carbon by shock-based synthetic methods. This is the allotrope of carbon that is

spiroconjugated in 3-D. Part of this analysis includes the prediction of the so-called 3-dimensional resonance structures of glitter, these are resonance forms that can be drawn over the tetragonal glitter unit cell. Chapter 3 includes a description of the chemical topology of the hydrocarbons and crystalline allotropes of carbon. The chemical topology principles are enunciated, based upon the Euler equations for graphs and patterns, and the results are applied to the glitter allotrope of carbon and the other crystalline allotropes of carbon including fullerenes, grapheme and diamond. This chemical topology scheme enables one to map the C allotropes in a topology space allowing them to be classified.

Chapter 4 is the final chapter of Part I and it develops a novel dynamic elasticity theory based upon the work of Feynman et al. The dynamic elasticity theory addresses questions like: What is the ultimate strength of materials? And What is the ultimate strong material? The theory is applied to cubic diamond and tetragonal glitter and the results of an approximate strength calculation show that glitter should actually rival cubic diamond in strength along its longest axis. Other allotropes of carbon, as models, including the hexagonite pattern are analyzed approximately as well.

Part II of *Computational and Experimental Chemistry: Developments and Applications* is entitled “New Developments in Computational and Experimental Chemistry”, and this part of the book narrates contemporary problems in theoretical chemistry and applied chemistry. Thus, Part II of this book contains several chapters that cover a wide range of topics from theoretical and computational chemistry to experimental applied chemistry. Part II, therefore, comprises the last eight chapters of the book and provides an interesting survey of contemporary problems in theoretical chemistry and experimental chemistry that include contemporary perturbation theory results for helium and helium-like ions, the investigation of so-called quantum breather ferroelectric materials by second quantization techniques, the study of magnetic field effects in small molecule organic systems, plasma surface modification in textile processing, the equalization principle in theoretical chemistry, and so on.

In Chapter 5, a successful application of second order many-body perturbation theory to estimate the CE for confined many-electron atoms has been depicted. The second order many-body perturbation theory proposed by Møller and Plesset and detailed implementation of code in GPU

proposed by Gazra et al. has also been discussed vividly. Finally the authors have made a comparative study between their results for helium-like atoms with more sophisticated techniques to find out the percent of correlation energy recovered by the MP2 method.

In Chapter 6, distance dependence of magnetic field effect (MFE) on donor-acceptor (D-A) pair inside a confined heterogeneous environment has been emphasized. In this study N, N-dimethyl aniline (DMA) and the protonated form of Acridine (Acr) have been treated as electron donor and electron acceptor respectively. In this chapter, Basu et al. have elaborately reported the mechanistic features of excited state proton transfer with the photoinduced electron transfer between Acr and DMA.

Nowadays, plasma surface modification is an active field of research. In Chapter 7, the various experimental approaches of plasma surface modification of polyester textile have been described. The improved quality plasma treatment mentioned in this chapter has potential to solve problems with synthetic polyester textile to expand their usefulness and this method is also very ecofriendly.

From the early days of theoretical chemistry, the equalization principle and its application in real field are very popular among researchers. In the Chapter 8, Chattaraj and his colleagues have analyzed the three important equalization principles in chemistry *viz.*, electronegativity equalization principle (EEP), hardness equalization principle (HEP), and principle of electrophilicity equalization (PEE). The qualitative nature and validation of three principles have been concluded nicely at the end of this chapter.

In Chapter 9, the authors have described the ring opening metathesis polymerization procedure that has potential application in cancer therapy. The synthesis and complete characterization of both norbornene derived doxorubicin (mono 1) and polyethylene glycol (mono 2) monomers have been clearly described. Secondly their copolymerization by ring-opening metathesis polymerization (ROMP) to get the block copolymer has been vividly elaborated. Similarly the NDB monomer as well as its homopolymer (NDBH) synthesis and complete characterization have been thoroughly discussed.

In Chapter 10, Chakraborty et al. have studied theoretically biological activity of newly synthesized mesoionic heterocycles. Invoking global and local reactivity based descriptors, the experimental mechanistic features

of mesoionic molecules have been nicely correlated with their theoretical counterparts.

In Chapter 11, Bandyopadhyay et al. have reported on the non-linear Klein-Gordon equation that is based on their discrete Hamiltonian in a typical array of ferroelectric domains. The effect of second quantization, in a particular environment, toward the nonlinearity has been described. This is considered useful for a future study in this new field of investigation of quantum breathers in ferroelectrics.

Finally, in the last chapter (Chapter 12) of Part II of this book, Ramon has studied the molecular quantum similarity (QS) measures involving three density functions. The necessary algorithms have been described here. General theory and computational feasibility of a hypermatrixial or tensorial representation of molecular structures associated to any molecular quantum object set (MQOS) have been nicely explained in this chapter. Secondly, generalized Carbó similarity indices (CSI) have also been studied. The theoretical and computational approaches have been supported by various suitable applicative examples.

Computational and Experimental Chemistry: Developments and Applications is a collection of chapters that has a wide and eclectic range of subject matter regarding the applications of theoretical and experimental chemistry in realistic, everyday settings. The research articles comprising this book are based upon established methods of theoretical and computational chemistry, and applied chemistry, and this subject matter is thus very important in the context of contemporary problem solving in chemistry. Finally, two of the chapters of this book, Chapters 7 and 9, have been included so as to cover important research in applied chemistry of textiles and polymers, and these topics were thus chosen for their importance in the everyday applications of chemistry.

— **Tanmoy Chakraborty, PhD, Michael J. Bucknum, PhD, and
Eduardo A. Castro, PhD**

PART I
Exotic Carbon Allotropes

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CHAPTER 1

SPIRO QUANTUM CHEMISTRY

MICHAEL J. BUCKNUM and EDUARDO A. CASTRO

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SUMMARY

A recent paper has described the structure of a hypothetical 3-,4-connected net termed glitter. This is a model of an allotrope of carbon in the form of a synthetic metal. That paper pointed to the importance of through-space p_σ interactions of adjacent olefin units in the net in understanding the electronic structure at the Fermi level. The present communication elucidates the role of spiroconjugation in understanding features of the electronic band structure and density of states of glitter. With this analysis of spiroconjugation in the 1-dimensional polyspiroquinoid polymer and the 3-dimensional glitter lattice, the foundations have been laid for a new type of quantum chemistry herein called spiro quantum chemistry. Spiro quantum chemistry complements traditional quantum chemistry which is focused on linear polyenes, circular annulenes, polyhexes, 2-dimensional graphene sheets and related structures including fullerenes, by focusing on spiroconjugated hydrocarbon structures in 1-,2-, and 3-D, including linear spiro[n]quinoids and polyspiroquinoid in 1D, circular cyclospiro[n]quinoids, spiro[m,n]graphene fragments and spirographene in 2D and [m,n,o] glitter fragments and glitter in 3D.

1.1 INTRODUCTION

In 1994, the structure of the all-carbon “glitter” lattice [1] was described along with B_2C and CN_2 phases adopting this structure-type. Glitter is a hypothetical tetragonal allotrope of carbon. The geometrical structure of the lattice (space group $P4_2/mmc$, # 131) is shown in Fig. 1.

The dimensions of the lattice are $a = 2.53 \text{ \AA}$ and $c = 5.98 \text{ \AA}$, these are constrained by the geometry of the 1,4-cyclohexadiene molecule upon which the structure is based [2]. It is a 3-,4-connected net [3] containing trigonal and tetrahedral atoms in a ratio of 2:1, with a calculated density of 3.12 g/cm^3 ; intermediate between graphite and diamond. Apparent in the structure are the ethylenic columns, which run perpendicular to each other to generate the 3-dimensional lattice.

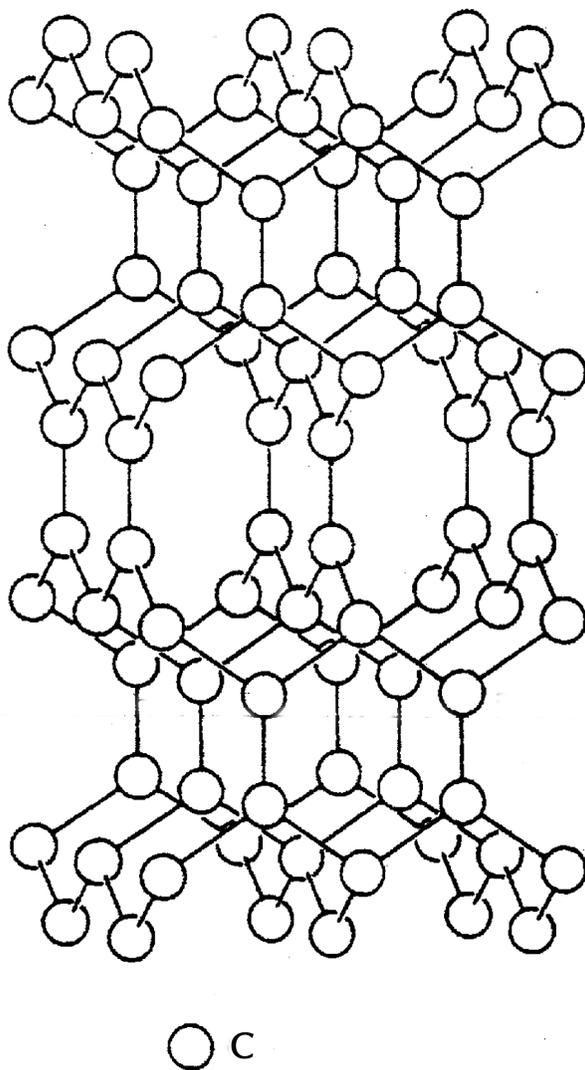


FIGURE 1 Structure of the glitter model in space group $P4_2/mmc$.

Merz et al. [4] have described the electronic band structures of several related 3-,4-connected nets each possessing stacked olefin units. Evolution of $\pi-\pi^*$ band overlap with the separation between adjacent units in an olefin stack is presented in their paper, this diagram is shown in Fig. 2. Note

the touching of the π and the π^* bands at an interaction distance of about 2.5 Å. From this diagram it is clear that the approximate density of states profile of glitter will be that of a metal, with a small π - π^* band overlap at the Fermi level.

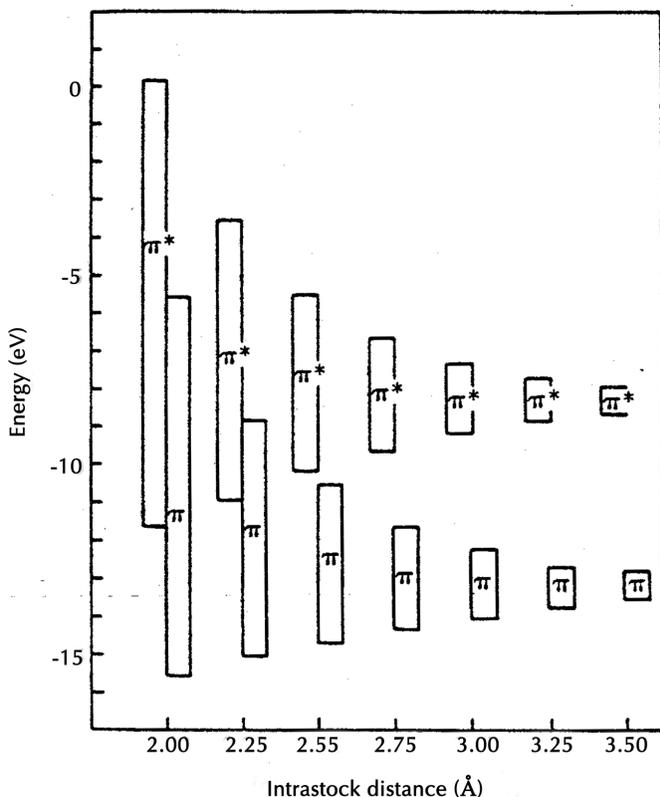


FIGURE 2 Evolution of π - π^* overlap with the separation between adjacent units in an olefin stack.

The structure shown in Fig. 1 also contains the 1,4-cyclohexadiene-oid molecular units linked through their tetrahedral vertices to adjacent rings. These linkages form chains. Each such chain is termed a “polyspiroquinoid” substructure of the “glitter” lattice. The electronic structure of a polyspiroquinoid model is described in connection with the concept of spiroconjugation.

Band structure calculations for this net were carried out using the extended Hückel method adapted for application to extended structures. [5] Electronic band structures of various sublattice models, including the polyspiroquinoid one, were presented in the original report of the glitter structure [1] in order to clarify the importance of through-space interactions in these lattices.

1.2 SPIROCONJUGATION IN 1-DIMENSION AND POLYSPIROQUINOID

Spiroconjugation [6] is claimed to occur in the electronic structure of the polyspiroquinoid chain. [1] This type of through-space interaction can be considered in terms of 4 p_{π} atomic orbitals held “spiro” to each other about a tetrahedral C atom (see Fig. 3). These four orbitals interact to form 4 combinations of differing symmetry with respect to the two perpendicular mirror planes dividing the tetrahedral C atom. One combination is symmetric under reflection in each mirror plane, labeled (SS), and there are also (SA), (AS) and (AA) combinations. The (AA) combination is shown, it is of the proper symmetry for a bonding spiro-type interaction.

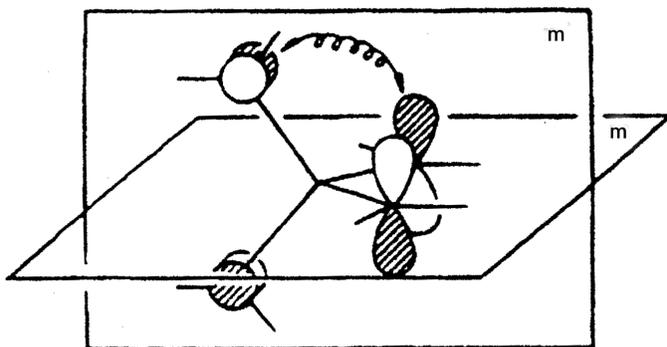


FIGURE 3 “Spiro” molecular orbitals derived from 4 p_{spiro} combinations.

From the original analyses of the effect of spiroconjugation in discrete molecular systems, including spiro [4.4] nonatetraene [7] the importance of it in stabilizing (and destabilizing) a frontier molecular orbital was of

primary interest. This work was based upon electronic spectra, chemical reactivity and electronic structure calculations [6]. From this background, in the original paper on the glitter structure [1], only the lowest-lying π^* band, the LUCO (lowest unoccupied crystal orbital) was considered in assessing the importance of through-space p_{spiro} interactions in the 1-dimensional polyspiroquinoid substructure of glitter.

The interaction diagram for spiro[4.4]nonatetraene, reported by Duerr and Kober [7h], is shown in Fig. 4. The diagram reveals that in a situation involving 8 p_{π} orbitals (four interacting π systems as opposed to four interacting p orbitals, as in Fig. 3), there are generated two sets of four butadieneoid π systems. These four butadieneoid π systems are of (AS), (AA), (AS) and (AA) symmetry, unlike the archetypal system diagrammed in Fig. 3. Interaction of these four π systems through the spiro C atom, yields eight molecular orbitals over the skeleton of the spiro [4.4] nonatetraene molecule.

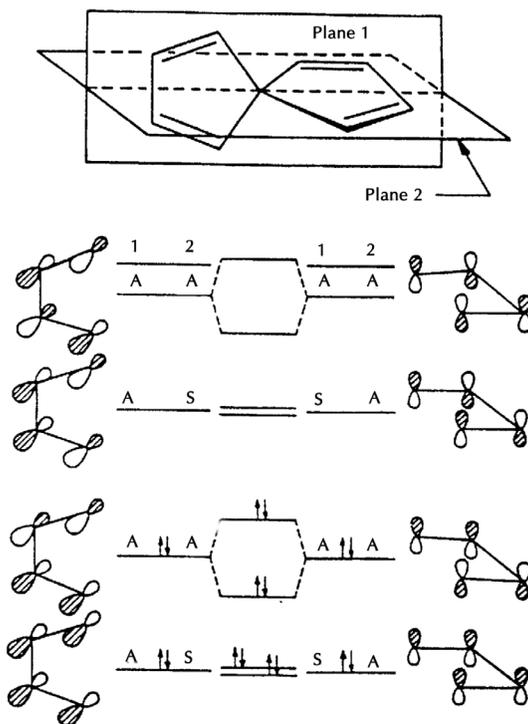


FIGURE 4 Molecular orbitals of spiro[4.4]nonatetraene.

Note the presence of the two (AA) combinations, one derived from the interaction of the HOMO (highest occupied molecular orbital) π levels of butadiene and one derived from the interaction of the LUMO+1 (next highest to the lowest unoccupied molecular orbital), π^* levels of butadiene. There are thus four levels in which the effects of spiroconjugation could be important, two down in the bonding manifold and the other pair in the anti-bonding manifold. The splitting of these pairs of (AA) combinations results from one spiro [4.4] nonatetraene orbital carrying a bonding p_{spiro} interaction and its sibling carrying an anti-bonding p_{spiro} interaction.

An analogy exists between the interaction diagram of the spiro [4.4] nonatetraene molecule and the unit cell of the polyspiroquinoid chain. Certain of the energy levels in both of these systems are comprised of 8 p_{π} atomic orbitals present in each structure. This analogy will be followed, which describes the stabilizing effects of spiroconjugation in the electronic band structure of polyspiroquinoid.

Figure 5 shows the structure of the model polyspiroquinoid chain (H atoms added to the glitter fragment to reach a realistic structure) and Fig. 6 is its electronic band structure. To the right in this diagram are appended the levels of the 3,3, 6,6-tetramethyl-1,4-cyclohexadiene molecule. This molecule is a reasonable model for the polymer, but one lacking the spiroconjugation interaction. The 2 π and 2 π^* levels in the molecule have been indicated alongside the 4 π and 4 π^* bands of polyspiroquinoid.

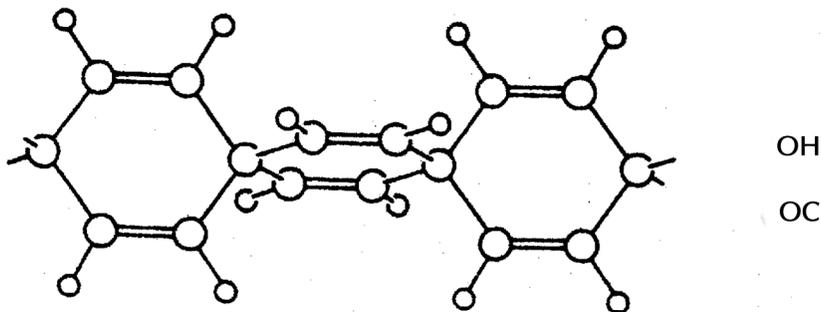


FIGURE 5 Structure of the polyspiroquinoid model.

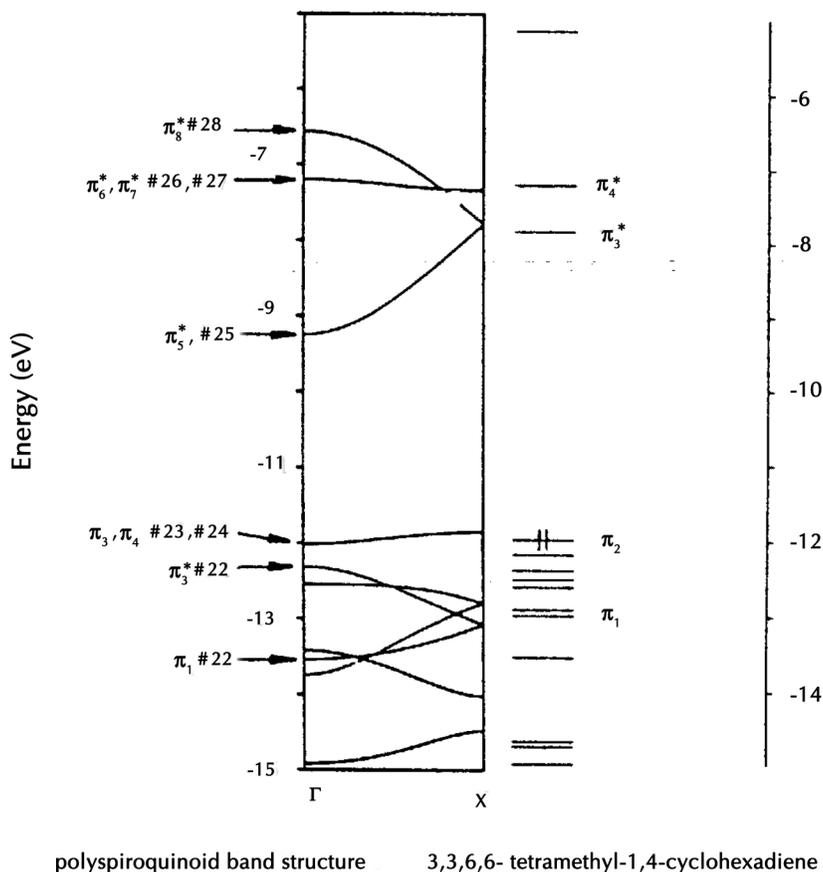


FIGURE 6 Electronic band structure of polyspiroquinoid and molecular orbitals of 3,3,6,6-tetramethyl-1,4-cyclohexadiene with π and π^* levels indicated.

As pointed out previously, [1] the lowest-lying π^* band in the electronic structure of the chain is of the proper symmetry, (AA), for there to be a bonding p_{spiro} interaction in that band. In addition, the lowest-lying π band is also of (AA) symmetry, so that there is a bonding p_{spiro} interaction in that occupied band as well. The relative importance of the effects of spiroconjugation in the chain will be posed with respect to the stabilization of the occupied π band compared to the energy level of the discrete π molecular orbital of 3,3,6,6-tetramethyl-1,4-cyclohexadiene from which it is derived.

In analogy with spiro [4.4] nonatetraene, the 8 p_π atomic orbitals in the unit cell of polyspiroquinoid generate 4 π crystal orbitals and 4 π^* crystal orbitals in its electronic band structure. At the zone center, half of these eight crystal orbitals are constructed from real coefficients of the same magnitude at each p_π atomic site in the unit cell. Because of their importance in the analysis of spiroconjugation in polyspiroquinoid, these four (AA) crystal orbitals are sketched exactly as they occur at the zone center, in Fig. 7. These are analogous to the four (AA) combinations from the spiro [4.4] nonatetraene analysis. They occur as band #18 (p_1), band #22 (p_2), band #25 (π_5^*) and band #28 (π_8^*).

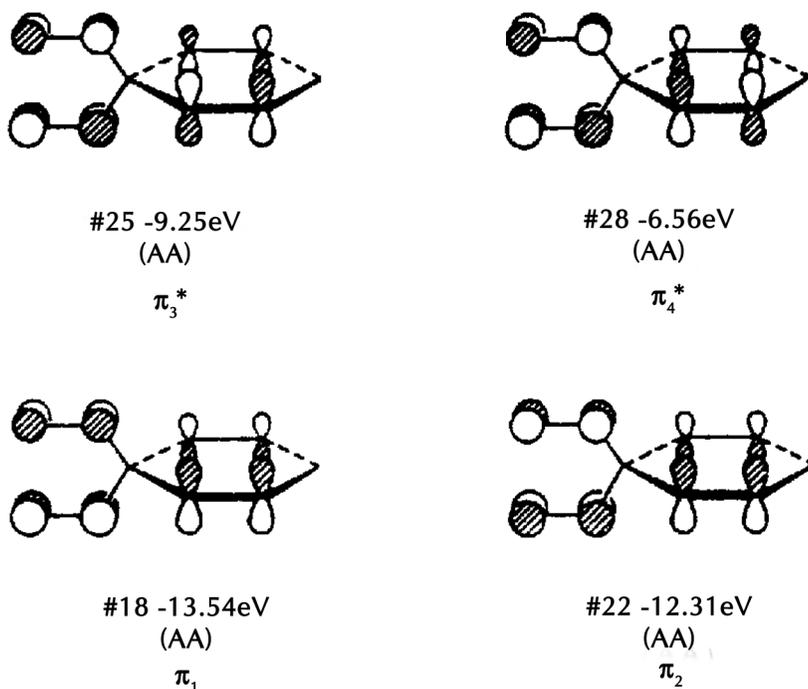


FIGURE 7 The p_π crystal orbitals of polyspiroquinoid sketched at the center of the Brillouin zone.

The four (AS) combinations occur in degenerate band pairs (compare to the orbital interaction diagram of spiro [4.4] nonatetraene) across the Brillouin zone of the chain. These are constructed from real coefficients of the same magnitude and sign at each p_π atomic site in one or the other ring of the polyspiroquinoid unit cell. Every other ring in the polymer possesses these π and π^* type interactions. The π and π^* interactions in half the unit cell are involved in σ or σ^* interactions with the adjacent ring, which maintain the (AS) symmetry of the crystal orbital. At the zone center they occur as bands #23 (p_3) and #24 (π_4), (the HOCO, highest occupied crystal orbital, levels) and as bands #26 (π_6^*) and #27 (π_7^*), (the LUCO+1 levels).

One can analyze the attendant orbital interactions of the (AA) combinations graphically from the sketches. In crystal orbital #18, the 4 bonding p_π combinations in the unit cell also possess a bonding p_{spiro} interaction about each of the spiro carbons in the chain. Comparison with crystal orbital #22, the sibling π band to crystal orbital #18, reveals their only difference is the presence of an anti-bonding p_{spiro} interaction in the higher-lying π band. Their energy difference at the zone center is 1.23 eV, this is the actual magnitude of the splitting of the (AA) combinations; this was predicted qualitatively in the orbital interaction diagram shown in Fig. 4.

In the 3,3,6,6-tetramethyl-1,4-cyclohexadiene model molecule, the lower-lying π (p_1) level is the “out-of-phase” π combination, it is of (AA) symmetry with respect to the two mirror planes dividing the spiro carbon atoms in the ring. Its sibling level (p_2) is the “in-phase” π combination, it is of (AS) symmetry. The 2 π (AA) levels in polyspiroquinoid are derived from the pure “out-of-phase” π combination of this model molecule, and the two (AS) levels are derived from the pure “in-phase” π combination. Crystal orbital #18 (p_1) occurs at -13.54 eV at the zone center and crystal orbital #22 (p_2) occurs at -12.31 eV. Therefore, the spiroconjugation band is stabilized by 0.55 eV with respect to the lower-lying π level in 3,3,6,6-tetramethyl-1,4-cyclohexadiene and its sibling π band, with anti-bonding p_{spiro} interactions, is destabilized by 0.68 eV.

Tracing the evolution of these bands along the symmetry line of polyspiroquinoid, one sees the two sibling bands meet at the zone edge where they are degenerate (*see* Fig. 6). This degeneracy occurs because of the presence of a 4_2 screw axis in the polyspiroquinoid unit cell. The band structure is “folded” in half due to the 4_2 screw axis. Across the Brillouin

zone crystal orbital p_1 , the spiroconjugation band, is stabilized with respect to the lower-lying π level in 3,3,6,6-tetramethyl-1,4-cyclohexadiene (p_1). At the zone edge, the degeneracy at -13.07 eV is just 0.08 eV below the corresponding molecular orbital (p_1) in the 3,3,6,6-tetramethyl-1,4-cyclohexadiene model molecule.

Figure 8 shows the density of states (DOS) diagram along with the band structure diagram (Fig. 6) of polyspiroquinoid. The shaded area is the contribution of p_π orbitals to the total DOS. It has a “spike” at an energy, which corresponds to the spiroconjugation band at the zone center (-13.5 eV). This spike indicates there is a large density of states in the electronic structure of the polymer at that energy. Evidently from the DOS diagram, there is not a corresponding spike coincident with the energy of the sibling pband, which possesses anti-bonding p_{spiro} interactions at the zone center. This is consistent with the small degree of dispersion (flatness) of band #18 in the neighborhood of the zone edge.

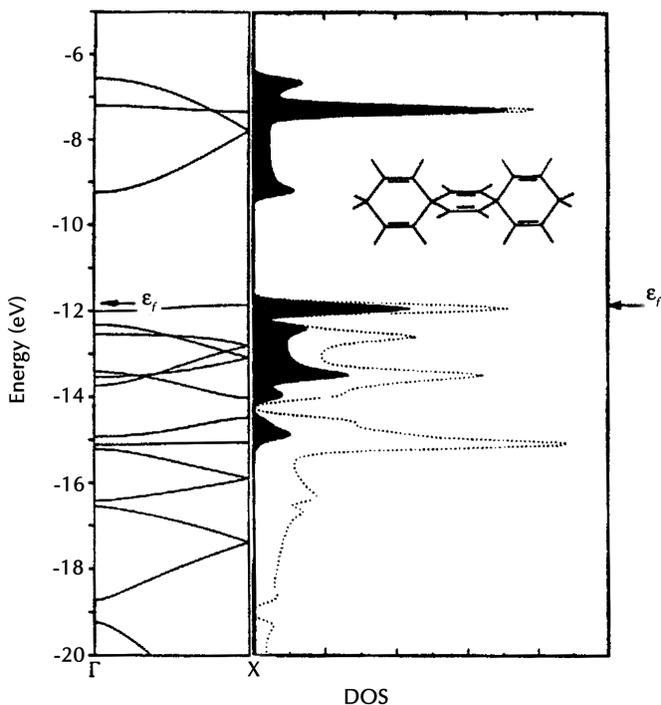


FIGURE 8 Electronic band structure and density of states (DOS) of the polyspiroquinoid model; shaded area indicates contribution of p_π orbitals to the total DOS.

1.3 SPIROCONJUGATION IN 3-DIMENSIONS AND GLITTER

In the full 3-dimensional glitter lattice shown in Fig. 1, it is obvious the polyspiroquinoid chains are linked together along the $[100]$ and $[010]$ directions of the lattice. Although through-space bonding p_s interactions are primary in the analysis of what occurs at the Fermi level of glitter, it turns out that the spiroconjugation effects seen in the 1-dimensional polyspiroquinoid substructure will carry over into the 3-dimensional structure.

As is implied in the model structural drawing on the inset of Fig. 9, through-space bonding p_o interactions are responsible for reducing the band gap (see Fig. 2) in the 1-dimensional polycyclophane substructure, which possesses the p_o interactions uniquely among the 1-dimensional substructures. Clearly in this substructure, which from its geometry is absent orbital interactions connected with spiroconjugation, the π and π^* crystal orbitals come in pairs, the HOCO-1 and the HOCO as the π bands, and the LUCO and the LUCO+1 as the π^* bands. These bands run down from the zone center, where they occur in nearly degenerate pairs, out to the zone edge, as shown in Fig. 9.

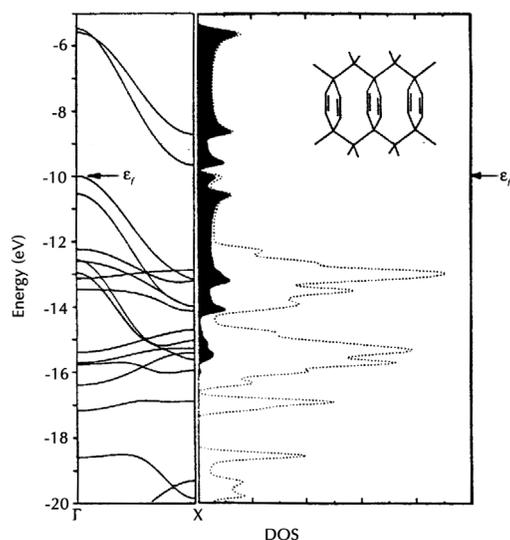


FIGURE 9 Electronic band structure and density of states (DOS) of the polycyclophane structure. Shaded area indicates the contribution of p_x orbitals to the total DOS. Structural model shown on onset.

Figure 10 shows the band structure of glitter, as there are 6 C atoms in the unit cell it consists of 24 bands, 12 of these bands are fully occupied. In order to assess the importance of through-space interactions in the lattice, including the importance of spiroconjugation, it is only necessary to consider the crystal orbitals derived from combinations of the p_p atomic orbitals present in the unit cell of glitter. These 4 p_π atomic orbitals, one such atomic orbital for each of the 4 trigonal planar C atoms in the unit cell, combine together to form 2 π crystal orbitals and 2 π^* crystal orbitals in the electronic band structure of the glitter lattice.

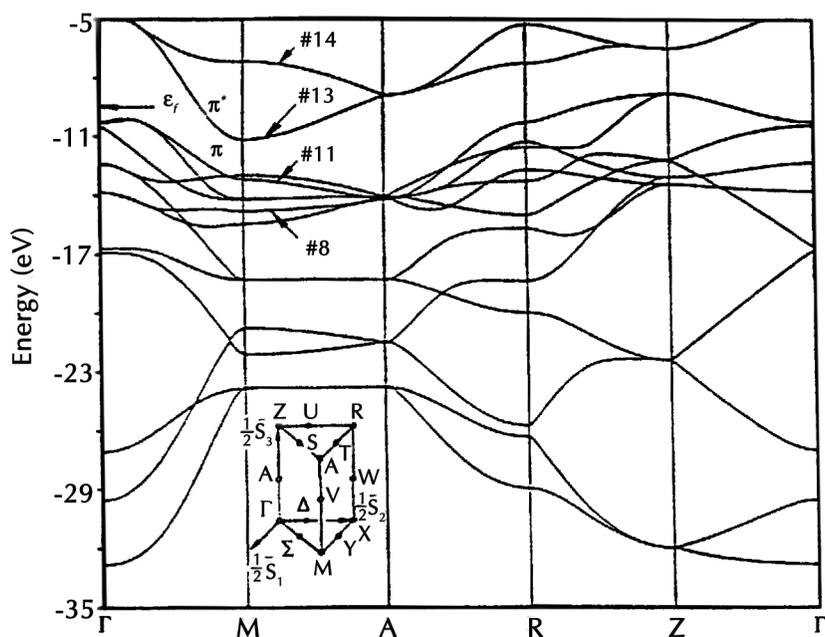


FIGURE 10 Electronic band structure of glitter. The π and π^* bands are indicated at symmetry point M of the Brillouin zone.

In analogy with the polycyclophane substructure, it would be expected that these π and π^* crystal orbitals would bracket the Fermi energy; that is they would occur as the HOCO-1, HOCO, LUCO and LUCO+1 (see Fig. 10). In the original report of the electronic structure of glitter, the authors pointed to the importance of through-space p_σ interactions, occurring

together with through-bond p_π interactions, at the short interaction distance of 2.53 Å present in the unit cell.

Comparison of the Brillouin zone of glitter to the unit cell of glitter in direct space, shown on the inset of Fig. 10, reveals that symmetry point M is analogous to the zone center in the Brillouin zone of the polyspiroquinoid model. The symmetry line from M to A corresponds to the symmetry line followed from the zone center to the zone edge in the electronic structure of the polyspiroquinoid model. The π and π^* bands in glitter, the π bands labeled as #8 and #11 and the π^* bands labeled as #13 and #14, at symmetry point M in the diagram, become degenerate pairs at symmetry point A. These degeneracies occur because of the presence of a 4_2 screw axis in the unit cell of glitter.

At symmetry point M in the Brillouin zone of glitter these 4 crystal orbitals enter with real valued coefficients of the same magnitude. It is possible to carry out a graphical examination of these 4 crystal orbitals derived from the 4 p_π atomic orbitals of glitter. They may be sketched exactly as they appear in the Brillouin zone at symmetry point M. From these sketches, which are shown in Fig. 11, the attendant orbital interactions may be analyzed graphically.

Labeling the 4 π crystal orbitals at high symmetry point M in the Brillouin zone, using their symmetry with respect to the 4_2 screw axis and the c glide plane of the unit cell, there are four combinations: p_1 (SS), p_2 (AA), p_3^* (AA) and π_4^* (SS). Using the twomirror planes along $[001]$ to assign the symmetries of the π crystal orbitals, instead of their behavior with respect to the space symmetry elements, they would all be of symmetry (SS), this represents an inversion of symmetry from the polyspiroquinoid (AA) combinations. Had the unit cell been chosen with $[100]$ and $[010]$ rotated through 45° from the present unit cell, all four combinations would be of (AA) symmetry with respect to the twomirror planes along $[001]$. This is entirely analogous to the four (AA) combinations of the polyspiroquinoid model, although not strictly homologous to the electronic structure of the polymer, as is discussed later. At any event, the present choice of unit cell makes visualization of the orbital interactions more clear to the reader.

From these sketches, one can see the presence of p_π interactions within the unit cell and also the presence of inter-cell and intra-cell p_σ and p_{spiro} interactions. Band #8 is the lowest-lying π crystal orbital (-14.87 eV),