Pure Appl. Chem., Vol. 82, No. 4, pp. 905–915, 2010.
doi:10.1351/PAC-CON-09-10-29

Electronic structure of higher acenes and polyacene: The perspective developed by theoretical analyses*

Holger F. Bettinger‡

Institute for Organic Chemistry, University of Tübingen, 72076 Tübingen, Germany

Abstract: The hypothetical polymer obtained by linear annelation of benzene units, polyacene (PAC) $(C_4H_2)_n$, has received considerable attention over the last 50 years. This interest is due to the unusual electronic structure that is assumed to result in usual physical properties. The review summarizes the theoretical investigations of PAC research. The most recent computational analyses available in the literature are based on density functional theory (DFT) for PAC and on the complete active space self-consistent field (CASSCF) method for oligoacenes and suggest an undistorted symmetrical structure with an antiferromagnetic (AFM) coupling of electrons.

Keywords: electronic structure theory; oligoacene; polyacenes; polycyclic aromatic hydrocarbon; solid state.

INTRODUCTION

The chemistry of the higher acenes **1**, compounds composed of laterally fused benzene rings, dates back 80 years when Clar and John first reported the synthesis and properties of pentacene **2** ($n = 5$) [1]. Clar and Marschalk independently reported the synthesis of hexacene **3** in 1939 [2], and Clar attempted the synthesis of heptacene **4** in 1942 [3]. Subsequent work Bailey et al. [4] on heptacene seemed to confirm Clar's work, but Marschalk [5] and Clar himself cast some doubt on his earlier results [6]. The existence of heptacene remained dubious until 2006 when Neckers and co-workers employed a photochemical precursor embedded in polymethylmetacrylate matrix to generate heptacene [7].

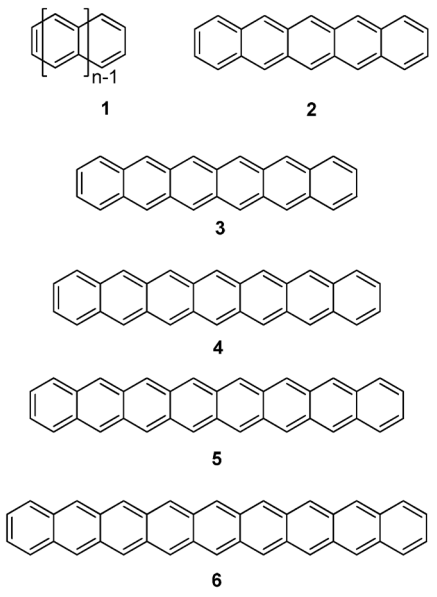
Parent acenes larger than heptacene have been considered by Clar to be not accessible [8]. This was nonetheless very recently achieved by our group using the photobisdecarbonylation strategy employed earlier by Neckers and co-workers, but required the application of matrix isolation techniques in cryogenic argon for the stabilization of octacene **5** and nonacene **6** [9].

The hypothetical polymer that can be constructed from the acenes, polyacene (PAC) ($n \rightarrow \infty$ in **1**), has received considerable attention since its first study by Salem and Longuet-Higgins in 1960 [10]. Since then, a sizeable number of theoretical investigations on the properties of this polymer have been published, and recent years have seen again an increased interest in this polymer. This is certainly driven by the current attention on carbonaceous materials like graphene in general and the acenes in particular [11–15]. However, it also appears that a computational investigation by Bendikov et al. [16] in 2004 was very influential in triggering a number of further theoretical studies on the properties of higher

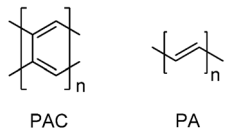
Pure Appl. Chem.* **82, 757–1063 (2010). An issue of reviews and research papers based on lectures presented at the 13th International Symposium on Novel Aromatic Compounds (ISNA-13), 19–24 July 2009, Luxembourg City, Luxembourg on the theme of aromaticity.
‡E-mail: holger.bettinger@uni-tuebingen.de

acenes and on PAC. In this review, the computational investigations that focus on the geometric and electronic structure of PAC and higher acenes are summarized.

In the remainder of this paper, the term "polyacene" (PAC) is reserved for the (infinite) polymer in analogy to the use of "polyacetylene" (PA) (see Scheme 2), while finite acene molecules are called "oligoacenes" (**1**).



Scheme 1 The oligoacenes **1** and the members pentacene **2** to nonacene **6** studied under the conditions of matrix isolation.



Scheme 2 Lewis formulas of the polymers PAC and PA.

GEOMETRICAL DISTORTIONS IN POLYACENE: TO BE OR NOT TO BE

The foundations for an understanding of PAC were laid in 1960 by Salem and Longuet-Higgins [10]. They previously had investigated long polyenes [17] (or PA) with respect to bond-length alternation (BLA) and extended their study to PAC, a so-called ladder polymer as it consists of two polyene chains linked by C–C bonds, sometimes called rung bonds. Their analysis of long polyene molecules is nowadays textbook knowledge [18,19]: any very long polyene must have alternate bonds unequal in length in the most stable configuration. In a molecular orbital theory picture, equal bond lengths in a long polyene chain result in a degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This degeneracy is expected to result in a Jahn–Teller distortion. In solid-state physics, the same condition is termed differently [19]. The polyene is a 1D system with a partly filled band. Peierls has shown that for such systems one can always find a distortion which breaks the degeneracy at the Fermi level [20]. This geometric distortion is nowadays known as (first-order)

Peierls distortion. As a result of the Peierls distortion, the polymer assumes a structure with BLA as is well known for polyenes or PA.

Salem and Longuet-Higgins applied Hückel molecular orbital (HMO) theory to obtain and analyze the band structure of the symmetric form (**A**) of PAC (see Fig. 1). They concluded that (a) BLA is *not* inevitable; (b) the symmetrical equilibrium configuration with external bond lengths of $R_1 = R_2 =$ 1.410 Å and rung bond lengths of $R_3 = 1.438$ Å is stable with respect to geometrical distortion. They included the caveat that their second conclusion depends upon how rapidly the resonance integral of a C–C bond varies with its length, but used the best value available at that time for the distance dependence of the resonance integral.

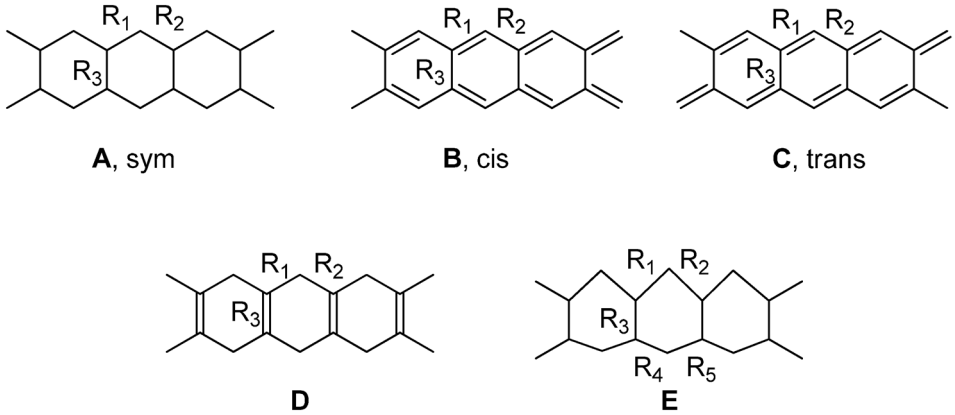
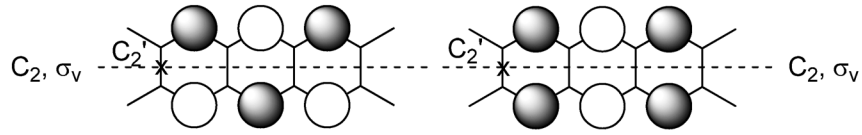


Fig. 1 Schematic structures considered for PAC. Double lines represent relatively shorter bonds. **A** is the undistorted polymer with equal bond lengths R_1 and R_2 (following common practice, double bonds are not indicated in this form); **B** is the *cis*-distorted polymer with $R_1 \neq R_2$; **C** is the *trans*-distorted polymer with $R_1 \neq R_2$; **D** is a distorted polymer with short rung bonds R_3 and $R_1 = R_2$; **E** is a distorted polymer with equal lengths on either strand ($R_1 = R_2$ and $R_4 = R_5$), but with $R_1 \neq R_4$ and $R_2 \neq R_5$. The numbering is taken from Kivelson and Chapman [21].

The explanation given by Salem and Longuet-Higgins for their finding that PAC does not necessarily need to undergo a geometric distortion **B** (see Fig. 1) is easily rationalized by symmetry arguments: the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) are of different symmetries before and after a symmetric distortion of the polymer (see Fig. 2). They therefore cannot interact within the framework of reduced symmetry, and thus there is no driving force for a distortion. In other words, there is no reason for the system to undergo a Peierls distortion, although it cannot be excluded either. This situation has been termed a "conditional instability" later.

In addition to the *cis* distortion **B** considered by Salem and Longuet-Higgins, a *trans* distortion **C** was taken into account. Boon argued in 1971 that in the *trans*-distorted form, a Peierls distortion should be allowed by symmetry [22]. But Whangbo, Hoffmann, and Woodward [23] demonstrated that the symmetry arguments brought forward by Salem and Longuet-Higgins also apply to the *trans*-distorted form **C** of PAC, i.e., also a *trans* distortion is not inevitable. In contrast, however, to the conclusions of Salem and Longuet-Higgins, the study by Whangbo et al. [23] using extended Hückel theory (EHT) found symmetrical PAC to be of highest energy while the *trans* configuration was the lowest energy form. In addition, the EHT study found that there is a crossing of bands at the Fermi level for the symmetric form, a result that was confirmed by Lowe et al. [24]. The origin of this crossing was discussed further by Kertesz and Hoffmann in 1983, and the consequences of *trans* distortions were analyzed in terms of the HMO model [25]. The loss of symmetry upon *trans* distortion allows mixing of the HOCO and the LUCO+1 as well as that of HOCO–1 and LUCO. Most notably, the size of a bandgap E_g was



A (C_2', C_2, σ_v):	SSA	AAS
B (C_2, σ_v):	SA	AS
C (C_2'):	S	A

Fig. 2 HOCOs (left) and LUCOs (right) at the Fermi surface of the symmetrical form of PAC. The symmetry properties (asymmetric A or symmetric S) of these orbitals with respect to the available symmetry operations in the three most important forms of PAC are given below the orbitals. This clearly shows that in **A–C** the frontier orbitals are of different symmetry properties and thus cannot interact directly.

obtained to be proportional to the second power of a small distortion δ: $E_g \sim \delta^2$. Its actual magnitude depends on the elastic forces of the σ framework [25].

The HMO and EHT conclusions drawn concerning the structural stability of PAC were basically in agreement with results obtained with other theories. Tyutyulkov et al. [26] used the alternant molecular orbital (AMO) method in 1975 and concluded that BLA should not be very pronounced. Brédas et al. [27] employed the valence effective Hamiltonian (VEH) technique for polymers and arrived at low or zero bandgaps for the three isomers **A–C** of PAC in 1982, while Kao and Lilly [28] obtained a slightly larger bandgap using the same method but different geometry.

Likewise, the study of Tanaka et al. [29], who used the CINDO/2 (closed-shell intermediate neglect of differential overlap) approximation in a self-consistent field (SCF)-crystal orbital framework, found that the *trans*-isomer is lowest in energy, followed by the slightly less stable *cis* form. The symmetric PAC is least stable at this level of theory. In contrast to the results of the HMO and EHT investigations, however, these authors found that the bands do not touch at the boundary of the Brillouin zone or even cross; rather a finite bandgap was obtained and ascribed to result from the inclusion of third nearest-neighbor interactions [29]. Kertesz et al. critically discussed the problem associated with bandgaps obtained with SCF or Hartree–Fock (HF)-based theories, including the semiempirical approximations MNDO (modified neglect of differential overlap) or PPP (Pariser–Parr–Pople) that were used in PAC research [30]. These authors were aware of the general overestimation of the energy gap by HF theory for solids and traced the large gap obtained for *sym* PAC to the nonlocal exchange term. Kertesz et al. therefore cautioned that the overestimation of the energy gap of *sym* PAC by HF-based theories will also have a "dramatic effect on the relative stabilities of the other forms" [30]. In other words, the relative energies of PAC isomers obtained with HF-based theories are questionable. The error should be decreased by including electron correlation, but such theories were not available for systems like PAC for some time. Hence, Kertesz et al. also applied MNDO in spite of some deficiencies, as it was assumed to provide still more reliable results than those obtained previously at non-SCF levels.

While the *trans* form was the most stable isomer in almost all of the early investigations, the *cis* form was found to be lowest in energy at the MNDO level by Kertesz et al. [30]. This result that was confirmed by Chandrasekhar and Das using periodic boundary conditions (PBCs) and sampling of k space at the MNDO level [31].

The structural instability of PAC was further investigated by Srinivasan and Ramasesha using the Hubbard model within the projector quantum Monte Carlo (PQMC) method [32]. The Hubbard model improves upon the Hückel or tight-binding (TB) approximation by considering electron–electron interactions to some extent. In this PBC study, the lattice was kept frozen (static lattice approximation) and

the BLA was imposed by alternation of the transfer integrals t_{ij} by using an alternation parameter δ that modifies the transfer integrals. The effect of increasing correlation strengths was studied by varying the interaction strength U/t for a number of values of δ. It was found that the *cis* and *trans* forms are stabilized with respect to the *sym* PAC to the same extended at the Hückel level, i.e., without considering electron correlation. Increasing the electron–electron interaction further stabilizes the distorted states, with the *cis* form being more stabilized than the *trans* from. There is no indication that the system has a tendency to destroy the imposed BLA patterns [32]. Similar conclusions were drawn several years later by Raghu et al. [33]. These authors utilized the density matrix renormalization group (DMRG) approach for the ground state of PAC oligomers within the PPP approximation. Again, an alternation parameter δ was introduced that modified the transfer integrals t, and the response of the system to variation of δ and the electron–electron interaction strength U/t was probed. Both *cis* and *trans* distortions are favored over the symmetric form, and the *cis*-distorted form is the most stable isomer of PAC [33]. However, for both forms the instability is conditional, i.e., its extent depends on the stiffness of the σ framework. This, however, was not investigated by the authors [33].

An energetic preference of the *cis* form was also obtained by Niehaus et al. in 2005 [34]. These authors considered long oligoacenes up to $n = 30$ in the context of a TB-based Green's function approach. The *sym* form of PAC was found to be the most stable isomer only for $n \leq 19$. For larger oligomers and (though not explicitly stated by the authors) presumably the infinite polymer, the *cis*-distorted form is lower in energy [34]. No energy differences were given in the work of Niehaus et al. [34], but the BLA reported is only 0.008 Å.

A completely different approach to gain information on the energies and structures of PAC was taken by Cioslowski [35]. He considered the parent oligoacene molecules up to hexacene, and their amphi- and ortho-quinone derivatives at the HF and MP2 levels in conjunction with the 6-311G** basis set. Data for PAC were obtained by extrapolating to the infinite polymer limit using the Padé approximation. Interestingly, the *trans*-isomer is lowest in energy at the HF level. This is in agreement with the statement of Madjarova and Yamabe, who obtained a *trans*-distorted form from unspecified cluster calculations at the HF/6-31G* level [36]. Upon consideration of electron correlation, the undistorted *sym* form is preferred in Cioslowski's study [35]. Though less sophisticated with respect to the extrapolation scheme, the hybrid density functional study of Houk et al. at the B3LYP/6-31G* level on the structures of oligoacenes up to [13]acene could not find an indication for the formation of distorted structures [37].

Two additional distortions **D** and **E** were brought into play by Kivelson and Chapman [21] in their 1983 study employing a nearest-neighbor TB approach. This is equivalent to HMO theory used earlier. One of the distorted isomers, **D**, also preserves the symmetry operations that exclude interaction of HOCO and LUCO and thus is not expected to be of interest. But the reflection symmetry of the system is removed in the other isomer **E**, and this in principle allows for the usual (first-order) Peierls distortion. The distorted form **E** was further investigated by Božović using the TB approximation and line group symmetry arguments [38]. His major conclusion was that this distortion of the PAC chain, that is rather unusual and counterintuitive for chemists, should open a gap at the Fermi level that is linear with respect to the size of the distortion. PAC should thus undergo a conventional Peierls distortion to give **E**. However, Kertesz et al. [30] could not obtain any indication for the existence of **E** using the MNDO approximation. On the other hand, these authors cautioned that MNDO theory might not be appropriate for the problem: the bandgap at the MNDO level is not zero to begin with and thus the prerequisite for a Peierls distortion is not given within the framework provided by this theory. It appears that the distorted isomer **E** has not been considered further in the literature.

FINITE BANDGAP WITHOUT STRUCTURAL DISTORTIONS?

The preceding summary of research on the electronic and geometric structure of the PAC polymer is incomplete. The early understanding that in contrast to PA the Peierls instability is only conditional in

PAC has led to a number of investigations that probe other mechanisms that create a gap in this quasi-linear polymer. This work is summarized below, and as it turns out a number of papers already cited in the first section are again of importance here.

In the HF treatment of a system with an even number of electrons a number of constraints can be imposed. The one most often used is the spin-restricted HF (RHF) approximation where electrons of opposite spin are paired in molecular orbitals. The monodeterminantal wavefunction obtained from the self-consistent procedure may or may not correspond to a minimum. In the former case, the wavefunction is stable, while in the latter case it has an instability that is characterized by the constraint that needs to be lifted to obtain a lower energy solution [39,40]. Today, many computer chemistry codes allow the routine investigation of the stability of the HF or Kohn–Sham density functional theory (DFT) solutions by determining the lowest eigenvalues of the stability matrix [39,41].

In 1970, Čížek and Paldus investigated the stability of the HF solutions for oligoacenes within the PPP semiempirical Hamiltonian and derived stability rules for the oligoacenes [42]. They found that acenes having an even number of rings always have singlet-stable symmetry adapted HF solutions [42]. An odd number of rings in the oligoacene, however, allows for the possibility of singlet instabilities since there is no Kekulé structure having D_{2h} symmetry for these molecules. Singlet instabilities are associated with charge density fluctuations, and their existence implies that another nonsymmetry-adapted HF solution can be found that is lower in energy and that is a pure singlet.

If a lower energy solution can be found by releasing the constraint that electrons of opposing spin occupy the same spatial orbital, the RHF wavefunction is said to have a triplet instability. In the spin-unrestricted (UHF) wavefunction, different spatial orbitals are used for each α and β spin. This UHF solution, however, no longer corresponds to a pure spin state as the UHF wavefunction is not an eigenfunction of the total spin-squared operator $\hat{S}^2$. In molecular systems, the appearance of a triplet instability is not uncommon. For example, Dehareng and Dive [40] published a compilation of molecules that have a triplet instability at the HF level and investigated the factors that might contribute to the appearance of the triplet instability. Most important in the context of PAC is their conclusion that all oligoacenes, including benzene, have a triplet instability at the HF level. Further, the reoptimized UHF wavefunction presents an alternant spin density on the atoms involved in π delocalization and thus includes some degree of electron correlation [40]. Typical cases, besides the oligoacenes mentioned above, are 1,3-dipoles that have considerable diradical character [43]. The occurrence of a triplet instability in molecules is commonly considered to be an indication that the single determinant approximation of HF theory is inappropriate for the description of the electronic structure of the molecular system. For molecules with a strong diradical character, a multiconfiguration SCF approach that covers nondynamic correlation usually provides a reasonable starting point for a qualitatively correct description of the electronic structure.

For infinite or very large systems, however, the HF triplet instability implies a real phase transition to a spin-wave distorted ground state [44]. This is produced by the Coulomb repulsion between non-equal spin electrons, and it results in spin-density waves (SDWs). The system then features an antiferromagnetic (AFM) ordering of spin electrons, just as discussed above for the oligoacene molecules. Formation of an SDW produces a gap without the need for BLS. Indeed, it is known that BLS and SDWs are competitive with each other: BLA resists the charge separation between electrons of opposite spin [44].

These ideas were applied to PAC for the first time in 1983 by Baldo et al. [45]. They investigated the oligoacenes with n = 2–5, assuming all equal bonds, and determined the lowest eigenvalue of the stability matrix in the framework of the PPP approximation. From their analysis that applied various values of the resonance integral β and repulsion integrals γ, Baldo et al. concluded that "triplet instability must appear for long enough linear PAC, and thus it is very likely that the PAC polymer has a spin-wave distorted ground state and consequently an electron gap $\Delta \neq 0$" [45]. Using the AMO method and the Hubbard approximation, Baldo et al. [45] arrived at a gap of roughly 1.7 eV for symmetric PAC.

The origin of the triplet instability of the HF solution in the acene series was the subject of an investigation by Mestechkin et al. [46].

In their 1983 study, Kivelson and Chapman also investigated the possibility of other phase transitions than the Peierls distortion to form a gap in PAC with a focus on a superconductivity instability. However, due to the low level of theory the authors could only conclude "that the Peierls and superconducting transition temperatures are equal to each other within a large theoretical uncertainty" [21]. They further studied magnetic ordering. A ferromagnetic or an AFM ground state was considered to be likely if electron–electron repulsions are the dominant interactions.

The hypotheses of Kivelson and Chapman were further probed by Kimura et al. [47]. These authors also concluded that bond alternation is not likely in PAC. Kimura et al. then analyzed the condensed phase of PAC by considering singlet superconducting (SSC), charge density wave (CDW), and SDW instabilities. This allowed giving phase diagrams for the various possible condensed phases depending on interaction parameters. While the SSC state was found to be able to exist over a wide range of parameters, it was concluded that with the most likely set of parameters only the SDW phase can exist [47].

O'Connor and Watts-Tobin used the TB scheme and the Hubbard model in 1988 [48]. The Hubbard model improves upon the TB approximation by considering electron–electron interactions to some extent. This is achieved by including on-site repulsion U that arises from Coulomb interactions between electrons. Within this model, the PAC will distort for $U = 0$, i.e., in the TB approximation, but for $U > 0$, it will undergo a transition from a distorted structure to an undistorted structure with an SDW [48]. This picture of PAC changed when O'Connor and Watts-Tobin [48] considered correlation effects by using an exponential form of the ground-state wavefunction based on a reference function obtained with an effective TB Hamiltonian. A distorted structure with BLA of 0.04 Å and a bandgap of about 0.4 eV was obtained after including correlation. As common for such semiempirical theories, the results depend on the value of U/t, and for smaller values also this correlated model predicts an undistorted structure with an SDW. Employing DMRG within the PPP approximation, the preference of PAC to *cis* distortion was stressed by Raghu et al. in 2002 [33]. On the other hand, an analysis of the symmetric form of PAC in terms of correlation functions gave no indication for the susceptibility of the system to form bond order waves (BOWs), SDWs, or CDWs [33].

RECENT RESULTS IN PAC RESEARCH

The discussion above summarizes the knowledge up to 2002. At that time, an AFM (or SDW) symmetric ground-state structure with a non-zero gap had already been discussed in the literature, but most analyses available preferred Peierls distorted ground states with small or vanishing gaps.

In 2004, Bendikov et al. [16] reported that the oligoacenes have a triplet instability at the hybrid DFT (B3LYP/6-31G*) level of theory from heptacene on. The finding of an spin-unrestricted Kohn–Sham (UKS) solution, sometimes also called broken symmetry solution, is analogous to the earlier observation of Baldo et al. [45] and Dahareng and Dive [40] discussed above for HF-based theories. It is well known today that (hybrid) DFT solutions are more robust with respect to triplet instabilities than HF wavefunctions, and indeed the RB3LYP solutions of shorter oligoacenes were found to be stable by Bendikov et al. [16]. The work by Bendikov et al. changed the view of organic chemists on oligoacenes. The discussion of AFM ordering of spins and formation of SDWs in the ground state of PAC was largely confined to the solid-state community. Even Bendikov et al. did not cite the closely related work by Baldo et al. Organic chemists, who are primarily thinking in molecular terms, concluded from extrapolations of experimental data [49] and from HF and (hybrid) DFT calculations [37] that used the spin-restricted formalism that oligoacenes would prefer high spin (triplet) ground states from nonacene on. Bendikov et al. [16] arrived at singlet ground states for these molecules with an AFM ordering. They explained the energetic preference of the singlet over the triplet state by well-known arguments that were introduced into physical-organic chemistry [18] to explain the ground-state multi-

plicities of organic diradicals. Bendikov et al. [16] obtained two singly occupied nonbonding orbitals from their spin-unrestricted UB3LYP calculations that are localized on either long edge of the oligoacene. Alternatively, the normalized sum and difference of the degenerate orbitals depicted in Fig. 2 for the symmetric form yield two new orbitals that are maximized at either edge (Fig. 3) [24]. These orbitals are disjoint, i.e., they occupy different sets of atoms. In such cases, the exchange integrals are of similar size in the singlet and triplet states, but electron correlation usually prefers the singlet over the triplet state. Hence, diradicals with disjoint orbitals usually have singlet electronic ground states. In analogy to other well-studied organic diradicals, the authors called the oligoacenes diradicals with open-shell singlet ground states [16]. The study proved to be very important as it appears to have initiated further studies on the structure of large oligoacenes and PAC.

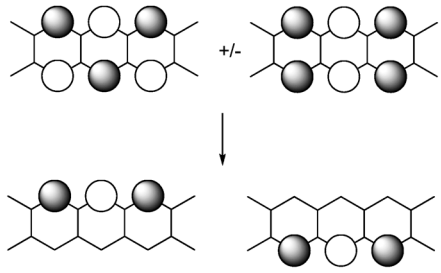


Fig. 3 Linear combination of the degenerate HOCO and LUCO of the symmetric form of PAC gives two degenerate disjoint nonbonding orbitals. Coefficient sizes are not drawn to scale for clarity.

The most sophisticated investigation was reported by Hachmann et al. [50]. This group studied oligoacenes up to dodecacene using complete active space (CASSCF) calculations in the framework of the DMRG algorithm [50]. This allowed the consideration of very large active spaces including all π-electrons in all π-orbitals. The CASSCF calculations were performed using optimized geometries obtained at the UB3LYP/6-31G* level as reported by Bendikov et al. [16]. In agreement with this study, singlet ground states were obtained by Hachmann et al. for the larger oligoacenes, and by extrapolation, also for PAC. Future inclusion of dynamic electron correlation is expected to further stabilize the singlet with respect to the triplet state. The electronic structure was analyzed in terms of the occupation number of the CASSCF natural orbitals obtained with the STO-3G basis set. The larger oligoacenes are best considered as polyradical species having "one unpaired spin with every five to six rings" [50]. The analysis of the electronic structure in terms of correlation functions revealed an AFM ordering: the orbital under investigation has a strong tendency toward single occupation while the neighboring orbitals also show a strong tendency toward single occupation with an AFM coupling. It is noteworthy that there is not an abrupt change in the properties with increasing system size. The AFM correlation increases with the acene length from naphthalene (n = 2) to dodecacene (n = 12). Hachmann et al. analyzed the bonding of the polyradical ground state in the acenes in terms of valence bond theory. They offered the view that the electronic structure may be best considered to arise from a resonance of predominately covalent valence bond structures.

The analysis of Hachmann et al. [50] is supported by more recent investigations. Jiang and Dai [51] have studied the electronic structure of PAC and oligoacenes up to n = 40 using spin-polarized DFT based on plane wave basis sets and the PBE general gradient approximation functional. The PBC calculations of PAC arrive at an undistorted AFM ground state with $R_1 = R_2 = 1.406$ Å and $R_3 = 1.459$ Å. For the finite oligoacenes, the polyradical character was confirmed. A valence-bond study of large oligoacenes up to n = 40 by Qu et al. [52], that utilized the DMRG technique, came to the conclusion that the ground state is of open-shell character or polyradical nature in the terminology of Hachmann et al. [50]. Qu et al. found that the geometries of singlet and triplet states for the larger oligoacenes are

very similar. Furthermore, this group concluded that the spin density distribution along the edge in the triplet state resembles a soliton [52], in agreement with the statements of Bendikov et al. [16]. The singlet can then be considered to have a soliton–antisoliton pair at the edges, and the antiparallel spins result in a stabilizing interaction that makes the singlet state lower in energy than the triplet state [52].

Finally, the study by dos Santos [53] applied PBCs in conjunction with the B3LYP hybrid functional for PAC, but running AFM states is nontrivial with the Gaussian 03 code under PBCs. Therefore, his finding of a *trans*-distorted geometry for PAC and an additional higher-energy metastable symmetric isomer should be taken with some caution. In the investigation of large oligoacenes, dos Santos appears to have not used spin-polarized or spin-unrestricted formalisms. His observation of BLA close to the central rings in oligoacene is in line with the results of Bendikov et al. [16] and Jiang and Dai [51]. These authors found that the transition from a spin-restricted to a spin-unrestricted description results in a reduction of the BLA for the central rings of the oligoacene.

SUMMARY

The theoretical research on the hypothetical polymer PAC has seen various phases. The conditional nature of the Peierls instability was quickly recognized and accepted. In view of the importance of geometrical structures, the chemical community was naturally for a long time focused on the geometric distortion and on the preferred distorted structure of PAC. The solid-state physics community, on the other hand, explored alternative mechanisms, such as superconductivity or magnetic ordering, that create a gap without the need of a geometrical distortion. However, analyses that were based upon Hubbard models including correlation effects or PPP Hamiltonians arrive at distorted geometries with a preference of *cis* configuration.

The most recent investigations employ DFT or even very large-scale CASSCF theory that includes the entire π space for oligoacenes up to $n = 12$. According to these computations, the ground state geometry of PAC should be considered to be symmetric and have an AFM coupling of electrons. A number of authors favor the co-existence of distorted and undistorted regions in PAC, a proposition that is reasonable in view of the similar energies of the competing forms.

In a chemical sense, the ground states of higher oligoacenes (and PAC by extension) may be considered to be polyradicals whose electronic structure can be represented by resonance of predominantly covalent valence bond structures [50]. In this context, it is very interesting that already in 1930 Clar and John [1] described their novel hydrocarbon, now known as pentacene, as a "radical." They did not imply an odd electron compound, but a species current terminology would call a diradical, just as Schlenk's [54] hydrocarbon that was already known at that time. Clar and John concluded from the investigation of the chemical properties of pentacene: "Man muss es wohl … als das beständigste aller bisher dargestellten organischen C-Radikale betrachten" [1].

Although the PAC is far from experimental realization, recent progress in the synthesis of nonacene **6** brings yet larger oligoacenes into reach [55]. This will allow experimental probing of the theoretical predictions.

REFERENCES

1. E. Clar, F. John. *Ber. Dtsch. Chem. Ges. B* **63**, 2967 (1930).
2. (a) E. Clar. *Ber. Dtsch. Chem. Ges. B* **72**, 1817 (1939); (b) C. Marschalk. *Bull. Soc. Chim.* **6**, 1112 (1939).
3. E. Clar. *Chem. Ber.* **75**, 1330 (1942).

"It should be considered to be the most persistent among all organic C-radicals synthesized to date."

4. W. J. Bailey, C.-W. Liao. *J. Am. Chem. Soc.* **77**, 992 (1955).
5. C. Marschalk. *Bull. Soc. Chim.* **10**, 511 (1943).
6. B. Boggiano, E. Clar. *J. Chem. Soc.* 2681 (1957).
7. R. Mondal, B. K. Shah, D. C. Neckers. *J. Am. Chem. Soc.* **128**, 9612 (2006).
8. E. Clar. *Polycyclic Hydrocarbons*, Academic Press, London (1964).
9. C. Tönshoff, H. F. Bettinger. *Angew. Chem., Int. Ed.* (2010). doi:10.1002/anie200906355.
10. L. Salem, H. C. Longuet-Higgins. *Proc. R. Soc. London A* **255**, 435 (1960).
11. M. Bendikov, F. Wudl, D. F. Perepichka. *Chem. Rev.* **104**, 4891 (2004).
12. F. Würthner. *Angew. Chem., Int. Ed.* **40**, 1037 (2001).
13. F. Würthner, R. Schmidt. *ChemPhysChem* **7**, 793 (2006).
14. J. E. Anthony. *Chem. Rev.* **106**, 5028 (2006).
15. J. E. Anthony. *Angew. Chem., Int. Ed.* **47**, 452 (2008).
16. (a) M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, F. Wudl. *J. Am. Chem. Soc.* **126**, 7416 (2004); (b) Erratum: M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, F. Wudl. *J. Am. Chem. Soc*. **126**, 10493 (2004).
17. H. C. Longuet-Higgins, L. Salem. *Proc. R. Soc. London A* **251**, 172 (1959).
18. E. V. Anslyn, D. A. Dougherty. *Modern Physical Organic Chemistry*, University Science Books, Sausalito, CA (2006).
19. R. Hoffmann. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, Wiley-VCH, New York (1988).
20. R. Peierls. *Quantum Theory of Solids*, Oxford University Press, London (1955).
21. S. Kivelson, O. L. Chapman. *Phys. Rev. B* **28**, 7236 (1983).
22. M. R. Boon. *Theor. Chim. Acta (Berl.)* **23**, 109 (1971).
23. M.-H. Whangbo, R. Hoffmann, R. B. Woodward. *Proc. R. Soc. London A* **366**, 23 (1979).
24. J. P. Lowe, S. A. Kafafi, J. P. LaFemina. *J. Phys. Chem.* **90**, 6602 (1986).
25. M. Kertesz, R. Hoffmann. *Solid State Commun.* **47**, 97 (1983).
26. N. N. Tyutyulkov, O. E. Polansky, J. Fabian. *Z. Naturforsch., A: Phys. Sci.* **30**, 1308 (1975).
27. J. L. Brédas, R. R. Chance, R. H. Baughman, R. Silbey. *J. Chem. Phys.* **76**, 3673 (1982).
28. J. Kao, A. C. Lilly. *J. Am. Chem. Soc.* **109**, 4149 (1987).
29. K. Tanaka, K. Ohzeki, S. Nankai, T. Yamabe, H. Shirakawa. *J. Phys. Chem. Solids* **44**, 1069 (1983).
30. M. Kertesz, Y. S. Lee, J. J. P. Stewart. *Int. J. Quant. Chem.* **35**, 305 (1989).
31. J. Chandrasekhar, P. K. Das. *J. Phys. Chem.* **96**, 679 (1992).
32. B. Srinivasan, S. Ramasesha. *Phys. Rev. B* **57**, 8927 (1998).
33. C. Raghu, Y. A. Pati, S. Ramasesha. *Phys. Rev. B* **65**, 155204 (2002).
34. T. A. Niehaus, M. Rohlfing, F. Della Sala, A. Di Carlo, T. Frauenheim. *Phys. Rev. A* **71**, 022508 (2005).
35. J. Cioslowski. *J. Chem. Phys.* **98**, 473 (1993).
36. G. Madjarova, T. Yamabe. *J. Phys. Chem. B* **105**, 2534 (2001).
37. K. N. Houk, P. S. Lee, M. Nendel. *J. Org. Chem.* **66**, 5517 (2001).
38. I. Bozovic. *Phys. Rev. B* **32**, 8136 (1985).
39. R. Seeger, J. A. Pople. *J. Chem. Phys.* **66**, 3045 (1977).
40. D. Dehareng, G. Dive. *J. Comput. Chem.* **21**, 483 (2000).
41. R. Bauernschmitt, R. Ahlrichs. *J. Chem. Phys.* **104**, 9047 (1996).
42. J. Čížek, J. Paldus. *J. Chem. Phys.* **53**, 821 (1970).
43. S. D. Kahn, W. J. Hehre, J. A. Pople. *J. Am. Chem. Soc.* **109**, 1871 (1987).
44. H. Fukutome. *Prog. Theor. Phys.* **40**, 998 (1968).
45. M. Baldo, G. Piccitto, R. Pucci, P. Tomasello. *Phys. Lett. A* **95**, 201 (1983).
46. M. M. Mestechkin, G. E. Vaiman, A. L. Vul'fov. *J. Struct. Chem.* **25**, 164 (1985).

47. M. Kimura, H. Kawabe, K. Nishikawa, S. Aono. *J. Chem. Phys.* **85**, 3090 (1986).
48. M. P. O'Connor, R. J. Watts-Tobin. *J. Phys. C: Solid State Phys.* **21**, 825 (1988).
49. H. Angliker, E. Rommel, J. Wirz. *Chem. Phys. Lett.* **87**, 208 (1982).
50. J. Hachmann, J. J. Dorando, M. Avilés, G. K.-L. Chan. *J. Chem. Phys.* **127**, 134309 (2007).
51. D. Jiang, S. Dai. *J. Phys. Chem. A* **112**, 332 (2008).
52. Z. Qu, D. Zhang, C. Liu, Y. Jiang. *J. Phys. Chem. A* **113**, 7909 (2009).
53. M. C. dos Santos. *Phys. Rev. B* **74**, 045426 (2006).
54. W. Schlenk, M. Brauns. *Ber. Dtsch. Chem. Ges.* **48**, 661 (1915).
55. A persistent, highly substituted nonacene was recently reported: I. Kaur, M. Jazdzyk, N. N. Stein, P. Prusevich, G. P. Miller. *J. Am. Chem. Soc.* **132**, 1261 (2010).

