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Fully Conjugated Heteroatomic Non- and Quasi-Alternant Polyradicals

Sergi Betkhoshvili [1], Jordi Poater [1,2,*], Ibério de P. R. Moreira [3,*] and Josep Maria Bofill [1,*]

[1] Departament de Química Inorgànica i Orgànica & IQTCUB, Universitat de Barcelona, Martí i Franquès 1–11, 08028 Barcelona, Spain; sbetkhbe73@alumnes.ub.edu
[2] ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
[3] Departament de Ciència de Materials i Química Física & IQTCUB, Universitat de Barcelona, Martí i Franquès 1–11, 08028 Barcelona, Spain
* Correspondence: jordi.poater@ub.edu (J.P.); i.moreira@ub.edu (I.d.P.R.M.); jmbofill@ub.edu (J.M.B.)

Abstract: In this work, we present fully π-conjugated diradical(oid)s and tetraradical(oid)s with five-membered non-alternant cyclopentadienyl and quasi-alternant thiophene rings, the latter of which is used as a source of aromatic stabilization. By controlling the topology of the π-systems, we can restrict the lower-bound number of unpaired electrons. Aromaticity and/or antiaromaticity in the different configurations of the compounds can be used to design conjugated compounds with high open-shell characters. We also designed the diradical(oid) based only on the five-membered rings, without any terminal radical groups. This work exemplifies the application of our theory of rational design of polyradicals to heteroatomic and non/quasi-alternant organic systems. The ability to create polyradicals with different classes of organic compounds establishes the possibility of creating multifunctional organic materials with tunable magnetic properties.

Keywords: non-alternant polyradicals; heteroatomic magnetic systems; thiophene-based polyradicals; organic magnetic materials

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1. Introduction

Organic polyradicals with more than two unpaired electrons comprise interesting classes of compounds with applications in molecular and quantum technologies [1–9]. In our recent works, we showed how to make the leap from diradicals to tetraradicals via the topological control of π-conjugation [10], we described a planar and fully π-conjugated tetraradical(oid) [11], and we formulated the theory of the rational design of fully π-conjugated organic polyradicals with any number of unpaired electrons and any ground-state multiplicity. Our method allows for the algorithmic design of polyradicals from the fragments of γ-graphyne, polycyclic aromatic hydrocarbons (PAHs), and any admixture of fully π-conjugated compounds [12]. In biological systems, heteroatomic aromatic compounds and heteroatomic conjugated systems are common and it is interesting to explore how to create polyradicals from similar building blocks. Such chemical classes of compounds are also quite underexplored in the context of magnetic properties. Thus, we designed fully π-conjugated thiophene-based quasi-alternant and non-alternant diradical(oid)s and tetraradical(oid)s with different open-shell characters and a low-energy spectrum as a consequence of the topological control of π-conjugation and following the rules of the rational design of polyradicals, as formulated in our recent publications. Our chemical model requires that the designed polyradicals possess a fully conjugated π-system

(including unpaired electrons), ensuring stabilization through delocalization and aromaticity. Also, each pair of directly π-conjugated unpaired electrons should be bridged by a system possessing aromatic resonance energy equivalent to at least two benzene-like rings, which may be shared among different pairs.

The topological principles through which we analyze the modes of conjugation in the π-systems allowed for the rational design to apply not only to the alternant hydrocarbons for which it is simple to predict the ground state using Ovchinnikov's rule [13], but also to the non-alternant systems which have multiple paths of direct π-conjugation, possibly leading to conflicting spin configurations when following the Coulson–Rushbrooke pairing theorem, also known as the "mirror theorem" [14,15]. Nonetheless, following the application of the topological principles that allowed for the design of polyradicals with any open-shell properties, we can also predict the ground state by analyzing the valence bond forms (VBFs) of the presented compounds and the paths of direct π-conjugations between unpaired electrons that **can lead to on-bond pairing /allow the shell to be closed.** The presented polyradicals contain five-membered rings, such as non-alternant cyclopentadineyl and quasi-alternant thiophene rings, the latter of which has an aromatic configuration that can be used to stabilize the open-shell structure of the designed compound. By employing the topological and resonance factors, we designed the heteroatomic polyradicals, which exemplify how our theory of polyradical creates the possibility of designing heteroatomic polyradicals, which could have important applications in organic magnetic materials and devices.

2. Results and Discussion

Through the application of the theory of the rational design of polyradicals, we designed parallel- and cross-conjugated tetraradical(oid)s, which contain five-membered cyclopentadienyl and thiophene rings. The aromatic stabilization of thiophene and the topology of the π-systems leads to high open-shell characters in the designed compounds, as the results show. The resonance structures of parallel-conjugated thiophenic tetraradical(oid) $\mathbf{PT}_{0,4}$ are shown in Figure 1a and those of cross-conjugated thiophenic tetraradical(oid) $\mathbf{CT}_{2,4}$ are shown in Figure 1b.

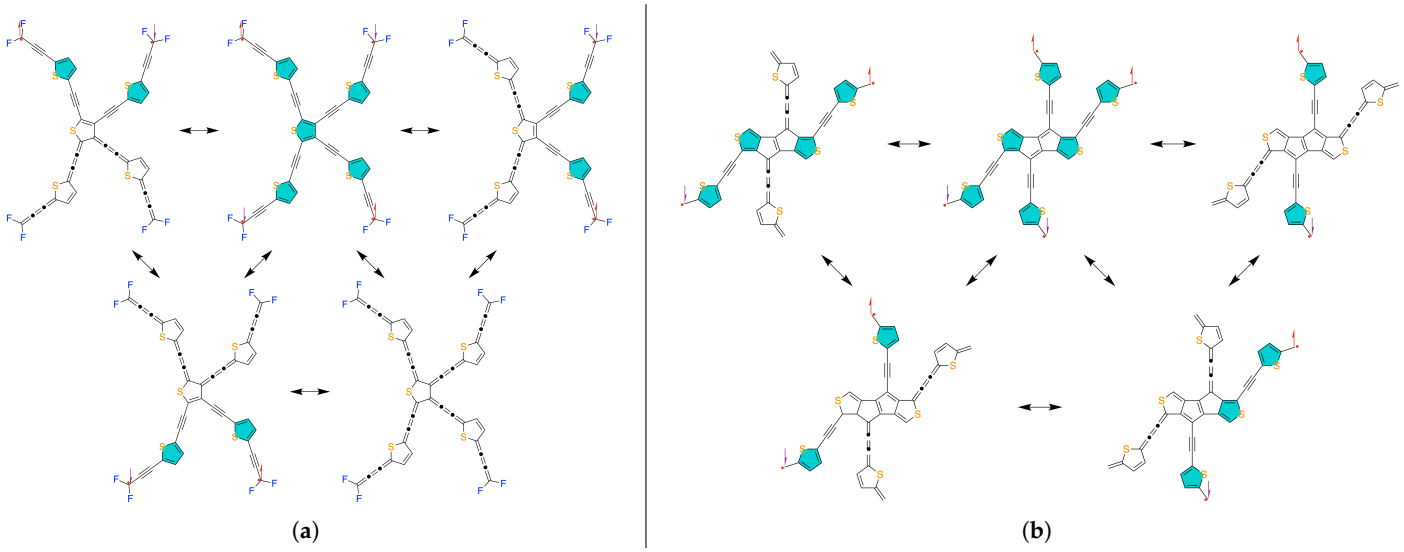
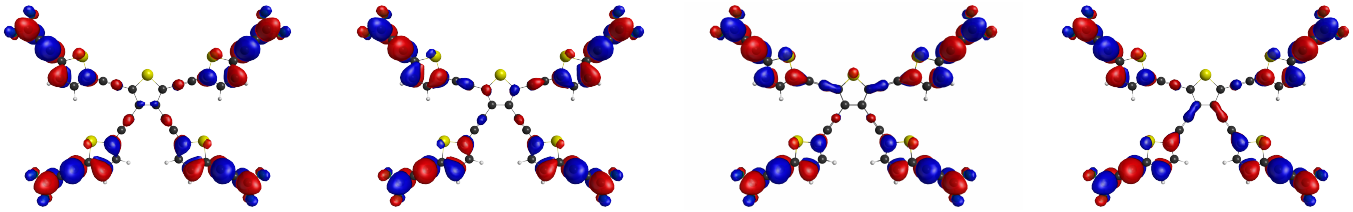


Figure 1. The resonance structures of (**a**) parallel-conjugated quasi-alternant and (**b**) cross-conjugated non-alternant heteroatomic tetraradical(oid)s. The aromatic configuration with six π electrons in the thiophenic ring in each valence bond form is emphasized by the filled color in the corresponding rings.

Upon analysis of the valence bond forms of $\mathbf{PT}_{0,4}$ in Figure 1a, we can note that there is no lower-bound restriction for this compound to have open shells. Nonetheless, in a diradical structure compared to a closed-shell structure, two additional thiophene rings assume an aromatic configuration with six π-electrons. In the tetraradical valence bond form, three more thiophene rings assume an aromatic configuration compared to diradical VBFs (Figure 1a). Our theory of polyradical design says that we need the aromatic resonance energy from at least two-three benzene rings to offset the energy of the broken π bond upon opening the shell, and the aromatic resonance energy of benzene is about 151 kJ/mol while the thiophene's is about 121 kJ/mol [16]. Thus, about 2.5–3.75 thiophene rings are needed to bridge directly π-conjugated unpaired electrons to maintain the high open-shell character. Moreover, as apparent from the resonance structures of $\mathbf{PT}_{0,4}$ in Figure 1a, each unpaired electron is directly π-conjugated to two other unpaired electrons, so that, in some valence bond forms, each such electron could be paired with any of the other directly π-conjugated electrons, closing the corresponding shell. If every unpaired electron becomes paired, the aromatic configuration of all five thiophene rings is lost. This co-dependence between aromaticity and the open-shell character leads to high diradical and tetraradical characters for the $\mathbf{PT}_{0,4}$. We computed the electronic structure of $\mathbf{PT}_{0,4}$ with a complete active space self-consistent field (CASSCF) [17–24] calculations using Dunning's correlation consistent double-ζ basis set [25], which showed that the low-energy spectrum of $\mathbf{PT}_{0,4}$ has a narrow spectral range of 72 cm^{-1}, a singlet ground state (GS) with a quintet highest-energy spin state (HS), and a singlet-triplet gap of 29 cm^{-1}, as shown in Table 1 (more computational details are presented in Section S2 of the Supporting Information). The natural orbitals (NOs) are eigenvectors of the first-order density matrix and their occupation numbers are corresponding eigenvalues [26]. Each of these orbitals shows the electron density distribution of the average number of electrons occupying it. Frontier NOs of $\mathbf{PT}_{0,4}$ with symbolic assignations are presented in Figure 2.



(**a**) (**b**) (**c**) (**d**)

Figure 2. The frontier CASSCF NOs of tetraradical(oid) $\mathbf{PT}_{0,4}$ describing the density distribution of unpaired electrons indicated by NO occupation numbers: (**a**) C_0, (**b**) C_1, (**c**) $C_1^{'}$, and (**d**) C_2.

Table 1. CASSCF(12,12)/cc-pVDZ states of $\mathbf{PT}_{0,4}$ using quintet UKS/DFT-optimized geometry.

State	Symmetry	HONO − 1		HONO		LUNO		LUNO + 1		ΔE from GS (cm^{-1})
S_0	A	$C_1^{'}$	1.050	C_2	1.043	C_0	0.958	C_1	0.948	0.00
T_0	A	L_+	1.037	R_-	1.012	R_+	0.989	L_-	0.962	29.34
T_1	A	C_2	1.024	$C_1^{'}$	1.017	C_0	0.983	C_1	0.975	44.18
S_1	A	L_+	1.018	R_-	1.010	R_+	0.993	L_-	0.979	58.31
T_2	A	R_-	1.011	L_+	1.008	L_-	0.991	R_+	0.990	64.25
Q_0	A	$D_1^{'}$	1.000	D_2	1.000	D_0	1.000	D_1	0.999	72.21

These NOs describe the electron density distribution in the spin states of the low-energy spectrum presented in Table 1. In the symbolic assignation, the analogy with the open-shell orbitals of cyclobutadiene is used with a different number of nodes, selected

according to the orbital phases. Orbital symbols assigned $L_{\pm}$ or $R_{\pm}$ denote the left-hand side or right-hand side of the molecule, with two radical centers with the same phase (+) or the opposite phase (−). The symbolic assignation of distorted orbitals (D) is based on the analogy to cyclobutadiene orbitals. The electron density distribution is not approximately equal in every radical center per orbital, but the overall frontier orbital electron density is the same as that of orbitals C_0 to C_2. As is evident from the frontier NO occupation numbers of $\mathbf{PT}_{0,4}$, even in the singlet ground state, four of the n_{NO} values are very close to 1, which means there are almost four unpaired electrons. Diradical and tetraradical characters, y_0 and y_1, as special cases of polyradical character index y_n, vary from $y_n = 0$ (fully closed shell) to $y_n = 1$ (fully open shell); we calculate them based on their frontier NO occupation number according to the method of Yamaguchi [27]. For $\mathbf{PT}_{0,4}$, the diradical character $y_0 = 0.92$ and tetraradical character $y_1 = 0.90$, implying an almost fully open-shell electronic structure with four unpaired electrons. Even though there is no topological restriction for this compound regarding its open-shell electronic structure, the electrons remain unpaired because the collective aromatic resonance energy of the thiophene rings offsets the energy that would have been gained by π bonding if these electrons paired.

Having characterized the parallel-conjugated tetraradical(oid), let us now focus on the cross-conjugated thiophenic tetraradical(oid) $\mathbf{CT}_{2,4}$, which includes not only thiophene rings but also fused cyclopentadienyl rings so that its five-membered rings are only based on the carbon atom. It is important to emphasize that we cannot create true cross-conjugation with only five-membered heterocyclic aromatic rings (furan, pyrrole, thiophene, etc.), as shown in Figure 1a. This is because paths of direct π-conjugation can diverge in such geometries. However, if we have five-membered rings where each atom is able to form single or double bonds within and outside the ring, we can create geometries where the connected terminal sites have converging paths of direct π-conjugation, which can be used to create the topological restriction on the lower-bound number of unpaired electrons. This property was employed when designing $\mathbf{CT}_{2,4}$, whose resonance structures are shown in Figure 1b. Notably, from these structures, it is evident that closing the shell between the unpaired electrons on the opposite sides of the pentaleno[1,2-c:4,5-c']dithiophene subsystem only destroys the aromatic configuration of two thiophene rings, while any other on-bond pairing destroys at least three. Moreover, regarding the diradical VBFs of the $\mathbf{CT}_{2,4}$, which have an equal number of π bonds, one of them has highest amount (four) of thiophene rings with an aromatic configuration. Thus, by extension of the Clar's rule [28], this should be the most important contributor to diradical VBFs. In contrast, there are no such differences between the diradical valence bond forms of $\mathbf{PT}_{0,4}$. Hence, $\mathbf{CT}_{2,4}$ might have a preferred open-shell subsystem in some of the states, as is evident from the S_0 and T_0 states described by Table 2. This concept allows us to control the tendency of modulation between open-shell characters (diradical, tetraradical, etc.) and the energy gaps between lower-energy states and relatively higher-energy states within the spin spectrum of polyradicals.

The CASSCF results for different spin states and their characteristics based on frontier NOs and occupation numbers are shown in Tables 2 and 3, and CASSCF frontier NOs with symbolic assignations are shown in Figure 3. The orbital symbols refer to the symmetrical cyclobutadiene open-shell orbitals with a number of nodes increasing from 0 to two. The spin-state spectrum for the triplet UKS/DFT and quintet UKS/DFT-optimized geometries (TG and QG, respectively) is presented in Figure 4b. The results show that in the CASSCF(12,12), the singlet ground state obtained for the triplet UKS/DFT-optimized geometry has two unpaired electrons and the two unpaired electrons are found in specific parts of the molecule, as shown by the first resonance structure (top left) in Figure 1b. This is because this resonance structure has the most thiophene rings in the aromatic config-

uration among the diradical VBFs and the triplet UKS/DFT-optimized geometry favors this configuration. However, when energies are sufficiently close (almost the degenerate region of potential energy surface), when the quintet UKS/DFT-optimized geometry is used for CASSCF(12,12) calculations, the singlet ground state has almost four unpaired electrons according to the NO occupation numbers of the S_0 state. The diradical character is $y_0 = 0.98 - 1.00$ and tetraradical character is $y_1 = 0.61$ (for QG). The comparison of these results shows that since $\mathbf{CT}_{2,4}$ is topologically restricted to be diradical, its diradical character is higher than that of $\mathbf{PT}_{0,4}$, which does not have such restrictions. However, since the tetraradical valence bond form of $\mathbf{PT}_{0,4}$ has three more thiophene rings in its aromatic configuration compared to the diradical valence bond forms, while the tetraradical VBF of $\mathbf{CT}_{2,4}$ has only two more thiophene rings in its aromatic configuration compared to one of the diradical VBFs, the tetraradical character of $\mathbf{PT}_{0,4}$ is higher. A comparison of the structure of the low-energy spectra of these tetraradical(oid)s is presented in Figure 4. The detailed CASSCF results for these compounds are provided in Section S3 of the Supporting Information. This is an example of how to control the tendency of modulation among open-shell characters for two, four, and higher numbers of unpaired electrons. The topological control of π-conjugation used in conjunction with the control of aromatic stabilization per each pair of directly π-conjugated unpaired electrons allows for precise control over the open-shell properties of the unsaturated organic compounds.

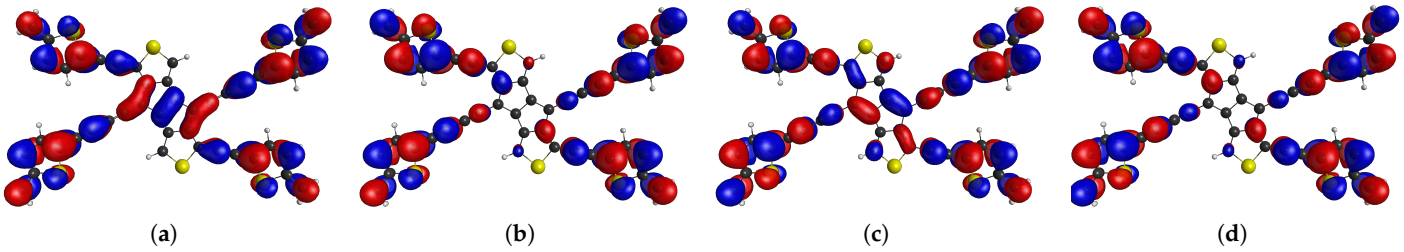


Figure 3. The frontier CASSCF NOs of tetraradical(oid) $\mathbf{CT}_{2,4}$ describing the density distribution of unpaired electrons indicated by NO occupation numbers: (**a**) C_0, (**b**) C_1, (**c**) $C_1^{'}$, and (**d**) C_2.

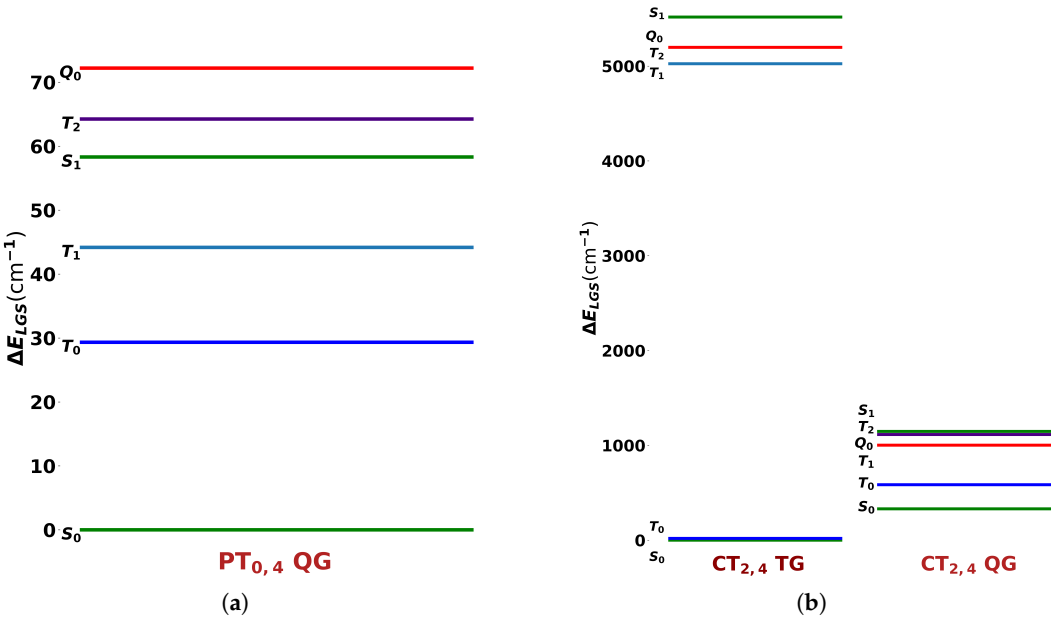


Figure 4. The CASSCF spectra of (**a**) $\mathbf{PT}_{0,4}$ with quintet-optimized geometry (QG) and (**b**) $\mathbf{CT}_{2,4}$ with triplet-optimized geometry (TG) and QG.

Table 2. CASSCF(12,12)/cc-pVDZ states of $\mathbf{CT}_{2,4}$ using triplet UKS/DFT-optimized geometry.

State	Symmetry	HONO − 1		HONO		LUNO		LUNO + 1		ΔE from GS (cm^{-1})
S_0	A_g	N	1.848	L_+*	1.012	L_-*	0.990	N	0.160	0.00
T_0	B_u	N	1.852	L_+*	1.001	L_-*	1.001	N	0.157	18.84
T_1	A_g	C_0	1.097	C_1	1.075	C_2	0.934	C_1'	0.898	5197.44
T_2	B_u	C_0	1.017	C_1	1.000	C_2	1.000	C_1'	0.985	5197.44
Q_0	A_g	C_0	1.017	C_1	1.000	C_2	1.000	C_1'	0.985	5197.44
S_1	A_g	C_0	1.025	C_1	1.012	C_2	1.011	C_1'	0.954	5517.36

* These orbital symbols mean the unpaired electrons are in the **long (L)** chain corresponding to the first resonance structure (top left) in Figure 1b.

Table 3. CASSCF(12,12)/cc-pVDZ states of $\mathbf{CT}_{2,4}$ using quintet UKS/DFT-optimized geometry.

State	Symmetry	HONO − 1		HONO		LUNO		LUNO + 1		ΔE from GS (cm^{-1})
S_0	A_g	C_0	1.202	C_2	1.002	C_1	0.999	C_1'	0.799	0.00
T_0	B_u	C_0	1.129	C_2	1.000	C_1	1.000	C_1'	0.872	254.64
T_1	B_u	C_0	1.006	C_1	1.000	C_2	1.000	C_1'	0.995	671.30
Q_0	A_g	C_0	1.006	C_1	1.000	C_2	1.000	C_1'	0.995	671.33
T_2	A_g	N/A *								
S_1	A_g	C_0	1.025	C_1	1.012	C_2	1.011	C_1'	0.954	817.11

* This CASSCF state did not converge for the quintet UKS/DFT-optimized geometry, but is available in CASSCF(12,12) results using the triplet UKS/DFT-optimized geometry presented in Table 2.

We also designed the diradical compound $\mathbf{TD}_{0,2}$ which contains only five-membered rings and no terminal methylene groups, as shown in Figure 5a, in which the cumulative aromaticity of the thiophene rings results in a high open-shell character, as verified by CASSCF(14,14)/cc-pVDZ calculations. Specifically, there is a diradical character y_0 = 0.95–0.97, with a singlet-triplet gap of ΔE_{S-T} = 5–12 cm^{-1}. This system is non-alternant, but due to the symmetry between the paths of direct π-conjugation and antiferromagnetic coupling, the singlet ground-state multiplicity can predicted.

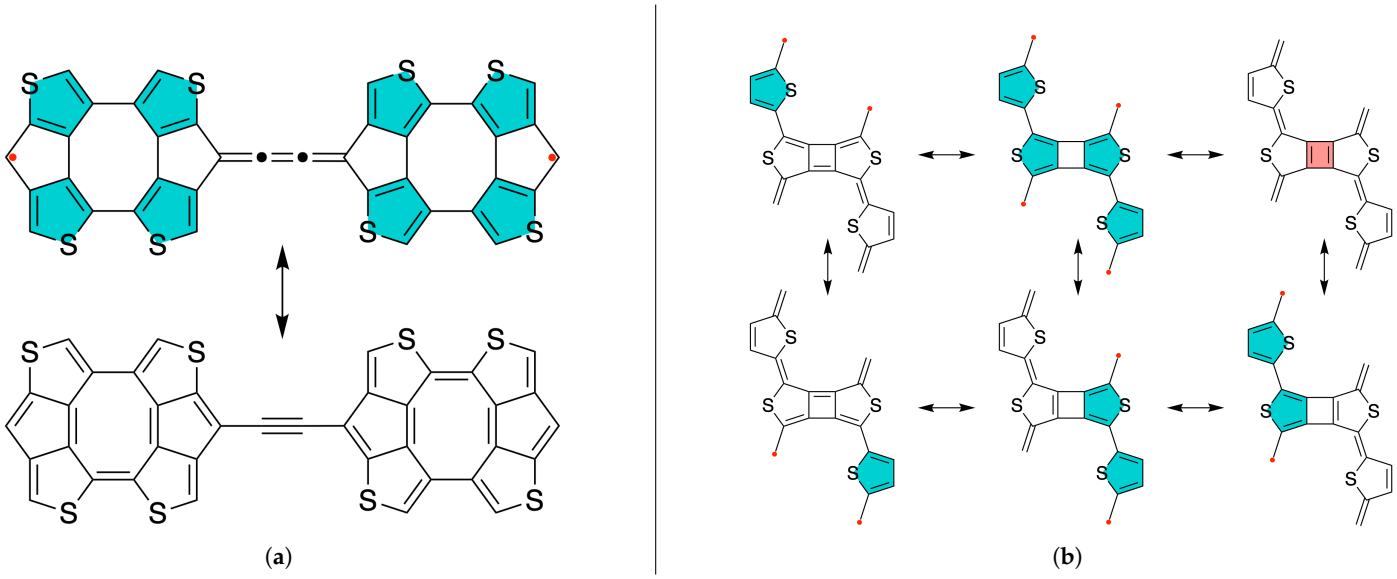


Figure 5. The resonance structures of (**a**) diradical $\mathbf{TD}_{0,2}$ and (**b**) cross-conjugated non-alternant heteroatomic tetraradical(oid) $_{0',4}$. The aromatic configuration with six π electrons in the thiophenic ring in each valence bond form is emphasized by the green fill in the corresponding rings. The antiaromatic configuration with four π electrons is shown in red.

In addition to taking advantage of aromaticity and topological restrictions to design compounds with high open-shell characters, we can also take partial or full advantage of antiaromaticity. In principle, any effect in the compound which stabilizes or destabilizes particular configurations can be used to control some of the properties of the compounds. If we are using aromaticity to stabilize open-shell configurations of the compounds, we can use the analogical strategy and use antiaromaticity to destabilize the closed-shell configurations and, in this manner, design compounds with a strong open-shell character. To exemplify this concept, we designed tetraradical(oid) $\mathbf{TR}_{0',4}$, which is expected to have a significantly stronger diradical character than tetraradical character, because two thiophene aromatic rings are not always sufficient to promote a very strong ($\geq$0.7) open-shell character, but the additional effect of antiaromaticity in closed-shell VBF compared to diradical VBF with two thiophene rings in the aromatic configuration provides a greater difference than diradical VBF compared to tetraradical VBF with four thiophene rings in the aromatic configuration. Hence, the additional difference due to the antiaromaticity of the cyclobutadiene creates a stronger diradical character than tetraradical character, even though each open shell is stabilized by two thiophene rings in an aromatic configuration according to the resonance structures in Figure 5b. As a consequence, the diradical character of this compound is $y_0 = 0.34 - 0.49$ and its tetraradical character is $y_1 = 0.013 - 0.058$, According to the CASSCF NO occupation numbers of the singlet ground state (S_0) determined by CASSCF(12,12)/cc-pVDZ calculations for triplet and quintet UKS/DFT-optimized geometries. The detailed CASSCF results for $\mathbf{TD}_{0,2}$ and $\mathbf{TR}_{0',4}$ are presented in Section S3 of the Supporting Information.

The CASSCF frontier NOs of these compounds are shown in Figure 6 and they clearly show the presence of unpaired electrons. The higher diradical character of $\mathbf{TD}_{0,2}$ compared to $\mathbf{TR}_{0',4}$ can be explained by the greater difference in $\mathbf{TD}_{0,2}$ in terms of the number of thiophenic rings in an aromatic configuration in diradical VBF compared to closed-shell VBF to offset the energy of the broken π bond that leads to unpaired electrons [29].

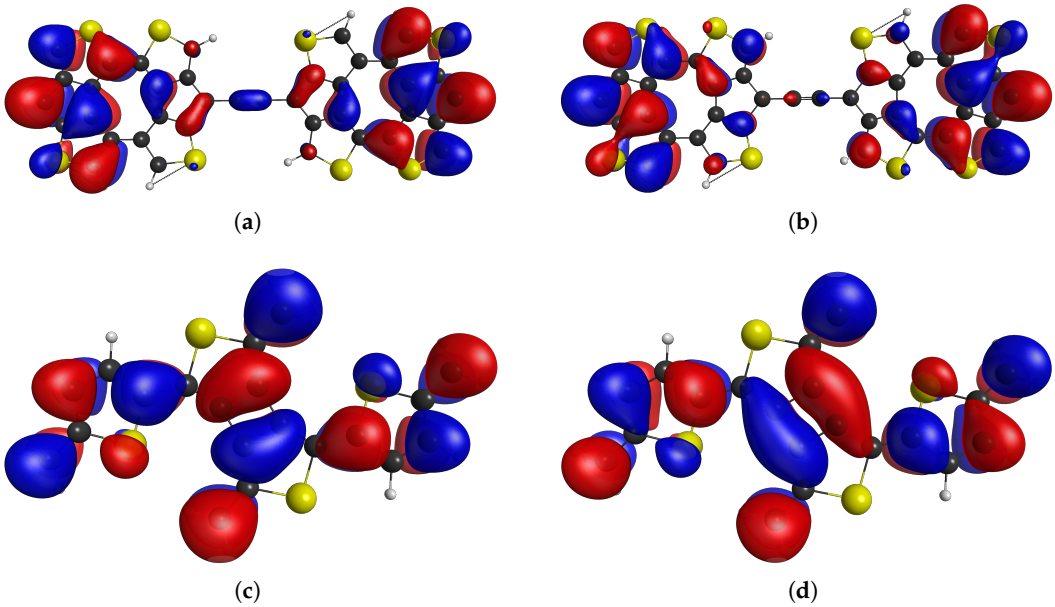


Figure 6. The CASSCF NOs of $\mathbf{TD}_{0,2}$ (**a**,**b**) and $\mathbf{TR}_{0',4}$ (**c**,**d**).

We can also use only the topological restriction and antiaromaticity in order to induce an open-shell character. Usually, compounds with antiaromatic parts that possess an open-shell character obtained this purely by virtue of having 4n π electrons in the cycle, which destabilizes the electronic structure according to Hückel's rule. However, we are using the principle that, in the ground electronic state, the molecule will assume the electronic

configuration which, if possible, avoids an antiaromatic configuration provided that the assumed electronic configuration is not more destabilizing than the antiaromaticity itself. This can be achieved using the system with an antiaromatic core that is fully conjugated to the rest of the π-system of the molecule. One example of such a compound, denoted $\mathbf{AP}_{2,2}$, is presented in Figure 7a. Notably, one can draw the fully closed-shell configuration of this molecule and by superficial analysis may incorrectly predict that the ground-state electronic configuration is closed-shell. However, according to the analysis of the VBFs, in an apparently closed-shell configuration, the pentalene core has 4n π electrons (8 π electrons), which, according to Hückel's rule, is antiaromatic. In such cases, within the cycle, the bonding on the last shell does not lower the energy of the system. Hence, the total binding energy of the π-system is less than it would be if there were localized π-bonds. In such case, repulsion between electrons is still present but there is no significantly stabilizing bonding interaction to compensate for this. Hence, this π-subsystem prefers to assume a non-aromatic configuration. Nonetheless, due to being bonded and fully π-conjugated to the rest of the molecule, this non-aromatic configuration of the pentalene core happens to be incompatible with the fully closed-shell configuration of the molecule. Hence, in order to avoid an antiaromatic core and minimize the electron–electron repulsion, the compound assumed a delocalized diradical configuration with a triplet ground state and close-lying singlet diradical state with two singly occupied natural orbitals, as shown in the Figure 7b. This distribution corresponds to the resonance structures shown in Figure 7a, which have the most π bonds (in this case, 15 π bonds) and no antiaromatic pentalene core. The calculated diradical character is $y_0 = 1.00$, with a triplet ground state and singlet-triplet gap of $\Delta E_{S-T} = -2050$ cm^{-1} (-5.85 kcal/mol).

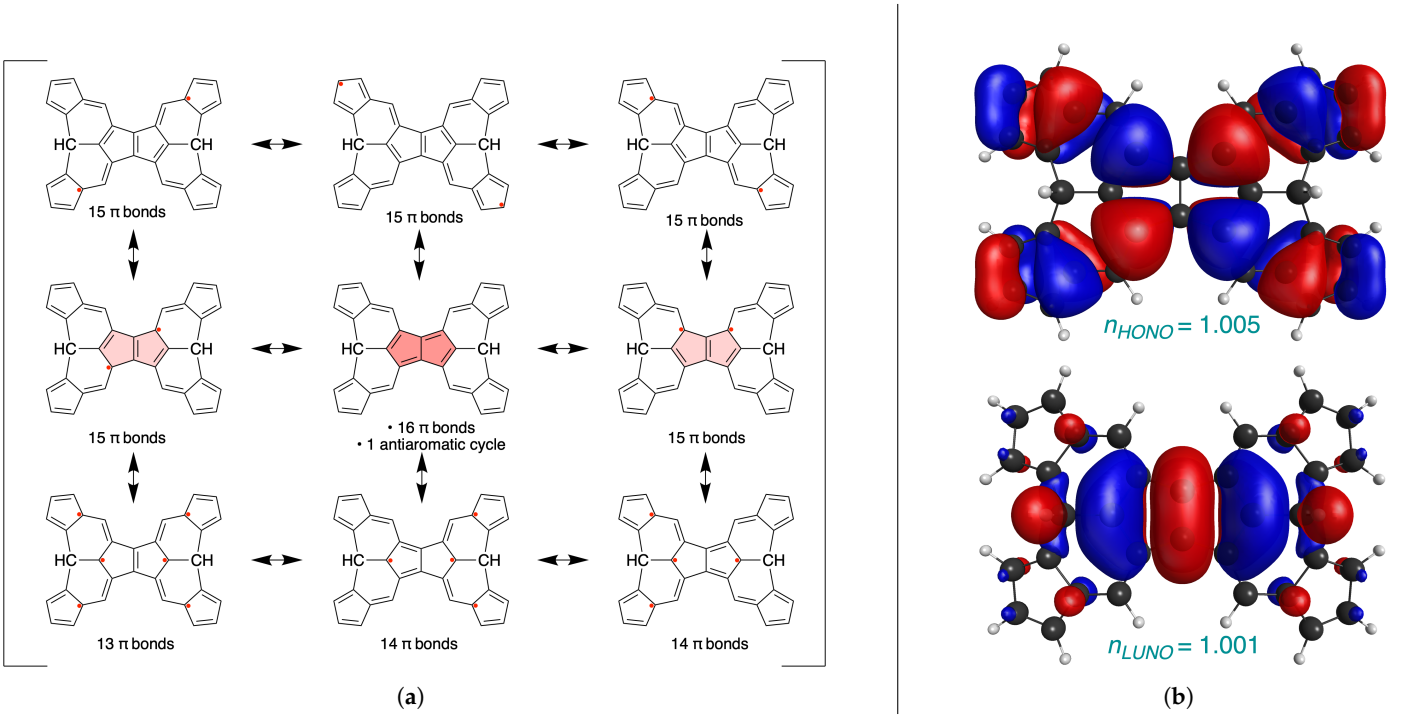


Figure 7. The resonance structures (**a**) and CASSCF(10,10)/cc-pVDZ triplet ground-state frontier natural orbitals with occupation numbers (**b**) of pentalene-containing diradical $\mathbf{AP}_{2,2}$. The antiaromatic configuration of pentalene is emphasized in brighter red.

Since we established the rules used to control the open-shell characters using aromaticity, antiaromaticity, and the topological control of π-conjugation, as well as the structure of the spin spectrum of the compounds, we can now create polyradicals with heteroatomic aromatic rings, and envisage multifunctional molecular materials with cross-dependent

effects between the magnetic response (diamagnetism versus ordered magnetism) and externally oriented electric field or mechanical stress.

3. Conclusions

In this work, we designed diradical(oid)s and tetraradical(oid)s with different geometries and topologies in the π-systems and, by taking advantage of their cross-conjugation, aromaticity and antiaromaticity, we were able to create compounds with moderate to high diradical and tetraradical characters. This study is an extension of our theory of the rational design of polyradicals and applies the rules of this theory in the context of quasi-alternant and non-alternant systems. We can thus conclude that the design rules in our theory are able to create polyradicals from the presented class of compounds. The idea is that any π-(sub)system that can assume different configurations can be used for bridging directly π-conjugated unpaired electrons. If there is a sufficient difference in the energies of these configurations (i.e., if the resonance energy is sufficient), we can expect that the electronic structure outside of this π-(sub)system will assume a configuration which is compatible with the more stable configuration of the π-(sub)system. This notion, along with the other rules of our theory, can serve as a guidebook for rationally designing polyradicals with any number of unpaired electrons and any ground-state multiplicity from different classes of organic compounds, which can lead to the development of multifunctional organic materials.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemistry7020045/s1, Introduction to the polyradicals with five-membered rings (Section S1); Methods and computational details (Section S2); CASSCF calculated results (Section S3); and Optimized geometries (Section S4) [30–41].

Author Contributions: Design: S.B. and J.M.B.; Computations: S.B.; Writing and editing: all authors. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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