Didehydrophenanthrenes: Structure, Singlet–Triplet Splitting, and Aromaticity

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In this work, we explore the geometries, relative stabilities, singlet–triplet (S–T) splittings, and local aromaticities of the 25 possible didehydrophenanthrenes (DDPs) at the BLYP/6-31G(d) level. The main aim is to understand their molecular structure and stability in terms of the electronic structure. To this end, we analyze the changes induced by didehydrogenation in molecular structure and local aromaticity and we investigate the coupling strength between radical centers in DDPs through the evaluation of S–T splittings. Further evidence for the repulsive character of the H–H interactions in phenanthrene’s bay region is gained from the relative energies of the triplet states of the different DDPs.

1. Introduction

There have been over the last century many studies relating to didehydroarenes (“arynes”) and their derivatives (for different reviews, see refs 1–3). The current renewed interest in these species comes mainly from the discovery that the biological activity of calicheamicin and related antitumor drugs4 is triggered by Bergman cyclization5 of an enediyne moiety that yields a p-benzyne derivative (see Scheme 1). Subsequent hydrogen abstraction from a sugar group in each strand of a double helix of DNA results in irreversible DNA damage and eventually to cell death. Moreover, arynes are also of interest because they are components of asphaltene aggregates.6 These aggregates are formed during oil extraction and may eventually lead to pipeline obstruction.7

Understanding the factors that control the reactivity of didehydroaranes is fundamental to improve the properties of current antitumor agents and to design procedures to avoid the formation of asphaltene aggregates. Despite the loss of two H atoms, the interaction between radical lobes makes didehydroaranes, in general, less reactive than monohydroaranes.8,9,10 The magnitude of the singlet–triplet (S–T) energy splitting, which reflects the degree to which spins at the dehydrocarbon atoms interact with one another,11 is a good indicator of the reactivity of these species. It has been found that there is a good correlation between the reactivity of singlet-state biradicals and the magnitude of the S–T energy splittings.8,9,12 In general, the reactivity of didehydroaranes increases as the biradical character increases, i.e., the singlet–triplet splitting decreases. The larger the S–T gap for a singlet ground state, the larger the interaction between the two radical lobes, the smaller the biradical character of the system, and, consequently, the smaller the reactivity of the arylene species. Thus, arynes are particularly stable when they have a closed-shell ground state structure with small biradical character, whereas active arylene antitumor agents show usually small S–T energy gaps and high biradical character.

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Scheme 1: Bergman Cyclization in Calicheamicin

The coupling between spins at the dehydrocarbon atoms takes place through-space when there is a large overlap between the two radical lobes like in o-benzyne or through-bond when there are appropriate unfilled σ* orbitals in the adjacent bonds that contribute to the hybrid biradical MO as in p-benzyne.11,13 The extent to which the two dehydro centers interact depends upon the separation distance, the relative orientation of the orbitals at the dehydro positions, and the number and orientation of the σ bonds that separate the two radical centers.11,13 Therefore, one can eventually fine-tune the reactivity of antitumor drugs by modifying the molecular structure of the p-benzyne derivative formed to get the desired S–T splitting. Although S–T splittings can be measured experimentally using gas-phase negative ion photoelectron spectroscopy (NIPES) techniques,14 quantum chemical computations turn out to be very helpful for providing access to such quantities. Indeed, in the quest for a better understanding of the effects that influence S–T splittings, a number of arylene derivatives have been...
TABLE 1: Experimental and Theoretical $\Delta E_{S-T}$ Energy Splittings (kcal/mol) for the Three Benzyne Species

<table>
<thead>
<tr>
<th>species</th>
<th>BLYP/6-31G(d)</th>
<th>BLYP/cc-pVTZ</th>
<th>B3LYP/6-31G(d)</th>
<th>CASPT2/cc-pVDZ$^a$</th>
<th>extpt</th>
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<tr>
<td>$\sigma$-benzyne</td>
<td>33.9</td>
<td>36.1</td>
<td>29.5</td>
<td>30.4</td>
<td>37.5 ± 0.3$^a$</td>
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<tr>
<td>$\mu$-benzyne</td>
<td>19.7</td>
<td>19.7</td>
<td>14.2</td>
<td>18.0</td>
<td>21.0 ± 0.3$^a$</td>
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<tr>
<td>$\rho$-benzyne</td>
<td>4.1$^b$</td>
<td>4.5$^b$</td>
<td>2.5$^c$</td>
<td>5.8</td>
<td>3.8 ± 0.5$^c$, 2.1 ± 0.4$^d$</td>
</tr>
</tbody>
</table>

$^a$ $\langle S^2 \rangle = 0.803$. Application of the sum rule leads to $\Delta E_{S-T} = 9.5$ kcal/mol$^{-1}$. $^b$ $\langle S^2 \rangle = 0.767$. Application of the sum rule leads to $\Delta E_{S-T} = 10.5$ kcal/mol$^{-1}$. $^c$ $\langle S^2 \rangle = 0.951$. Application of the sum rule leads to $\Delta E_{S-T} = 5.4$ kcal/mol$^{-1}$. $^d$ Reference 20. $^e$ Values at 298 K.$^{14}$ $^f$ Alternative value at 298 K.$^{14}$

Theoretically studied, such as didehydrobenzenes$^{10,13,15-21}$, didehydronaphtalenes$^{11,13,20}$, didehydroanthracenes$^{9}$, didehydrobiphenyls$^{13}$, didehydrophenylenes$^{22}$, didehydropropynes$^{22-24}$, didehydrotoluenes$^{25}$, didehydrobenzothiophenes$^{26}$, didehydrohydroxytoluenes$^{27}$, didehydropyridines$^{12,28}$, didehydrobenzoxoquinones$^{29}$, didehydrocubanes$^{30}$, didehydrohetero-substituted pentalenes$^{31}$, cyclooctatetraenes$^{31}$, and others$^{13,32}$.

To our knowledge there is only one previous theoretical study of phenanthyrenes that analyzes exclusively the 4,5-didehydrophenanthrene isomer using the extended Hückel method.$^{13}$ In this work, we have analyzed the molecular structure, stability, $S-T$ splittings, and local aromaticity of the 25 isomeric didehydrophenanthrenes (DDP) with three main goals: first, to analyze the molecular structure and stability of all possible phenanthyrenes; second, to compute their $\Delta E_{S-T}$ splittings that will provide a first indication of their reactivity; third, to compare the local aromaticity of phenanthyrenes with that of phenanthrene, to see whether there is a relationship between the nature of the phenanthrene formed and the increase or decrease of local aromaticity. To date this kind of analysis has been performed only in benzenes$^{16}$ and it has been found that the aromaticity rises when the distance between the diradical centers increases.

2. Computational Details

Full geometry optimizations have been carried out with the BLYP pure density functional$^{33,34}$ by means of the Gaussian 03 program$^{35}$ using the 6-31G(d) basis set.$^{36}$ For the analysis of benzenes, the Dunning’s correlation consistent augmented triple-$\zeta$ (cc-pVTZ) basis set$^{37}$ and the B3LYP method$^{34,38}$ have been also used. For all biradicals, we have computed the lowest lying closed-shell and open-shell singlet states as well as the lowest lying triplet state. For open-shell states, the geometry optimizations were performed within the unrestricted methodology, while for the closed-shell singlet states the restricted formalism was used. Theoretical treatment of singlet biradical species requires multiconfigurational or multireference methods due to strong static electron correlation. Unfortunately, however, these methods can only be applied to relatively small systems because they are extremely computationally demanding. As an alternative, we have used the unrestricted UB3LYP method in broken symmetry (BS, using GUESS = MIX)$^{39}$ This method improves the modeling of singlet biradical states at the expense of introducing some spin contamination from unwanted states of higher spin$^{19,21,29,32,40,41}$. Although this is not the most appropriate method to treat singlet biradical species, it has been shown that it can be used provided that the overlap between the open-shell orbitals is small (the unpaired electrons are located in separated atomic centers), as happens in most of the systems that show predominant biradical character studied in this work.$^{41}$ In addition, experience shows that this method provides a good combination of accuracy and efficiency especially considering the reduced computational effort needed in comparison with more elaborate calculations. In particular, previous authors have shown that pure density functionals like BLYP yield excellent geometries performing even better than the CASSCF method$^{19,25,29,31}$ as well as good energy differences that are improved as compared to those given by hybrid density functionals such as B3LYP.$^{15,25,42}$ According to some reports, BLYP and the 6-31G(d) are the functional$^{15}$ and the basis set$^{43}$ of choice for aromatic biradicals. Moreover, we have checked that as compared to experimental and high-level ab initio calculations, the BLYP/6-31G(d) method provides a good estimation of $\Delta E_{S-T}$ splittings in benzenes (see Table 1). Experimentally, benzyne species have singlet ground states, closed-shell for the $\sigma$- and $m$-benzenes and open-shell for $p$-benzyne. All methods agree with this experimental result as well as with the experimental order of stability,$^{14}$ namely, $\sigma$-benzyne > $m$-benzyne > $p$-benzyne. As can be seen in Table 1, the BLYP/6-31G(d) $\Delta E_{S-T}$ splittings are similar to those given by the BLYP/cc-pVTZ method and have smaller errors than those of the B3LYP/6-31G(d) values. This confirms that hybrid functionals are less appropriate than pure functionals for the study of $\Delta E_{S-T}$ splittings in open-shell singlet species. For $p$-benzyne, the application of the sum rule$^{44}$ to the energy of the biradical singlet state to remove the spin contamination error using the expression $E_S = 2E_{BS} - E_T$ (with $E_T$ computed at the geometry of the BS biradical singlet state) does not improve the results but rather leads to $\Delta E_{S-T}$ splittings with larger errors. In this line, some authors have shown that introduction of spin corrections into UB3LYP data completely breaks down the accord of the B3LYP and multireference ab initio methods.$^{45}$ For these reasons, throughout this paper, all $\Delta E_{S-T}$ splittings have been calculated without spin contamination corrections.

The evaluation of aromaticity has been performed using the NICS index, proposed by Schleyer and co-workers.$^{46}$ The NICS index is a magnetic measure of aromaticity which is based on the $\pi$-electron ring current that is induced when the system is exposed to external magnetic fields. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS value, the more aromatic the ring. The GIAO method$^{47}$ has been used to perform calculations of NICS at 1 Å above or below the center of the ring (determined by the nonweighted mean of the heavy atoms coordinates) taken into analysis (NICS(1)). It has been postulated that NICS(1) better reflects aromaticity patterns because at 1 Å the effects of the $\pi$-electron ring current are dominant and local $\sigma$-bonding contributions are diminished.$^{48}$ Finally, following the recommendation of using more than a single parameter to evaluate aromaticity,$^{49}$ for selected rings we have also computed the para-delocalization (PDI)$^{50}$ and the six-center (SCI) indices,$^{31}$ which are based on the electron delocalization properties of aromatic species.

3. Results and Discussion

The 25 possible DDPs derive from double H abstraction in phenanthrene (see Scheme 2). Figure 1 gives the BLYP/6-31G(d) optimized and X-ray molecular structure for phenanthrene
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in its singlet ground state. The BLYP/6-31G(d) and experimental (in parentheses) bond lengths (in Å) of phenanthrene are depicted in Figure 2. For the 25 DDPs, the ground state for all four DDPs, the less interacting o-BDDPs, the almost uncoupled o-BDDPs, and the highly coupled o-BDDPs, namely, 1,2-, 2,3-, 3,4-, and 9,10-DDPs, is depicted in Figure 2. For the 25 DDPs, the order of stability of the triplet states in o-benzene-like DDPs is 3,4-DDP > 2,3-DDP > 1,2-DDP > 9,10-DDP. Except for 3,4-DDP, the order of stability follows the expected order of \( C=C \) bond lengths; i.e., the larger the \( C=C \) bond lengths, the lower the exchange repulsion associated with the proximity of the two parallel spins, and the larger the stability of the triplet state. Again, the larger stability of the 3,4-DDP in its triplet state cannot be explained by the C3–C4 bond length and it obviously comes from the removal of the H⋯H repulsive interaction in the bay region of phenanthrene.

In the four o-benzene-like DDPs, the singlet ground state is substantially lower than the triplet state. The large \( \Delta E_{S\rightarrow T} \) splittings (from 32.0 to 38.1 kcal-mol\(^{-1}\)) indicate an important coupling between the two radical centers in o-benzene-like DDPs. The largest singlet–triplet gap is found in the 9,10-DDP. This can again be ascribed to the fact that the C9–C10 bond was already the shortest C–C bond in the phenanthrene parent molecule, which increases the stability of the singlet and.

result is identical for restricted and unrestricted calculations, and therefore, its wave function is spin-unrestricted stable. Through-bond interaction between the two didehydrocarbons drastically reduces the bond length connecting them to 1.25–1.26 Å, not far from the C–C bond length in ethyne (1.215 Å at the BLYP/6-31G(d) level). As compared to the values in phenanthrene, the \( C=C \) distance is reduced by 0.13–0.15 Å. The value of these bond lengths and the corresponding Mayer bond orders (Table 2) in phenanthrene and \( \alpha,\beta \)-DDPs indicate the partial formation of a triple bond in the latter.

In line with previous findings for benzynes\(^{14,21}\) and naphthalynes,\(^{11}\) o-benzene-like DDPs in their closed-shell singlet ground state are the most stable DDPs. The preference for the singlet state in the 3,4-DDP and 9,10-DDP is about 2.5 and 4.5 kcal-mol\(^{-1}\) larger than the corresponding preference in 1,2-DDP and 2,3-DDP, respectively. As noted previously for naphthalynes,\(^{11}\) the particular stabilization of the 9,10-DDP derives from the bond length alternation found in the original phenanthrene system. In phenanthrene (Figure 1), the 9,10-bond is already shorter than the 1,2- and 2,3-bonds, and therefore, the cost of deformation for the formation of the partial triple bond is smaller in the former than the two latter.\(^{11}\) The stabilization of the 3,4-DDP has a different origin. It derives from the fact that the bay H4 atom suffers a large steric repulsion in phenanthrene and, as a consequence, hydrogen abstraction becomes particularly favorable in this position.\(^{54}\) Proceeding from the fact that the C1–C2 and C3–C4 bond lengths are quite similar (Figure 1), one would expect similar energies for the closed-shell singlet 1,2- and 3,4-DDPs. However, because of the steric repulsion between bay hydrogens, the singlet 3,4-DDP becomes the most stable DDP species. This is an additional proof of the existence of H⋯H repulsions\(^{54,55}\) between the bay H atoms of phenanthrene and not H⋯H bonding as recently claimed in a recent AIM study\(^{56}\) on the basis of the presence of a bond critical point connecting these two H atoms and the lower atomic energy of these bay H atoms as compared to the rest of the H atoms in phenanthrene.

There are two aspects that differentiate singlet and triplet states of o-benzene-like DDPs. First, from a geometrical point of view, the geometry of the triplet states is almost the same as the original geometry of phenanthrene; i.e., double H atom abstraction to yield the triplet diradical has a small influence on the molecular structure of phenanthrene. Second, the energies of all triplet states of o-benzene like DDPs are similar, the largest difference being 2.5 kcal-mol\(^{-1}\) between 3,4- and 9,10-DDPs. The order of stability of the triplet states in o-benzene like DDPs is 3,4-DDP > 2,3-DDP > 1,2-DDP > 9,10-DDP. Except for 3,4-DDP, the order of stability follows the expected order of \( C=C \) bond lengths; i.e., the larger the \( C=C \) bond lengths, the longer the separation between same spin radical centers, the lower the exchange repulsion associated with the proximity of the two parallel spins, and the larger the stability of the triplet state. Again, the larger stability of the 3,4-DDP in its triplet state cannot be explained by the C3–C4 bond length and it obviously comes from the removal of the H⋯H repulsive interaction in the bay region of phenanthrene.

In the four o-benzene-like DDPs, the singlet ground state is substantially lower than the triplet state. The large \( \Delta E_{S\rightarrow T} \) splittings (from 32.0 to 38.1 kcal-mol\(^{-1}\)) indicate an important coupling between the two radical centers in o-benzene-like DDPs.\(^{11}\) The largest singlet–triplet gap is found in the 9,10-DDP. This can again be ascribed to the fact that the C9–C10 bond was already the shortest C–C bond in the phenanthrene parent molecule, which increases the stability of the singlet and.
reduces that of the triplet, leading to a large $\Delta E_{S-T}$ splitting. Another way of viewing this is that the additional bond that occurs after elimination of $H_2$ is strongest in the singlet $\pi,10-$DDP.

The aromaticity of the central ring in the reference system phenanthrene is smaller than that of the outer rings, as indicated by the NICS(1) values gathered in Table 3. In the order from phenanthrene to the singlet $R,\pi-$DPPs, there is an increase of aromaticity according to NICS(1) values in the ring bearing the two dehydrocarbon atoms, while the aromaticity of the other rings remains more or less unchanged. The same increase indicated by NICS was already observed in $o$-benzene as compared to benzene. It is worth noting that the reduction of NICS values may be attributed, in part, to the increase in the number of $\pi$-electrons in the ring with benzyne-like character that leads to more intense ring currents and, consequently, to a more negative NICS. To further support the increase of aromaticity indicated by NICS in the benzyne ring of $o$-benzyne like DDPs, we have computed two additional indices: the para-delocalization index (PDI) and the six-center index (SCI). We have found that, according to these indices, the aromaticity in the benzyne ring increases from 0.081 (PDI) and 0.049 (SCI) in phenanthrene to 0.102 and 0.051 in 1,2-DDP, 0.110 and 0.054 in 2,3-DDP, and 0.102 and 0.050 in 3,4-DDP (values not listed in Table 3). In 9,10-DDP, PDI (0.066) and SCI (0.100) also show an increase of aromaticity of the central ring with respect to phenanthrene (0.047 and 0.020, respectively).

Figure 2. BLYP/6-31G(d) bond lengths (in Å) for the singlet and triplet (in italics) states of $\alpha,\pi-$, $\alpha,\gamma-$, and $\alpha,\alpha-$phenanthrynes.

Like in pyrene and naphthalene diradicals, the singlet ground states of $m$-benzyne-like 1,3- and 2,4-DDPs have higher energies than those of the $o$-benzyne-like species (see Table 2). This is the result of a smaller coupling between the two radical centers in $m$-benzyne-like species. The mechanism of this coupling was first discussed by Hoffmann et al. and later...
TABLE 2: Relative Energies (in kcal·mol⁻¹) of the Lowest Lying Singlet (ΔEₛ) and Triplet (ΔEₜ) States with Respect to the 3,4-DDP Species in Its Ground State, (S²) Values for the Most Stable Singlet State, ΔEₛ–T Splittings, and Distances R(C–C) (in Å) and Mayer Bond Orders B(C–C) (in e) between the Didehydrocarbon Atoms

<table>
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<th>species type of interaction</th>
<th>ΔEₛ</th>
<th>(S²)</th>
<th>ΔEₜ</th>
<th>ΔEₛ–T</th>
<th>R(C–C)</th>
<th>B(C–C)</th>
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<td>1.2-DDP</td>
<td>αβ</td>
<td>2.90</td>
<td>0.000</td>
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<td>0.000</td>
<td>36.66</td>
<td>31.99</td>
<td>1.268</td>
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<td>3.4-DDP</td>
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<td>35.94</td>
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<td>0.000</td>
<td>38.44</td>
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<td>29.90</td>
<td>6.74</td>
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<td>8.10-DDP</td>
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a Computed at BLYP/6-31G(d). b Values in parentheses are for the phenanthrene parent molecule.

TABLE 3: NICS(1) Values (in ppm) for the Left, Central, and Right Rings of the Ground State of Phenanthrene and αβ-, αγ-, and αδ-like Didehydrophenanthrenes

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<td>2.3-DDP</td>
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a Computed at BLYP/6-31G(d). See Scheme 2 for definitions of species.

and 2,4-DDP species, the C1–C3 and C2–C4 bond distances of about 1.98 Å (0.45 Å shorter than in the original phenanthrene molecule) are not far from the values found for m-benzene and the corresponding 1,3-pyryne and 1,3-naphthalyne using pure DFT and highly correlated methods.11 The Mayer bond orders for the C–C bond are as large as 0.7 e (see Table 2), that is, not far from the value of a single C–C bond. This reveals the significant coupling between the two radical centers. All attempts to find BLYP/6-31G(d)-optimized bicyclic structures in 1,3- and 2,4-DDPs with shorter C1–C3 and C2–C4 bond lengths have failed.

The 1,3- and 2,4-DDPs have a strong preference for a closed-shell singlet ground state. Despite the slightly larger C–C distance and the smaller bond order in 2,4-DDP as compared to 1,3-DDP, the former is 1.7 kcal·mol⁻¹ more stable as a consequence of the relieve of the steric repulsion that the H4 bay hydrogen atom experiences in the phenanthrene parent molecule. Although 1,3-, 2,4-, and 1,10-DDPs all have only two σ bonds separating the two dehydro centers, the two former show a strong preference for the singlet state while the latter has almost degenerate singlet and triplet states. In 1,10-DDP, the coupling between the two radical centers is minor as a result of smaller overlap between the two radical lobes and less efficient mixing with the corresponding σ*(C–C) orbital (see structure B). This leads to a relative long C1–C10 separation and a Mayer bond order close to zero. The large spin contamination (see Table 2) of the 1,10-DDP wave function for the open-shell singlet state (approximated by the Slater
determinant constructed by using the corresponding Kohn—
Sham orbitals) is also consistent with a roughly speaking 1:1
mixture of singlet and triplet states and indicates significant
biradical character. The situation resembles that found for the
1,8-didehydrophthalene species.11

In the triplet state, the optimized structures of m-benzene-
like DDPs (and also for the rest of the DDPs) are very close to
each other and to that of phenanthrene (see Figure 2). The
relative order of stability of α,γ-DDPs in their triplet states is
1,10-DDP ≥ 2,4-DDP > 1,3-DDP. In line with what we find for
α,β-DDPs, the stability of α,γ-DDPs in their triplet state
increases as the C—C distances increase. According to the
C—C bond distance, the energy of triplet-state 2,4-DDP should
be more similar to triplet-state 1,3-DDP than to triplet-state 1,-
10-DDP. Again, the enhanced stability of triplet-state 2,4-DDP
comes from the release of steric repulsion after abstraction of
the H4 bay hydrogen atom. As expected from the discussion
about 1,10-DDP above, the ΔE_s–t splitting in 1,10-DDP is only
0.6 kcal·mol⁻¹; quite different from the values obtained in 1,3-
and 2,4-DDPs that are about 20 kcal·mol⁻¹.

Finally, NICS(1) values in Table 3 indicate that the aroma-
ticity of the rings that are not affected by H abstraction does
not change in α,γ-DDPs. As for α-benzene-like DDPs, the NICS
values indicate an increase in the aromatic character of the
didehydro rings in 1,3-DDP and 2,4-DDP as compared to
phenanthrene. In 1,10-DDP the two hydrogen atoms are
abstracted from two different rings, thus causing a lower increase of aromaticity in both rings as showed by NICS(1).

3.3. α,δ-DDPs (p-Benzene-like DDPs). The optimized
molecular structure of the lowest lying singlet and triplet states
of the five phenantrynes (1,4-, 2,10-, 4,5-, 4,10-, and 8,10-DDP)
with three α bonds separating the radical centers is depicted in
Figure 2. These five α,γ-DDPs have quite diverse electronic
ground states. The ground state of the 1,4-, 2,10-, 4,10-, and
8,10-DDP is a singlet open-shell, analogous to what has been
found for p-benzene at the BLYP/6-31G(d) and highly cor-
related1 levels of theory. Whereas the singlet and triplet states
are almost degenerate for 8,10-DDP, the singlet state is about
5 kcal·mol⁻¹ more stable than the triplet state for the 1,4- and
4,10-DDP. Interestingly, the 4,5-DDP has a singlet closed-shell
ground state. This can be interpreted as a partial single bond
connecting the two carbon atoms across the bay, as explained
in more detail later on.

1,4-DDP has the same topology as p-benzene and a similar
electronic structure. In this case, the through-bond mechanism
of coupling between the two spins of the two didehydrocarbon
atoms is more efficient than through-space interaction. Indeed,
p-benzene has destabilizing through-space and stabilizing
through-bond interactions.10,11,13,26 The through-bond coupling
proceeds via mixing of the two radical lobes with the two σ*(C—C)
orbitals of the two C–C bonds, one bond further away from the
didehydro positions as shown in structure C.11,13

Indeed, these two C–C bonds increase by about 0.04 Å when
going from phenanthrene to 1,4-DDP. This leads to an open-
shell singlet state as the ground state with relatively high
biradical character (about 65% in p-benzyne58). Interestingly,
the C1—C4 Mayer bond order increases only slightly from
phenanthrene to 1,4-DDP, thus indicating that some interaction
between these para-related carbon atoms existed before their
dehydrogenation. Indeed, this relatively large electronic delo-
calization between para-related carbon atoms in aromatic
molecules is the basis of the PDI.50,59 The triplet state is ca. 4
kcal·mol⁻¹ higher in energy, almost the same value found for
p-benzene at the same level of theory (see Table 1) and not far
from the 5.6 kcal·mol⁻¹ found for the equivalent 1,4-didehy-
 drophthalene at the CASPT2 level.11

A similar coupling mechanism is found in the 4,10-DDP. In
this case, however, the through-space antibonding interaction
is missing (radical lobes are not longer collinear, and the distance
that separates them is large) and the coupling takes places only
by the stabilizing through-bond interaction (see structure D).
This explains the larger stability by about 2.7 kcal·mol⁻¹ of
the open-shell singlet ground state of 4,10-DDP as compared
to that of the 1,4-DDP. The same situation is found when
comparing 1,4- and 1,5-didehydrophenanthrenes.11 The C–C
bond length of the σ*(C–C) orbital involved in this interaction
increases by 0.044 Å when going from phenanthrene to 4,10-
DDP. The triplet state of the 4,10-DDP, which is 6.7 kcal·mol⁻¹
above the singlet state, has almost the same energy as that of
the 1,4-DDP.

The 4,5-DDP is a particular case among α,δ-DDPs.13 In this
phenanthryne species, there is an important through-space
bonding interaction that leads to the formation of a partial single
C–C bond as denoted by the short C—C bond distance and
the relatively large Mayer bond order, which are not far from
those of m-benzene-like DDPs such as 1,3- and 2,4-DDP (see
Table 2). Because of this interaction, the ground state for this
system is a closed-shell singlet state, which is the most stable
among 1,4-DDPs. We have checcked that this closed-shell singlet
state is spin-unrestricted stable. One can interpret this C4–C5
connection as a strongly elongated single C–C bond. Indeed,
the C–C bond length of 1.67 Å is not far from that found in
semibulvalene (about 1.78 Å)60 and it is among the longest C–C
bonds ever found. The short C—C bond distance is followed by
an increase in the C9–C10 bond length and an important
decrease (by 0.085 Å) of the C–C bond length directly
connecting the two outer rings. The triplet state, on the other
hand, is almost isoenergetic with the triplet states of the rest of
1,4-DDPs because of two counteracting factors: the C—C
bond length that is the shortest among 1,4-DDPs (causing
relatively more repulsion between the two same-spin radical
electrons); the removal of steric repulsions after H4 and H5
hydrogen abstraction (causing extra stabilization relative to the
parent molecule phenanthrene). Thus, as a result of the enhanced
stability of the singlet state, 4,5-DDP has the largest singlet–
triplet splitting among α,δ-DDPs.

Finally, 2,10-DDP and 8,10-DDP are also interesting species.
From the depicted structure E, which corresponds to 8,10-DDP
(the situation for 2,10-DDP is analogous), one may assume that
some through-bond interaction is present in these species.
However, the small $\Delta E_{S-T}$ value of these biradicals points out a low coupling between the two radical centers. Hyperconjugation in 8,10-DDP takes place mainly from the radical lobe in C8 to the $\sigma^*(C-C)$ orbital (arrow $a$ in E) and from the radical lobe in C10 to the $\sigma^*(C-H)$ orbital of the adjacent CH group (arrow $b$ in E). Since the two sets of resulting molecular orbitals (i.e., $a$ and $b$) are almost orthogonal, the mutual overlap and thus the coupling between the two radical centers are weak. Finally, the triplet state of 2,10-DDP and 8,10-DDP are the least stable among $\alpha,\beta$-DDPs, despite having the largest separation between didehydrocarbon atoms. This may be ascribed to the fact that in these DDPs none of the bay H atoms are removed (and the associated H$\cdots$H repulsion is therefore not relieved), at variance with the situation for all other $\alpha,\beta$-DDPs.

With respect to aromaticity, for the ground state of 4,5-DDP species, NICS indicates an increase of aromaticity in the central ring and a decrease in the outer rings after formation of the C4$\cdots$C5 partial bond. In the case of all the other $\alpha,\beta$-DDPs, the NICS values indicate an increase of aromaticity in the central and the outer rings containing the dedydrocarbon atom(s). PDI and SCI values (not included in Table 3) support the NICS conclusions.

**3.4. $\alpha,\alpha$- to $\alpha,\beta$-DDPs (Weakly Coupled DDPs).** For all these systems, except for 7,10-DDP, we have essentially degenerate open-shell singlet and triplet states, i.e., low $\Delta E_{S-T}$ values, which is an indication of the low coupling between radical centers that are separated by more than 4 Å in all cases (Mayer bond orders between radical centers are in all cases lower than 0.04). The optimized C$\cdots$C bond lengths of open-shell singlet and triplet states in these systems differ by less than five thousandths of an Å and are very close to the C$\cdots$C bond lengths found in phenanthrene (differences are never larger than two hundredths of an Å; see Figure S1 in the Supporting Information). For all $\alpha,\alpha$- to $\alpha,\beta$-DDPs having C5 as a dehydro center, the energy of the open-shell singlet and triplet states is about 2 kcalmol$^{-1}$ lower than for the rest (28 vs 30 kcalmol$^{-1}$, approximately; see Table 2). The reason is, as pointed out above, relieve of steric repulsion between the bay H atoms of phenanthrene. For 7,10-DDP, the $\Delta E_{S-T}$ value of about 2 kcalmol$^{-1}$ indicates a preference for the singlet state and a nonnegligible spin$\cdots$spin coupling despite the significant separation between the two didehydrocarbon atoms. This is analogous to the situation found for 2,6-didehydronaphthalene. According to Squires and Cramer, the “W-like” topology found in 7,10-DDP favors a good overlap between orbitals along the path between the two radical centers, thus leading to nonnegligible coupling. Indeed, nuclear/nuclear and nuclear/electron coupling found in such “W-like” configurations is a well-known phenomenon in NMR and EPR spectroscopy, respectively.

In line with the small distortion found for these weakly coupled DDPs, the NICS values (provided as Supporting Information) indicate only slight changes upon didehydrogenation (less than 1 ppm) in the local aromaticity.

**4. Conclusions**

The relative stabilities of the singlet and triplet states of didehydrophenanthrenes (DDPs) are determined in the first place by the distance between radical centers: the closer the radical centers, the stronger the spins coupled and the stronger the extra bond formed. Thus, DDPs with radical centers separated by a small distance (like in o-benzene- and m-benzene-like structures) have singlet closed-shell ground states that are very stable and show a strong coupling between radical lobes as derived from the large singlet$\cdots$triplet (S$\cdots$T) splittings. The most stable DDPs are o-benzene-like structures in their singlet closed-shell ground states. For these systems, the $\pi$ bond is stronger if the original C$\cdots$C length in the parent phenanthrene is shorter. Thus, the second most stable o-benzene-like structure is 9,10-DDP that has the didehydro atoms separated by the smallest distance in the phenanthrene parent molecule. However, the most stable o-benzene-like DDP is the 3,4-DDP because of the relieve of steric repulsion between the bay hydrogen atoms after H4 removal. This is found in agreement with the fact that the abstraction of a single H atom in phenanthrene occurs with preference in one of the bay H atoms (Table S3). Interestingly, the 4,5-DDP with p-benzene-like structure has also a closed-shell singlet ground state with a short and relatively strong C4$\cdots$C5 bond. This bond can be considered as one of the longest C$\cdots$C single bonds reported to date.

For the triplet states, we have found that the longer the separation between radical centers, the larger the stability of the DDP. This leads to almost degenerate singlet open-shell and triplet states for DDPs with well-separated and weakly coupled spin radicals. Again those triplet states that involve removal of the bay hydrogen atoms are about 2 kcalmol$^{-1}$ more stable than those having similar C$\cdots$C separations. The stability of the different phenanthryne isomers in their triplet states shows that abstraction of the H atoms suffering the largest steric repulsions, i.e., those in the bay region of phenanthrene, leads to the most stable triplet phenanthryne isomers. The relative stabilities of didehydrophenanthrenes in their triplet states reinforce our previous conclusion that the H$\cdots$H bonding interaction between the bay H atoms of phenanthrene that was previously proposed by Bader and co-workers does not exist; instead there is H$\cdots$H steric repulsion.

Finally, it is worth mentioning that the minor changes in aromaticity induced by didehydrogenation in phenanthrene as reflected by NICS, PDI, and SCI values seem to indicate that aromaticity does not play a decisive role in determining the relative stabilities of DDPs.

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**Supporting Information Available:** Cartesian coordinates of all species occurring in this work, first and second dehydrogenation energies, NICS values for $\alpha,\alpha$- to $\alpha,\beta$-DDPs, and a figure with the geometries of $\alpha,\alpha$- to $\alpha,\beta$-DDPs. This material is available free of charge via the Internet at http://pubs.acs.org.