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Didehydrophenanthrenes: Structure, Singlet−Triplet Splitting, and Aromaticity

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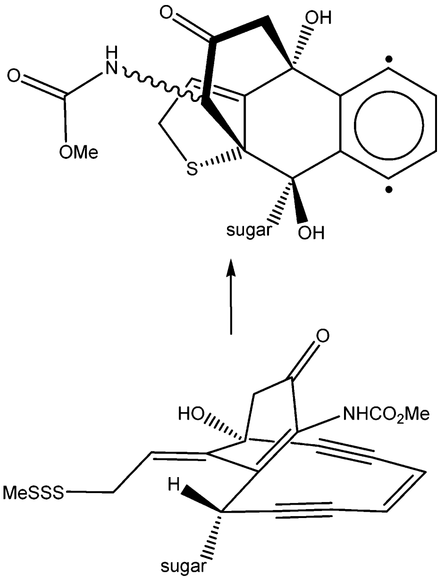
In this work, we explore the geometries, relative stabilities, singlet−triplet (S−T) splittings, and local aromaticities of the 25 possible didehydrophenanthrenes (DDPs) at the BLYP/6-31G(d) level. The main aim is to understand their molecular structure and stability in terms of the electronic structure. 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 drugs[4] is triggered by Bergman cyclization[5] 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 didehydroarenes 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 didehydroarenes, in general, less reactive than monodehydroarenes.[3,8−10] 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 didehydroarenes *increases* as the biradical character increases, i.e., as 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 aryne species. Thus, arynes are particularly stable when they have a closed-shell ground state structure with small biradical character, whereas active aryne antitumor agents show usually small S−T energy gaps and high biradical character.

SCHEME 1: Bergman Cyclization in Calicheamicin



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 aryne derivatives have been

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TABLE 1: Experimental and Theoretical ΔE_{S-T} Energy Splittings (kcal·mol^{-1}) for the Three Benzyne Species

species	BLYP/6-31G(d)	BLYP/cc-pVTZ	B3LYP/6-31G(d)	CASPT2/cc-pVDZ[d]	expt
o-benzyne	33.9	36.1	29.5	30.4	37.5 ± 0.3[e]
m-benzyne	19.7	19.7	14.2	18.0	21.0 ± 0.3[e]
p-benzyne	4.1[a]	4.5[b]	2.5[c]	5.8	3.8 ± 0.5,[e] 2.1 ± 0.4[f]

[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,[13] didehydropyrenes,[22−24] didehydrotoluenes,[25] didehydrophenols,[26] didehydrohydroxytoluenes,[27] didehydropyrydines,[12,28] didehydrobenzoquinones,[29] didehydrocubanes,[30] didehydrohetero-substituted pentalenes,[31] cyclooctatetraenes,[31] and others.[13,32]

To our knowledge there is only one previous theoretical study of phenantrynes that analyzes exclusively the 4,5-dehydrophenanthrene 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 phenanthrynes; second, to compute their ΔE_{S-T} splittings that will provide a first indication of their reactivity; third, to compare the local aromaticity of phenanthrynes with that of phenanthrene, to see whether there is a relationship between the nature of the phenanthryne formed and the increase or decrease of local aromaticity. To date this kind of analysis has been performed only in benzynes,[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 benzynes, the Dunning's correlation consistent augmented triplet-ζ (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 UBLYP 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 ΔE_{S-T} splittings in benzynes (see Table 1). Experimentally, benzyne species have singlet ground states, closed-shell for the *o*- and *m*-benzynes and open-shell for *p*-benzyne. All methods agree with this experimental result as well as with the experimental order of stability,[14] namely, *o*-benzyne > *m*-benzyne > *p*-benzyne. As can seen in Table 1, the BLYP/6-31G(d) ΔE_{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 ΔE_{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 ΔE_{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 ΔE_{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 π-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 π-electron ring current are dominant and local σ-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,[51] 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

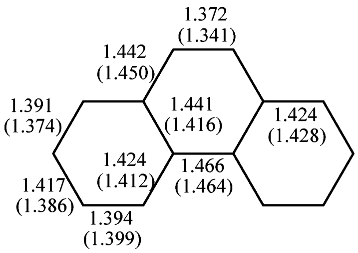
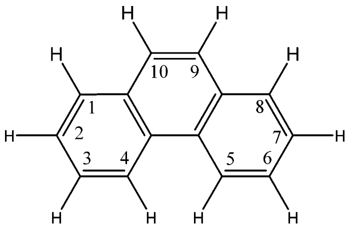


Figure 1. BLYP/6-31G(d) and experimental (in parentheses)[52] bond lengths (in Å) of phenanthrene.

SCHEME 2: Phenanthrene with Atom Numbering



in its singlet ground state. The BLYP/6-31G(d) and experimental bond lengths[52] agree well, the largest error being 0.03 Å.

The optimized molecular structure of the lowest lying singlet and triplet states of all possible DDPs are given in Tables S1 and S2 of the Supporting Information. Although we are particularly interested in the relative energies of DDPs, we have also optimized the geometry of the five possible monodehydrophenanthrenes in their doublet ground state. As a byproduct of this work, these calculations have provided the first and second dehydrogenation energies that can be found in Table S3 of the Supporting Information. The first dehydrogenation energy is found in between 115 and 116 kcal·mol^{-1} for removal of H1, H2, H3, or H10, and it reduces to ca. 113 kcal·mol^{-1} for H4. The 2 kcal·mol^{-1} difference has to be attributed to the relief of steric repulsions when H4 in the bay region of phenanthrene is removed. Similar results have been reported by Hemelsoet et al.[53] The second dehydrogenation energy is quite dependent on the interaction between the two radical centers formed (vide infra) varying from 85.5 to 115.7 kcal·mol^{-1}. Indeed, DDPs that result from abstraction of two adjacent H atoms (α,β-DDPs) have a more intense coupling between radical centers than those that are separated by two, three, or more σ bonds, and consequently, they have lower second dehydrogenation energies. For this reason, we have divided this section into four subsections that discuss separately the highly coupled α,β-DDPs, the less interacting α,γ-DDPs, the even less coupled α,δ-DDPs, and the almost uncoupled α,ϵ- to α,θ-DDPs.

3.1. α,β-DDPs (*o*-Benzyne-like DDPs). The molecular structure of the singlet ground state and the lowest lying triplet state of all possible *o*-benzyne-like DDPs, namely, 1,2-, 2,3-, 3,4-, and 9,10-DDP, is depicted in Figure 2. For the 25 DDPs, Table 2 gathers relative energies of the lowest lying singlet and triplet states with respect to the most stable DDP, i.e., the 3,4-DDP in its closed-shell singlet ground state, $\langle S^2 \rangle$ values for the lowest lying singlet state, $\Delta E_{\mathrm{S-T}}$ splittings, and distances and Mayer bond orders between radical centers for the lowest lying singlet states. The $\langle S^2 \rangle$ values for the open-shell singlet states vary from 0.701 in 4,10-DDPs to 1.013 for the 1,8-DDP. For the lowest lying triplet state of all 25 DDPs, $\langle S^2 \rangle$ never exceeded 2.016, so the contamination of the triplet states is always quite small. The analysis of the spin density in the triplet states reveals that it is strongly localized in the dehydrocarbon atoms.

The ground state for all four *o*-benzyne-like DDPs is closed-shell singlet. For these systems, we have checked that the final 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 α,β-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*-benzyne-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*-benzyne-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*-benzyne 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*-benzyne like DDPs is 3,4-DDP > 2,3-DDP > 1,2-DPP > 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*-benzyne-like DDPs, the singlet ground state is substantially lower than the triplet state. The large $\Delta E_{\mathrm{S-T}}$ splittings (from 32.0 to 38.1 kcal·mol^{-1}) indicate an important coupling between the two radical centers in *o*-benzyne-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

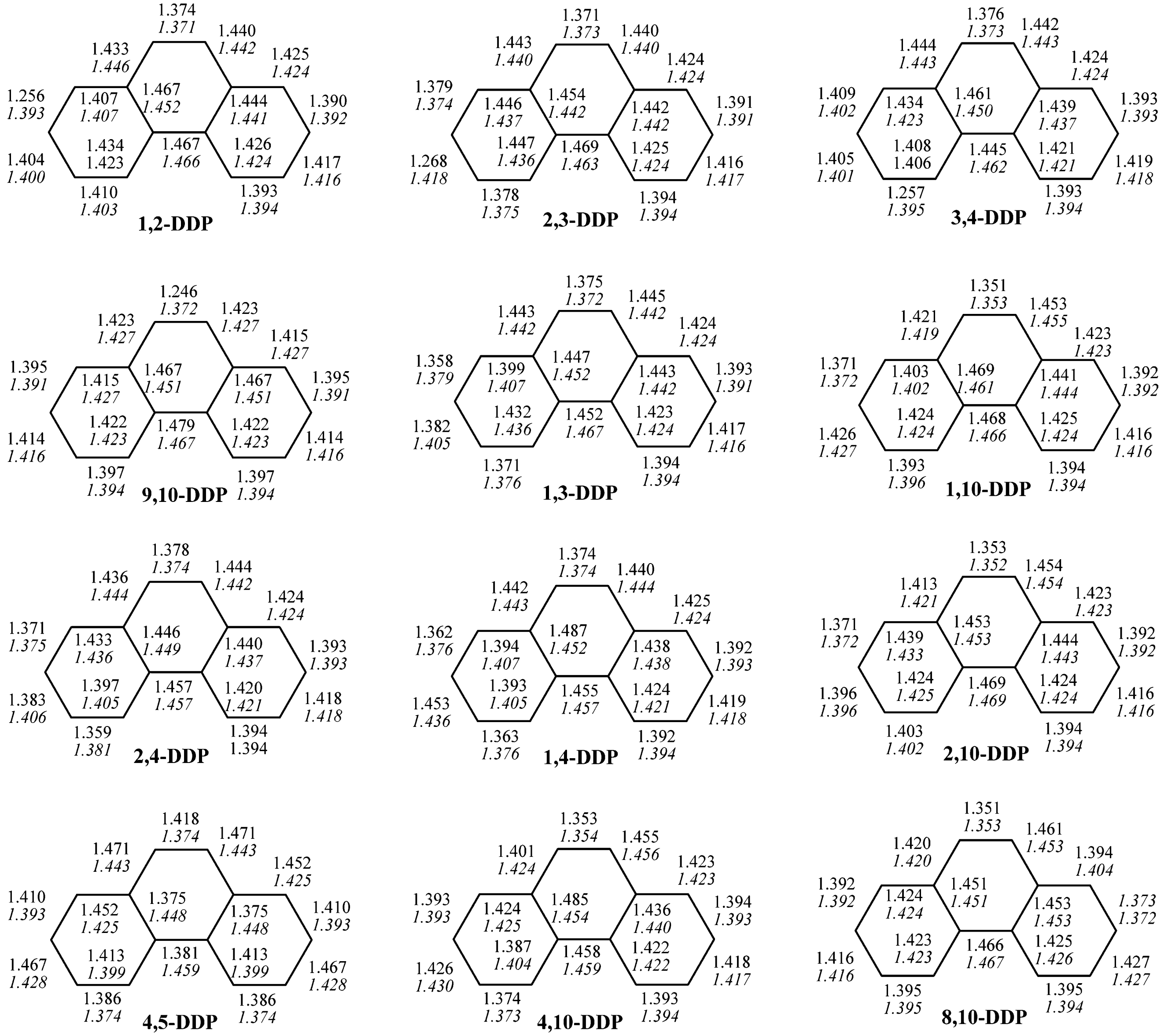


Figure 2. BLYP/6-31G(d) bond lengths (in Å) for the singlet and triplet (in italics) states of α,β-, α,γ-, and α,δ-phenanthrynes.

reduces that of the triplet, leading to a large ΔE_{S-T} splitting. Another way of viewing this is that the additional π bond that occurs after elimination of H_2 is strongest in the singlet 9,10-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.[57] In the order from phenanthrene to the singlet α,β-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.[16] It is worth noting that the reduction of NICS values may be attributed, in part, to the increase in the number of π-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(1) in the benzyne ring of *o*-benzyne like DDPs, we have computed two additional indices: the para-delocalization index (PDI)[50] and the six-center index (SCI).[51] 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).

3.2. α,γ-DDPs (*m*-Benzyne-like DDPs). There are three DDPs that have the radical lobes separated by a single C atom like *m*-benzyne, namely, the 1,3-, 2,4-, and 1,10-DDPs. The ground state of the two former is a singlet closed-shell, the same found for *m*-benzyne at the BLYP/6-31G(d) and highly correlated[1] levels of theory. On the other hand, 1,10-DDP has a singlet open-shell ground state with an almost degenerate triplet excited state, indicating the lack of interaction between the C1 and C10 radical centers. Neither its electronic nor its molecular structure indicate *m*-benzyne-like character for 1,10-DDP. The BLYP/6-31G(d)-optimized molecular structures of the three α,γ-DDPs are provided in Figure 2.

Like in pyrene[23] and naphthalene[11] 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.[13] and later

TABLE 2: Relative Energies (in kcal·mol^{-1}) of the Lowest Lying Singlet (ΔE_S) and Triplet (ΔE_T) States with Respect to the 3,4-DDP Species in Its Ground State, $\langle S^2 \rangle$ Values for the Most Stable Singlet State, ΔE_{S-T} Splittings, and Distances R(C•−C•) (in Å) and Mayer Bond Orders B(C•−C•) (in e) between the Didehydrocarbon Atoms[a]

species	type of interaction	ΔE_S	$\langle S^2 \rangle$	ΔE_T	ΔE_{S-T}	R(C•−C•)	B(C•−C•)[b]
1,2-DDP	α,β	2.90	0.000	37.83	34.93	1.256	2.279 (1.484)
2,3-DDP	α,β	4.67	0.000	36.66	31.99	1.268	2.141 (1.355)
3,4-DDP	α,β	0.00	0.000	35.94	35.94	1.257	2.263 (1.477)
9,10-DDP	α,β	0.37	0.000	38.44	38.07	1.246	2.360 (1.563)
1,3-DDP	α,γ	12.72	0.000	33.47	20.75	1.983	0.731 (0.009)
1,10-DDP	α,γ	30.40	0.956	31.04	0.64	2.540	0.011 (0.005)
2,4-DDP	α,γ	11.84	0.000	31.36	19.52	1.987	0.706 (0.005)
1,4-DDP	α,δ	25.86	0.797	29.88	4.02	2.718	0.117 (0.095)
2,10-DDP	α,δ	30.30	0.990	30.70	0.40	3.721	0.030 (0.025)
4,5-DDP	α,δ	17.88	0.000	29.05	11.17	1.670	0.753 (0.023)
4,10-DDP	α,δ	23.16	0.701	29.90	6.74	3.647	0.158 (0.012)
8,10-DDP	α,δ	29.44	0.985	30.55	0.62	3.702	0.051 (0.048)
3,5-DDP	α,ϵ	27.77	0.973	28.61	0.84	4.365	0.014 (0.000)
3,10-DDP	α,ϵ	30.27	1.009	30.14	-0.14	4.169	0.002 (0.000)
5,10-DDP	α,ϵ	28.14	0.999	28.26	0.11	4.185	0.005 (0.000)
7,10-DDP	α,ϵ	29.19	0.936	30.87	1.68	4.791	0.035 (0.002)
1,8-DDP	α,ζ	30.35	1.013	30.36	0.01	5.658	0.005 (0.006)
2,5-DDP	α,ζ	28.32	1.007	28.46	0.14	5.158	0.011 (0.011)
3,6-DDP	α,ζ	30.31	1.011	30.32	0.01	5.758	0.005 (0.006)
6,10-DDP	α,ζ	30.17	1.007	30.42	0.26	4.996	0.031 (0.035)
1,5-DDP	α,η	28.46	1.010	28.37	-0.09	4.942	0.000 (0.000)
1,7-DDP	α,η	30.57	1.010	30.54	-0.03	6.452	0.000 (0.000)
2,6-DDP	α,η	30.43	1.006	30.50	0.07	6.505	0.002 (0.000)
1,6-DDP	α,θ	29.90	0.989	30.49	0.59	6.154	0.011 (0.003)
2,7-DDP	α,θ	30.75	1.011	30.81	0.06	7.044	0.009 (0.011)

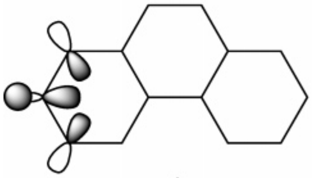
[a] Computed at BLYP/6-31G(d). [b] Values in parentheses are for the phenanthrene parent molecule.

TABLE 3: NICS(1) Values (in ppm) for the Left, Central, and Right Rings of the Ground State of Phenanthrene and α,β-, α,γ-, and α,δ-like Dedydrophenanthrenes[a]

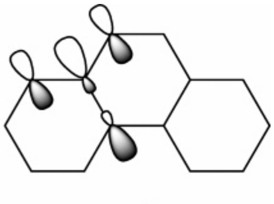
	NICS(1)		
species	left	central	right
phenanthrene	−11.6	−9.2	−11.6
1,2-DDP	−13.6	−9.4	−11.8
2,3-DDP	−14.3	−9.5	−11.7
3,4-DDP	−13.6	−9.5	−11.9
9,10-DDP	−11.5	−10.9	−11.5
1,3-DDP	−13.3	−9.6	−11.6
1,10-DDP	−12.6	−10.1	−11.8
2,4-DDP	−13.1	−9.0	−11.7
1,4-DDP	−14.5	−9.4	−11.6
2,10-DDP	−12.4	−10.2	−11.8
4,5-DDP	−7.1	−10.9	−7.1
4,10-DDP	−12.7	−10.4	−11.7
8,10-DDP	−11.6	−9.9	−12.6

[a] Computed at BLYP/6-31G(d). See Scheme 2 for definitions of species.

on adopted by Squires and Cramer.[11] According to these authors, in *m*-benzyne-like species there is a strong through-space interaction enhanced by the mixing with the σ*(C−H) orbital located between the two dehydrocarbon atoms (see structure **A**). The decrease of the distance between the dehydrocenters favors the coupling of the two radicals but increases the energy needed to distort the initial geometry. As a result of these and other[1,11] counteracting factors, the potential energy surface along the distance that connects the two radical atoms in 1,3-arynes is very flat and sensitive to the methodology used.[11,15,17,23] Thus, in the case of *m*-benzyne, the HF, LDA, and B3LYP methods favor the formation of a bicyclic structure with a small C−C bond length (by about 1.5−1.6 Å) between the two radical centers,[15,17,22,23] while pure DFT and highly correlated ab initio methods[1,11,15,22] yield a C−C separation of about 2 Å. The preference for a long C−C separation and not a bicyclic structure in *m*-benzyne has been confirmed experimentally from the band positions and relative intensities in the IR spectra.[1] In our 1,3- 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*-benzyne[15] and the corresponding 1,3-pyryne[23] 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.



A



B

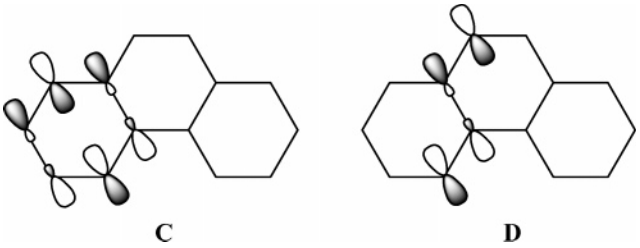
The 1,3- and 2,4-DDPs have a strong preference for a closed-shell singlet ground state. Despite the slightly larger C•−C• distance and the smaller bond order in 2,4-DDP as compared to 1,3-DDP, the former is 1.7 kcal·mol^{-1} more stable as a consequence of the relieve of the steric repulsion that the 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-didehydronaphthalene species.[11]

In the triplet state, the optimized structures of *m*-benzyne-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 $\geq$ 2,4-DDP $>$ 1,3-DPP. 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 aromaticity of the rings that are not affected by H abstraction does not change in α,γ-DDPs. As for *o*-benzyne-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). PDI values (not listed in Table 3) also show an increase of aromaticity of the didehydro ring in 1,3- and 2,4-DDPs (0.104 and 0.103, respectively), whereas SCI values (not listed in Table 3) are kept invariant (0.048) with respect to phenanthrene. For 1,10-DDP, the trends are opposite: thus, PDI (0.083 and 0.048 for the outer and middle ring containing the dehydro carbons, respectively) is almost unchanged whereas SCI shows a large increase in both dehydro rings (0.099 and 0.039, respectively).

3.3. α,δ-DDPs (*p*-Benzyne-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-DDPs) with three σ bonds separating the radical centers is depicted in Figure 2. These five α,γ-DDPs have quite divers electronic ground states. The ground state of the 1,4-, 2,10-, 4,10-, and 8,10-DDPs is a singlet open-shell, analogous to what has been found for *p*-benzyne at the BLYP/6-31G(d) and highly correlated[1] 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-DDPs. 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*-benzyne 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*-benzyne 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*-benzyne[58]). 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 delocalization 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*-benzyne 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-didehydronaphthalene at the CASPT2 level.[11]

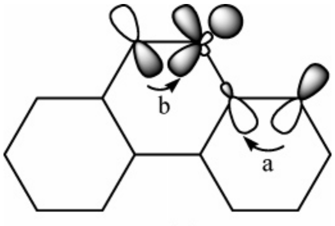


A similar coupling mechanism is found in the 4,10-DDP. In this case, however, the through-space antibonding interaction is missing (radical lobes are no longer collinear, and the distance that separates them is large) and the coupling takes places only by the stabilizing through-bond interaction (see 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-didehydronaphthalenes.[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*-benzyne-like DDPs such as 1,3- and 2,4-DDPs (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 checked 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 ΔE_{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 σ^*(C−C) orbital (arrow *a* in **E**) and from the radical lobe in C10 to the σ^*(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 α,δ-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−H repulsion is therefore not relieved), at variance with the situation for all other α,δ-DDPs.



E

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−C5 partial bond. In the case of all the other α,δ-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. α,ϵ- to α,θ-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 ΔE_{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 e). The optimized C−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−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 α,ϵ- to α,θ-DDPs having C5 as a dehydro center, the energy of the open-shell singlet and triplet states is about 2 kcal·mol^{-1} lower than for the rest (28 vs 30 kcal·mol^{-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 ΔE_{S-T} value of about 2 kcal·mol^{-1} indicates a preference for the singlet state and a nonnegligible spin−spin coupling despite the significant separation between the two didehydrocarbon atoms. This is analogous to the situation found for 2,6-didehydronaphthalene.[11] According to Squires and Cramer,[11] 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.[11]

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*-benzyne- and *m*-benzyne-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−triplet (S−T) splittings. The most stable DDPs are *o*-benzyne-like structures in their singlet closed-shell ground states. For these systems, the π bond is stronger if the original C−C length in the parent phenanthrene is shorter. Thus, the second most stable *o*-benzyne-like structure is 9,10-DDP that has the dehydrocarbon atoms separated by the smallest distance in the phenanthrene parent molecule. However, the most stable *o*-benzyne-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).[53] Interestingly, the 4,5-DDP with *p*-benzyne-like structure has also a closed-shell singlet ground state with a short and relatively strong C4−C5 bond. This bond can be considered as one of the longest C−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 kcal·mol^{-1} more stable than those having similar C−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[54,55] that the H···H bonding interaction between the bay H atoms of phenanthrene that was previously proposed by Bader and co-workers[56] does not exist; instead there is H···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 α,ϵ- to α,θ-DDPs, and a figure with the geometries of α,ϵ- to α,θ-DDPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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