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Theoretical Prediction of Benzyne-Like Species in Pyrene Diradicals

I. García-Cruz,*,† J. M. Martínez-Magadán,† J. M. Bofill,‡ and F. Illas†,§

Programa de Ingenieria Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, Colonia San Bartolo Atepehuacán, México D. F., 07730, México, Departament de Química Orgànica i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain, and Departament de Química Física i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain

The different products that can be obtained from pyrene dehydrogenation have been studied by means of hybrid density functional theory. Most of the didehydrogenated species exhibit a diradical character. This is supported by the closeness between the geometry and energy of singlet and triplet states and the open-shell nature of the singlet state. However, three didehydrogenated species have been found to exhibit a closed-shell singlet electronic ground state. The analysis of the electronic structure, the formation energy of these didehydrogenated species, and their geometrical structure reveals that these three didehydrogenated species are better described as benzyne-like moieties; two of them are of *o*- and one of *m*-benzyne character. The two *o*-benzyne species have lower energies than the *m*-benzyne and are favored upon diradical formation. This interpretation is fully supported by the analysis of multiconfigurational wave functions and the order of stabilities confirmed by second-order multireference perturbation theory calculations. A possible implication of the reactivity of these benzyne-like species in asphaltene formation is discussed.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are among the most abundant atmospheric pollutants. They are an important byproduct of the petroleum industry[1] and are also originated from incomplete combustion either in automobile engines, home fireplaces and industrial installations.[2] Moreover, these compounds are known to exhibit a strong mutagenic activity[2,3] and readily form relatively stable radical species.[4] Likewise, asphaltene moieties have been recently recognized as PAH.[5–8]

Despite the considerable amount of work devoted to the study of aromatic diradicals[9] there is almost no information about the various possible diradical species originated from PAH dehydrogenation.[4] In particular, benzene diradicals have been subject of many studies related to the formation of the *o*-, *p*- and *m*-benzyne compounds which indeed are known to be involved as intermediates in a large number of organic reactions.[10–13] The structure of these benzyne compounds has been clarified in the past few years. Nowadays, there is clear evidence of the existence of an *o*-benzyne species playing an important role as intermediate in the nucleophilic substitution rearrangement of halobencenes;[14] the structures of *m*-benzyne have been elucidated experimentally and confirmed with the help of accurate computational ab initio calculations,[15–18] and Marquardt et al.[19] have shown evidence for the formation of *p*-benzyne in a neon matrix, although in this case the long distance between the two radical centers prevents the formation of a chemical bond. Likewise, the electron affinities and singlet−triplet splitting of *o*-, *m*-, and *p*-benzyne have been determined experimentally

together with the ultraviolet photoelectron spectroscopy of the *o*-, *m*-, and *p*-benzyne negative ions and a careful theoretical study.[20] Finally it is worth mentioning two very recent related studies: one reporting the microwave spectrum[21] of *o*-benzyne and the other one reviewing the chemistry of aryne compounds.[22]

Benzyne-like compounds can also be produced by appropriate dehydrogenation of PAH although there seems to be no evidence for their existence. Pyrene (Figure 1) is one of the simplest polycyclic aromatic hydrocarbons; it consists of four fused benzene-like rings and may be defined as a Kekulé hydrocarbon. Pyrene ground-state electronic structure can be represented by closed-shell singlet resonant forms. Accordingly, it exhibits a strong aromatic character and a rather high stability. Nevertheless, pyrene readily forms radical species which have a broad interest, ranging from its interaction with DNA[23–25] to astrophysics.[26,27] Therefore, one may wonder whether pyrene diradical species would rather evolve up to benzyne-like structures, or, on the contrary, they maintain the diradical character with minimum changes in the molecular structure. This study has a basic interest because it is not at all clear that benzyne-like species derived from pyrene would resemble those obtained from benzene. The existence of the fused rings suggests already various possibilities not at all present in benzene. On the other hand, the possible existence of these species can be a technological relevant issue because they could be related to the formation of asphaltenes.[28] In fact, PAH diradicals can be formed spontaneously under the crude oil extraction processes.[4] Those radicals are short-lived and further reactions could produce other aromatic compounds such as asphaltene aggregates or larger asphaltene entities. Additionally, benzyne species have a different reactivity, they can react with other PAH compounds through a Diels−Alder coupling where the

* To whom correspondence should be addressed. E-mail: igarcia@imp.mx.
† Instituto Mexicano del Petróleo.
‡ Departament de Química Orgànica i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona.
§ Departament de Química Física i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona.
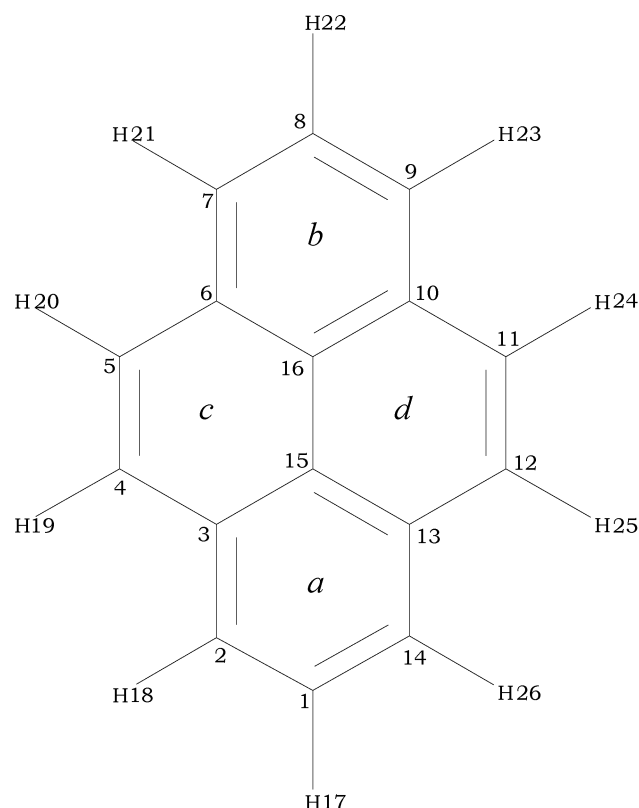
Figure 1. Schematic representation of pyrene.

benzyne-like molecule plays the role of the olefin and the PAH that of the dienophile moiety.[10,11,29] This coupling is very favorable under crude oil extraction conditions, thus leading to a variety of compounds which may eventually also condense to asphaltenes.

Because of the high reactivity and short lifetime of pyrene radicals and diradicals it is very difficult to carry out a systematic experimental study aimed to classify the different radical species in terms of electronic structure and relative stability. From EPR experiments[30,31] on molecular crystals of pyrene triplet lifetimes are 6 ms. Hopefully, modern quantum chemistry computational techniques have reached a level of accuracy which permits us to investigate these radical species and provide reliable estimates of their structure and relative stability. This is precisely the aim of the present study. To this end, density functional theory calculations have been carried out for the 16 different pyrene diradicals which can be formed from the three unique mono-radical species.

Computational Details

Different sophisticated methods have been recently proposed to accurately describe the electronic structure of open-shell molecules exhibiting diradical character although analytical gradients are not always available for geometry optimization.[32−34] The B3LYP hybrid density functional theory method[35−36] with the 6-31++G** basis set[37] has been selected in an attempt to reach a compromise between accuracy and computational feasibility. Notice that a total of 352 basis functions are involved for the diradical species and that more than 30 molecular structures are investigated. Moreover, the hybrid B3LYP level of theory has proven to accurately predict the thermochemistry of a large number of organic compounds[38] including complex open-shell systems such as nitroxide diradicals[39] or the oxover-dazyl radical and of the diradical obtained by joining two

identical units.[40] Therefore, the optimum geometry of pyrene radicals resulting from hydrogen abstraction on positions C_1, C_2, C_4 (Figure 1) and diradicals formed by abstraction of (C_1,C_2), (C_1,C_4), (C_1,C_5), (C_1,C_7), (C_1,C_8), (C_2,C_4), (C_2,C_5), (C_2,C_7), (C_2,C_8), (C_2,C_9), (C_2,C_{11}), (C_2,C_{12}), (C_2,C_{14}), (C_4,C_5), (C_4,C_{11}), and (C_4,C_{12}) has been obtained from geometry optimization carried out at the hybrid B3LYP/6-31++G** level of theory. Unrestricted spin calculations were carried out for the open-shell systems; these involve the doublet states of the C_1, C_2, C_4 radicals and the triplet and broken-symmetry open-shell "singlet" solutions of all diradicals. In most cases, the ground-state singlet is obtained from a broken symmetry solution and corresponds to a diradical species. However, in some special situations, one finds that the lowest singlet has a closed-shell character. This is one of the key points of the present work and will be discussed in detail in the forthcoming section. In the case of diradical species, the singlet−triplet energy difference is calculated as twice the energy difference between the triplet and broken symmetry solutions.[41] Although there is evidence that DFT provides a reliable description of some diradicals[39,40] including the singlet−triplet energy gap in some benzynes,[42] the fact that DFT leads to an incorrect description of the electronic structure of some related species[17,20] requires an additional careful check of the reliability of the DFT predictions on the systems studied in this work. Hence, it is important to point out that, in all cases studied in the present work, the spin density is highly localized around the carbon radical centers, and the distance between these centers is large enough so that a negligible overlap between the open-shell Kohn−Sham orbitals exists. Cremer et al.,[43,44] have shown that under these circumstances hybrid DFT provides a reasonable description of diradicals as well. This interpretation is fully supported by complete active space self-consistent field (CASSCF) and second-order multireference perturbation theory calculations carried out using the CASSCF as a zero-order wave function (CASPT2).[45−46] These calculations have been carried out using a complete active space containing two electrons and two orbitals and considering the B3LYP-optimized geometry. Hence, for the singlet state, two configurations are considered which are equivalent to the neutral and ionic Heitler and London valence bond forms of the hydrogen molecule. Two different situations are possible which are also reminiscent of the hydrogen molecule; these are the closed-shell singlet equivalent to the wave function of H_2 at the equilibrium distance (domi-nated by a single configuration) and the open-shell singlet equiv-alent to H_2 at large internuclear separation (dominated by two configuration with nearly equal contributions). The CASSCF and CASPT2 single point calculations have been carried out using the (3s2p1d) and (2s1p) atomic natural orbital basis sets.[47] In the CASPT2 calculations the C (1s2) core electrons have not been correlated and excitations are limited to virtual orbitals with an orbital energy smaller than 1 hartree.

To interpret the relative stability of the different diradicals, the nuclear independent chemical shifts[48] (NICS), at the center of each aromatic ring, have been computed for selected diradicals. For comparative purposes a NICS analysis has also been carried out for pyrene. As usually, the NICS are defined as the absolute magnetic shielding computed at the ring center which in turn is defined as the weighted average of the heavy atom coordinates. To have a correspondence with the familiar nuclear magnetic resonance (NMR) chemical shift convention, negative NICS denote aromaticity. The NICS have been calculated using the continuous set of the gauge transformation method[49−50] within the B3LYP approach and basis sets used in the geometry optimization process. Here it is worthwhile to point

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TABLE 1: X-ray and Calculated Geometrical Parameters of Pyrene

parameter	X-ray[56]	B3LYP/6-31++G** [a]
	Bond Length (Å)	
C_1-C_2	1.396	1.395
C_2-C_3	1.406	1.406
C_3-C_4	1.424	1.439
C_4-C_5	1.363	1.363
C_1-C_{14}	1.396	1.395
$C_{11}-C_{12}$	1.363	1.363
$C_{12}-C_{13}$	1.396	1.439
$C_{15}-C_{16}$	1.430	1.428
C_1-H_{17}	0.980	1.086
C_2-H_{18}	0.990	1.087
C_5-H_{20}	1.000	1.087
$C_{11}-H_{24}$	0.970	1.087
$C_{14}-H_{26}$	1.000	1.087
	Bond Angle (deg)	
$C_1-C_2-C_3$	121.0	120.7
$C_2-C_3-C_4$		122.4
$C_2-C_3-C_{15}$	119.0	119.0
$C_2-C_1-C_{14}$	120.4	120.6
$C_3-C_{15}-C_{16}$	119.7	120.1
$C_5-C_6-C_{16}$	118.6	118.6
$C_{12}-C_{13}-C_{14}$		122.4
$C_{13}-C_{15}-C_{16}$		120.1
$C_{14}-C_{13}-C_{15}$	119.1	119.0

[a] Present work.

TABLE 2: Optimized B3LYP/6-31++G Geometrical Parameters of Relevant Dehydrogenated Pyrene Compounds in the Triplet State[a]**

parameter	pyrene	(C_1,C_8)	(C_1,C_2)	(C_4,C_5)	(C_2,C_{14})
		Bond Length (Å)			
C_1-C_2	1.395	1.374	1.396	1.394	1.382
C_2-C_3	1.406	1.414	1.389	1.407	1.389
C_3-C_4	1.439	1.437	1.442	1.425	1.438
C_4-C_5	1.363	1.363	1.362	1.362	1.363
C_1-C_{14}	1.395	1.374	1.377	1.396	1.382
$C_{11}-C_{12}$	1.363	1.363	1.364	1.363	1.363
$C_{12}-C_{13}$	1.439	1.437	1.438	1.439	1.438
$C_{15}-C_{16}$	1.428	1.430	1.428	1.429	1.428
C_1-H_{17}	1.086			1.086	1.088
C_2-H_{18}	1.087	1.087		1.085	1.087
C_5-H_{20}	1.087	1.087	1.087		1.087
$C_{11}-H_{24}$	1.087	1.087	1.087	1.087	1.087
$C_{14}-H_{26}$	1.087	1.087	1.087	1.087	
		Bond Angle (deg)			
$C_1-C_2-C_3$	120.7	117.3	121.8	120.2	125.7
$C_2-C_3-C_4$	122.4	121.9	123.4	123.4	124.9
$C_2-C_3-C_{15}$	119.0	119.2	117.4	119.6	115.9
$C_2-C_1-C_{14}$	120.6	126.4	121.6	120.8	115.4
$C_3-C_{15}-C_{16}$	120.1	119.8	119.5	120.6	119.5
$C_5-C_6-C_{16}$	118.6	118.9	118.7	116.9	118.9
$C_{12}-C_{13}-C_{14}$	122.4	121.8	122.0	122.3	124.8
$C_{13}-C_{15}-C_{16}$	120.1	119.8	120.0	120.0	119.4
$C_{14}-C_{13}-C_{15}$	119.0	119.2	119.3	119.2	116.0

[a] Pyrene structure in the singlet state is included for comparison.

out that the NICS provides information about the relative stability of these polycyclic π-conjugated systems. However, one must point out that this agreement between NICS predictions and relative stability is not universal. This is because the NICS values provide information arising from the ring current contributions. There are several examples in the literature showing that the magnetic criterion of aromaticity does not always follow the energy one.[51−53]

All DFT calculations have been carried out using the Gaussian98 suite of programs,[54] whereas CASSCF and CASPT2 calculations have been carried out using MOLCAS 5.4 program.[55]

Results and Discussion

The close agreement between X-ray structure[56] and the B3LYP/6-31++G** optimized geometry of isolated pyrene (Table 1) provides the first evidence of the reliability of this level of theory. The pyrene singlet−triplet gap is 48.5 kcal/mol. The geometry optimization process results in a canonical form in which the *a* and *b* rings (Figure 1) have a localized sextet, respectively; whereas the *c* and *d* ones have double bonds in C_4-C_5 and $C_{11}-C_{12}$ (1.363 Å), respectively. Accordingly, NICS analysis gives −14.6 and −6.9 ppm of aromatic character, for the benzenic and nonbenzenic rings, respectively, as detailed below. Therefore, the prediction of the existence of benzyne-like moieties in pyrene didehydrogenated species cannot be directly predicted from the analysis of the benzyne species formation from benzene. In particular, different didehydrogenated pyrene compounds can be formed depending on the two carbon atoms chosen to extract the hydrogen atoms.

The structure of the three different monoradicals does not evidence significant changes and the total energy of these radicals differ in less than 0.5 kcal/mol, C_1 and C_4 radicals having the same energy and that of the C_2 one being only slightly higher. Within the present computational approach the three monoradicals should be considered isoenergetic. Next, the different didehydropyrene species in the triplet and singlet states are analyzed. In the triplet state, the optimized structure of all different dehydrogenated pyrene compounds is very close to

that of pyrene. The analysis of spin density reveals that it is strongly localized on the carbon atoms where atomic hydrogen has been extracted. This result provided evidence of the diradical character of all these species. Table 2 reports a summary of structures for a selected group of diradicals and confirms the above statement. From the pyrene open-shell singlet diradicals, (C_1,C_8) is taken as a prototypal case, the optimized structure is also very close to that obtained for the triplet state. Moreover, the energy of the broken symmetry solution used to find the open-shell singlet energy[39,41,57] is nearly degenerate compared to that of the triplet state; as expected[58] the spin density exhibits a localized character, as in the triplet state, and differs from that of the triplet state only in the fact that, here, the two unpaired electrons have opposite spin. Moreover, the expectation value of the square of the total spin operator (which strictly speaking should not be used in DFT) for the broken symmetry solution is close to one. This indicates that the electronic structure of these species, although calculated as a broken symmetry solution which effectively corresponds to roughly 50% mixture of singlet and triplet states,[41,57] can in fact be described as an open-shell singlet of diradical character. As pointed out above, the proper description of this open-shell singlet involves at least two electronic configurations, each of closed-shell nature but the resulting wave function with two natural orbitals with occupation numbers close to one. This is fully confirmed by the CASSCF and CASPT2 results reported in Table 3 for the (C_1,C_8) compound. Notice that for these diradicals, the energy of the singlet state is obtained from the broken symmetry solution and using the appropriate projection.[41] Nevertheless, one must realize that such projection is based on the expectation value of the square of the total spin operator, which as pointed out above, is not directly obtained in DFT.[59,60]

For three didehydrogenated pyrene compounds—(C_1,C_2), (C_2,C_{14}), and (C_4,C_5)—the situation is completely different from that for the rest of didehydropyrene compounds. In fact, it is found that, for these three didehydropyrenes, the lowest singlet corresponds to a closed-shell electronic structure. In this case the closed-shell singlet can be properly described with a single configuration with occupied natural orbitals with occupation

TABLE 3: Summary of CASSCF and CASPT2 Energies (in kcal/mol) of Relevant Didehydrogenated Pyrene Species in the Triplet and Lowest Singlet State Relative to that of the (C_4,C_5) Species in the Lowest Singlet State[a]

	CASSCF			
	triplet		singlet	
compound	CAS(2,2)	CAS(4,4)	CAS(2,2)	CAS(4,4)
(C_1,C_2)	55.2	41.7	9.4 (97.3; 2.7)	8.6 (97.0; 1.5)
(C_1,C_8)	12.9	4.8	12.9 (50.1; 49.9)	4.8 (79.1; 9.0; 8.0)
(C_2,C_{14})	63.3	6.4	34.5 (97.8; 2.2)	19.7 (93.5; 2.0; 1.8)
(C_4,C_5)	43.4	20.1	0.0 (96.5; 3.5)	0.0 (96.2; 3.5)

	CASPT2			
	triplet		singlet	
compound	CAS(2,2)	CAS(4,4)	CAS(2,2)	CAS(4,4)
(C_1,C_2)	58.7	58.1	5.2	3.8
(C_1,C_8)	34.5	31.7	34.5	31.5
(C_2,C_{14})	67.9	28.4	16.6	13.3
(C_4,C_5)	54.4	32.1	0.0	0.0

[a] For the singlet state numbers in parentheses the composition of the CASSCF wave function given in percent, in the CAS(4,4) only contributions larger than 1.5% are given. In all cases (C_1,C_2), (C_2,C_{14}) and (C_4,C_5) have natural orbital occupations ∼2.0 whereas for (C_1,C_8) there are two natural orbitals with occupations ∼1.0.

TABLE 4: Optimized B3LYP/6-31++G Geometrical Parameters of Relevant Dehydrogenated Pyrene Compounds in the Lowest Singlet State[a]**

parameter	pyrene	(C_1,C_8)	(C_1,C_2)	(C_4,C_5)	(C_2,C_{14})
	Bond Length (Å)				
C_1-C_2	1.395	1.374	1.249	1.398	1.358
C_2-C_3	1.406	1.414	1.393	1.396	1.384
C_3-C_4	1.439	1.437	1.429	1.420	1.442
C_4-C_5	1.363	1.363	1.364	1.234	1.369
C_1-C_{14}	1.395	1.374	1.382	1.392	1.358
$C_{11}-C_{12}$	1.363	1.363	1.362	1.362	1.369
$C_{12}-C_{13}$	1.439	1.437	1.440	1.439	1.442
$C_{15}-C_{16}$	1.428	1.430	1.429	1.440	1.408
C_1-H_{17}	1.086			1.086	1.084
C_2-H_{18}	1.087	1.087		1.085	
C_5-H_{20}	1.087	1.087	1.087		1.087
$C_{11}-H_{24}$	1.087	1.087	1.087	1.087	1.087
$C_{14}-H_{26}$	1.087	1.087	1.084	1.087	
	Bond Angle (deg)				
$C_1-C_2-C_3$	120.7	117.4	126.9	119.9	144.8
$C_2-C_3-C_4$	122.4	121.9	129.7	129.9	129.3
$C_2-C_3-C_{15}$	119.0	119.2	109.9	120.7	113.2
$C_2-C_1-C_{14}$	120.6	126.4	128.6	120.7	89.9
$C_3-C_{15}-C_{16}$	120.1	119.8	118.3	122.4	122.9
$C_5-C_6-C_{16}$	118.6	118.9	119.2	109.3	118.2
$C_{12}-C_{13}-C_{14}$	122.4	121.8	120.4	121.7	129.3
$C_{13}-C_{15}-C_{16}$	120.1	119.8	119.8	119.7	122.9
$C_{14}-C_{13}-C_{15}$	119.0	119.3	121.4	119.4	113.2

[a] Pyrene structure in the singlet state is included for comparison.

numbers equal to two. Again, this is confirmed by the CASSCF and CASPT2 calculations described in Table 3; notice that in this case the contribution of the dominant configuration is larger than 95%. Table 4 reports the geometrical structure of these didehydropyrene species and also includes the prototypal (C_1,C_8) structure in the broken symmetry state for comparison. Comparing the triplet and singlet structures of the (C_1,C_2) and (C_4,C_5) didehydropyrene species, one readily notices that there is a very large difference in the C_1-C_2 and C_4-C_5 distances (see numerals marked in bold in Table 4). Obviously, while the triplet state of these three species has a clear diradical character, the singlet state of these three compounds does not exhibit diradical character at all.

First, not taking into account the (C_1,C_2), (C_4,C_5) and (C_2,C_{14}) didehydropyrenes, which will be further discussed below, the

average energy cost to form the diradical species in the triplet/singlet state plus molecular hydrogen is 124.9/124.4 kcal/mol with a standard deviation of 0.3/0.8 kcal/mol, only. This clearly shows that all these species are nearly isoenergetic and both singlet and triplet states can be properly described as diradicals. Indeed, the singlet−triplet gap never exceeds 3 kcal/mol, as can be expected for a prototypal diradical.[58] Now, for the (C_1,C_2), (C_2,C_{14}), and (C_4,C_5) didehydropyrenes the singlet state energy is substantially lower than that of the triplet state. In these three cases the B3LYP singlet−triplet gaps are 31.2, 35.8, and 9.5 kcal/mol strongly suggesting that these three species have a marked benzyne character. Notice, however, that while the general trends predicted by B3LYP and the more accurate CASSCF and CASPT2 methods are the same, the B3LYP triplet states corresponding to these three didehydrogenated pyrene compounds appear at energies which are significantly lower than those predicted from the CASSCF and CASPT2 methods. This apparent contradiction is due to the fact that the triplet states of these three didehydropyrene compounds require a larger CAS because of the coupling between the two π-systems, the one corresponding to the aromatic system and the one corresponding to the broken bond. Results obtained including four electrons and four orbitals in the active space lead to singlet−triplet differences in a much better agreement with the B3LYP results (Table 3). However, in all cases, the CASSCF wave function exhibits a clear dominants configuration and hence a single-reference character. Moreover, the CASSCF and CASPT2 single-triplet differences for the (C_1,C_2) compound seems to be still too large, indicating that further extension of the CAS is needed to properly describe this electronic state through these explicitly correlated methods. Surprisingly, the single-reference B3LYP method provides results that are similar to those predicted by the CASPT2 one and at a lower computational cost. The B3LYP energy cost to form the closed-shell electronic structure for the (C_1,C_2), (C_4,C_5), and (C_2,C_{14}) dehydropyrenes in the singlet state plus molecular hydrogen, drops from ∼125 kcal/mol for all other cases discussed above to 100.8, 97.4, and 118.1 kcal/mol, respectively. These values are significantly lower than the experimental energy cost to didehydrogenate ethene and benzene, 135.7 and 190.9 kcal/mol, respectively, to form ethyne and o-benzyne, respectively.[61] The case of the (C_2,C_{14}) didehydropyrene deserves a further comment since accurate explicitly correlated calculations show that B3LYP and other DFT schemes give poor results for m-benzyne.[17,20] However, one must notice that while in the case of m-benzyne, DFT favors the bicycle species; this is not the case for the (C_2,C_{14}) species.

These results can be rationalized in accordance with the pyrene electronic structure analysis along with the examination of the geometrical parameters as follows: First of all, the (C_1,C_2) and (C_2,C_{14}) didehydropyrenes can be properly defined as benzynes, these are formed from a conjugate bond region whereas the (C_4,C_5) comes from a double bond. Thus, the most stable didehydropyrene compound with benzyne character is obtained away from the benzenic aromatic region. Notice that this cannot not be inferred from the analysis of the benzyne species coming from the benzene molecule. Additionally, the analysis of the geometrical parameters will permit us to understand why these species exhibit a closed-shell singlet electronic ground state. A summary of B3LYP energies relative to the most stable species is reported in Table 5.

From the above discussion it appears that singlet state (C_1,C_2) and (C_4,C_5) are the most stable compounds that will be formed upon pyrene dehydrogenation. The analysis of the geometrical

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TABLE 5: Summary of B3LYP/6-31++G** Energies (in kcal/mol) of the Different Didehydrogenated Pyrene Species in the Triplet and Lowest Singlet[a] State Relative to that of the (C_4,C_5) Species in the Lowest Singlet State (-614.472796 au)

compound	triplet	singlet
(C_1,C_2)	34.5	3.4
(C_1,C_4)	27.0	27.1
(C_1,C_5)	25.6	26.4
(C_1,C_7)	27.6	27.5
(C_1,C_8)	27.1	27.1
(C_2,C_4)	28.1	28.1
(C_2,C_5)	27.7	27.3
(C_2,C_7)	27.9	27.9
(C_2,C_8)	27.6	27.5
(C_2,C_9)	27.1	27.6
(C_2,C_{11})	27.1	27.1
(C_2,C_{12})	27.9	27.6
(C_2,C_{14})	30.1	20.7
(C_4,C_5)	35.8	0.0
(C_4,C_{11})	26.7	26.9
(C_4,C_{12})	25.5	25.4

[a] Singlet energies are obtained from the broken symmetry (BS) and triplet (T) energies as $E_S = 2E_{BS} - E_T$ (cf. refs 41 and 57).
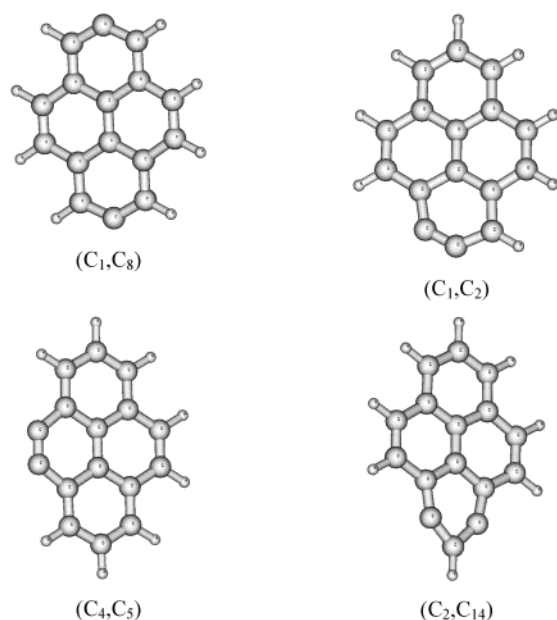
Figure 2. Optimized structures of the (C_1,C_8), (C_1,C_2), (C_2,C_{14}), and (C_4,C_5) pyrene diradicals in the lowest singlet state.

parameters in Table 4 reveals that in the closed-shell ground state the C_1-C_2 and C_4-C_5 distances are much shorter than in the triplet state with values close to those encountered in typical $C-C$ triple bonds; see also Figure 2. Therefore, these two structures are better described as *o*-benzyne-like compounds. Similarly, the strongly distorted structure of the (C_2,C_{14}) singlet species suggests that this compound is better described as *m*-benzyne derivative although, in the view of previous results for *m*-benzyne,[17,20] this assignment has to be taken with care. Notice that the $C_1-C_2-C_{14}$ bond angle becomes $\sim90°$, and the C_2-C_{14} distance 1.919 Å; even shorter than that reported for *m*-benzyne.[15] Hence, the present calculations suggest to rule out the existence of a bicyclic structure, at least for this pyrene derivative. Therefore, it can be concluded that the formation of benzyne-like species is the responsible for the closed-shell electronic structure of the (C_1,C_2), (C_4,C_5), and (C_2,C_{14}) diradical singlet species and, compared to the triplet diradicals, for their lower energy. Moreover, the fact that both the (C_1,C_2) and (C_4,C_5) compounds can be described as *o*-benzyne derivatives

explains their relative stability with respect to (C_2,C_{14}). To have an approximate idea of the different reactivity of the different didehydropyrene compounds, we examine the thermochemistry of the reaction between didehydrobenzene and pyrene to give benzene plus didehydropyrene. The pyrene + 1,2-didehydrobenzene → 4,5-didehydropyene + benzene reaction is exoergic by 3.8 kcal/mol whereas pyrene + 1,2-didehydrobenzene → 1,2-didehydropyene + benzene is almost isoenergetic, only 0.3 kcal/mol exoergic. Finally, the reaction involving pyrene + 1,2-didehydrobenzene → 2,14-didehydropyene + benzene is endoergic by 16.9 kcal/mol. In principle the two former reactions are likely to occur in the gas phase, (provided the energy barrier is sufficiently low) whereas the later is unfavored. For all other didehydropyrenes with diradical character, the reaction is endoergic by ∼31 kcal/mol. Therefore, the present results strongly suggest that once a benzyne species is formed, it will interact with other PAHs in such a way that the benzyne moiety can be transferred from one molecule to the other. Nevertheless, one must appreciate that the didehydropyrene compounds with diradical character will exhibit a higher reactivity.

Finally, the NICS values computed at the center of each aromatic ring are used to estimate the stability provided by aromaticity. Hence, NICS values computed for the (C_1,C_2) and (C_4,C_5) *o*-benzyne derivatives will be compared with those reported above for pyrene. For the (C_1,C_2) *o*-benzyne species, the NICS value at the *a* ring, where the C≡C bond is located, is -22.3 ppm, even larger than in pyrene. This is a clear indication of the stability of this *o*-benzyne derivative. For (C_4,C_5), the most stable *o*-benzyne species, the NICS value is smaller (-20.7 ppm) indicating a decrease in the aromaticity of the *a* and *b* rings and an increase in the *c* one; notice again that this is the ring containing the C≡C bond. In this case, the NICS value is smaller because this benzyne is formed over a double bond ring. Therefore, the calculated NICS value at the ring where the C≡C bond is located permits to rationalize the different stability of these two *o*-benzyne derivatives.

Summary and Conclusions

The geometry and electronic structure of the different compounds that can be formed upon pyrene dehydrogenation have been studied by means of the B3LYP density functional method which has proven to accurately predict the thermochemistry of a large number of organic compounds. The interpretation of the B3LYP electronic structure of the different types of didehydropyrene compounds has been confirmed by CASSCF and CASPT2 calculations. At first glance one would expect the formation of diradical species and, hence, geometry optimization was carried out for the lowest singlet and triplet states. For the compounds where two hydrogen radicals (H•) have been removed from the (C_1,C_4), (C_1,C_5), (C_1,C_7), (C_1,C_8), (C_2,C_4), (C_2,C_5), (C_2,C_7), (C_2,C_8), (C_2,C_9), (C_2,C_{11}), (C_2,C_{12}), (C_4,C_{11}), and (C_4,C_{12}) carbon atom pairs (Figure 1), the geometry and energy of the singlet and triplet states are very close. Indeed, in these cases the singlet state has a clear open-shell character. Hence, the resulting species can be described as pyrene diradicals and the B3LYP energy cost to form them (singlet or triplet) plus the hydrogen molecule is always ∼125 kcal/mol. However, for the compounds formed by removing two H• radicals from the (C_1,C_2), (C_2,C_{14}), and (C_4,C_5) carbon atom pairs the lowest singlet exhibits a closed-shell electronic structure. In these three cases, inspection of the geometrical structure led us to suggest that these species are better described as benzyne derivatives. Clearly, the *o*-benzyne compounds— (C_1,C_2) and (C_4,C_5)—are more stable than the (C_2,C_{14}) *m*-

benzyne. These *o*-benzynes have energies 24 and 27 kcal/mol, respectively, lower than the average energy of the family of pyrene diradicals described above; the different stability being nicely explained by the computed NICS values. The fact that *ortho* species exhibit a significant greater stability than the corresponding pyrene diradicals has important chemical consequences. Being thermodynamically favored, these benzyne species are likely to be formed under crude oil extraction conditions. However, these species should exhibit a high reactivity. In particular, they are susceptible of Diels−Alder condensation. We suggest that this is a possible mechanisms contributing in and to the formation of asphaltene phases and aggregates.

Supporting Information Available: Tables of Cartesian coordinates and total energies for the hydrogen molecule, pyrene, the three distinct pyrene radicals, and the different dehydrogenated compounds in their lowest singlet or triplet state and the CASSCF and CASPT2 energies of relevant didehydrogenated pyrene species in the triplet and lowest singlet state relative to that of the (C4,C5) species in the lowest singlet state. This material is available free of charge via the Internet at http://pubs.acs.org.

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