

# Triplet fluoranthenes: Aromaticity versus unpaired electrons

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**Abstract** Three fluoranthenes and one substituted fluoranthene, 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene, were investigated using the unrestricted symmetry-broken and complete active space methods. It was shown that four Kekuléan hydrocarbons are diradicals, implying that their ground state is a triplet. In the energetically less favorable singlet state these hydrocarbons exhibit pronounced diradical character. This occurrence is explained with the tendency of the investigated molecules to delocalize their  $\pi$ -electrons. This leads to aromatic stabilization which is stronger than destabilization due to unpaired electrons. Our results for 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene are in excellent accord with experimental findings of McMaster et al. concerning this compound.

**Keywords** Complete active space calculation · Diradical · Singlet diradical · Triplet state · Unrestricted symmetry-broken method

## Introduction

Fluoranthene is a well-known conjugated hydrocarbon present in large amounts in coal tar [1]. It consists of a benzene and naphthalene unit, joined through a five-

membered ring. Other polycyclic conjugated hydrocarbons consisting of two benzenoid units joined through a five-membered ring are referred to as fluoranthenes [2]. Interest for nonalternant polycyclic compounds of this kind has recently much increased, after the discovery that these are formed from benzenoid hydrocarbons in flash vacuum pyrolysis experiments (see [3, 4] and the references cited therein).

A polycyclic conjugated hydrocarbon is said to be *Kekuléan* if it possesses at least one Kekulé structure, i.e., a resonance formula in which all carbon atoms are pairwise joined by double bonds [5, 6].

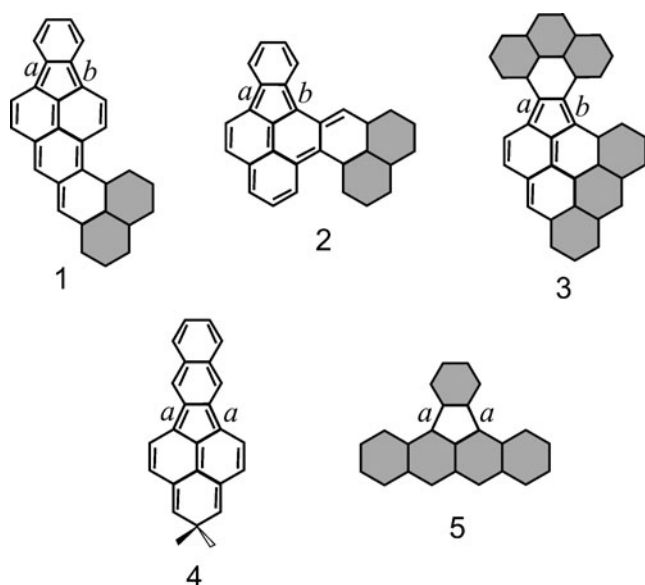
While studying  $\pi$ -electron properties of fluoranthenes [7–9], we observed that there is a class of such compounds that possesses unusual Kekulé structures [10]. The Kekulé structures of these fluoranthenes possess a significant number of fixed single and double bonds. Some characteristic representatives of these species are the fluoranthene congeners 1–3, depicted in Fig. 1.

Since the compounds 1–3 are Kekuléan, one would expect a singlet ground state for them. Surprisingly, however, our DFT calculations indicated that 1–3 are diradicals, implying that their triplet ground states are energetically more favorable than the singlet states. In addition, their singlet ground states exhibit a significantly large amount of diradical character.

A singlet diradical can be defined as a molecular species that has all paired electrons, but a pair of these electrons occupy different parts of space with a small sharing region. The ground state of such species is a singlet, yet they exhibit a pronounced diradical character. On the other hand, a diradical is a molecular species with two electrons occupying degenerate, or nearly degenerate, molecular orbitals (resulting in a triplet ground state). In this paper we will focus on Kekuléan diradical hydrocarbons.

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**Fig. 1** Triplet (1 – 4) and singlet (5) Kekulé fluoranthene-type polycyclic conjugated hydrocarbons. The shaded parts represent the domains without fixed single and double bonds, i.e., domains in which – according to the Kekulé model – the  $\pi$ -electrons are delocalized

Electronic structure of singlet diradicals with Kekulé structures has attracted significant attention [11–24]. Diradical character of Chichibabin’s hydrocarbon [11], substituted fluoranthenes [13], linear polyacenes [14, 17, 19, 24], phenalenyl-based hydrocarbons [15, 16, 18, 21–23], and zethrenes [20] was investigated using experimental and theoretical methods. On the other hand, the question whether Kekulé system can exist in a triplet ground state was examined less extensively. The assumption that a sufficiently small HOMO-LUMO gap should allow the promotion of an electron to give a diradical, resulted in proposing cyclohepta[*def*]fluorene [25], nonacene, and higher linear polyacenes [26–28] as possible representatives of triplet Kekulé hydrocarbons. However, cyclohepta[*def*]fluorene has never been synthesized. In addition, it was shown [14] that the RB3LYP wave function becomes unstable for as small a polyacene as hexacene, and all higher polyacenes. A reoptimization applying the unrestricted symmetry-broken method was performed, revealing that higher polyacenes exist in a singlet state with a large amount of diradical character. In agreement with these findings, high level *ab initio* calculations showed that the ground state of linear polyacenes is a singlet for all chain lengths from naphthalene to dodecacene [19]. Furthermore, the assumptions that anthracene-2,3-dimethylene [29], cyclopenta[*a*]cyclopenta[*i*]anthracene [30], as well as pleiadene and benzopleiadene [31–34] are triplet Kekulé hydrocarbons have never been confirmed.

To our best knowledge, the only known triplet Kekulé hydrocarbon is 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene (4 in Fig. 1) [13, 35]. This compound was generated

photochemically, and examined spectroscopically in a cryogenic matrix and in solution using nanosecond laser flash photolysis. On the basis of spectroscopic measurements, trapping experiments, and DFT calculations, the singlet-triplet gap for 4 was estimated to be 3.3 – 5.4 kJ mol<sup>-1</sup> in favor of the triplet [13, 35]. It is worth mentioning that the DFT calculation was actually performed on the relative of 4 in which the methyl groups were replaced with H atoms for the sake of computational feasibility.

In this work we report the results of a DFT study of three fluoranthene diradicals. Diradical 4 and the well-defined singlet indeno[1,2,3-*fg*]naphthalene (5 in Fig. 1) were also investigated using the same method. The electronic structure of diradical hydrocarbons in their singlet and triplet states is discussed in detail.

## Computational methods

All calculations were performed with the GAUSSIAN 03 W, version 6.1, program package [36], at the B3LYP/6-311G(d,p) level of theory [37, 38]. The effect of diffuse functions was examined by applying the B3LYP/6-311G++(d,p) method on singlet fluoranthene 5 and compound 4 whose triplet state has been confirmed experimentally [13, 35]. The frequency calculations showed that the examined structures have no imaginary vibrational frequencies. The hydrocarbons were calculated in their singlet and triplet states, using the restricted and unrestricted schemes for close-shell and open-shell calculations, respectively.

The singlet diradical character of the investigated hydrocarbons was estimated using a CASSCF(6,6) method in the RB3LYP/6-311G(d,p) optimized geometry, and a symmetry-broken UB3LYP/6-311G(d,p) method along with geometry optimization. The diradical index  $y$  was determined according to the NOON (natural orbital occupation number) analysis [39], i.e., on the basis of the occupation number ( $n$ ) of the LUMO, resulting from the CAS calculation. The diradical index ranges from 0% for close-shell states to 100% for pure diradical states. The applicability of the diradical index was tested on the basis of the results for singlet 5 and triplet 4.

## Results and discussion

The results of our investigation are summarized in Table 1. This table shows that the application of the 6-311G++(d,p) basis set to the compounds 4 and 5, i.e., the addition of diffuse functions, invokes only negligible structural and energetic changes. For this reason, all further discussion will be based on the B3LYP/6-311G(d,p) calculations.

**Table 1** Difference in total energy ( $\text{kJ mol}^{-1}$ ) between open shell symmetry-broken singlet and close shell RB3LYP solution ( $\Delta E_{\text{OS-CS}}$ ), singlet – triplet gap ( $\Delta E_{\text{T-OS}}$ ), spin contamination for the open shell singlet ( $\langle S^2 \rangle$ ), occupation number in the LUMO ( $n_{\text{LUMO}}$ ) resulting

from the complete active space calculation, and bond lengths ( $\text{\AA}$ ) for a and b (Fig. 1) resulting from the calculations for open shell symmetry-broken singlet (OS) and triplet (T) state

| Compound | $\Delta E_{\text{OS-CS}}^x$ | $\Delta E_{\text{T-OS}}^y$ | $\langle S^2 \rangle$ | $n_{\text{LUMO}}$ | $a_{\text{OS}}$                            | $b_{\text{OS}}$ | $a_{\text{T}}$   | $b_{\text{T}}$ |
|----------|-----------------------------|----------------------------|-----------------------|-------------------|--|-----------------|------------------|----------------|
| 1        | -36.5                       | -16.1                      | 1.03                  | 0.495             | 1.461                                      | 1.468           | 1.466            | 1.469          |
| 2        | -37.3                       | -16.5                      | 1.03                  | 0.431             | 1.460                                      | 1.471           | 1.464            | 1.472          |
| 3        | -5.4                        | -5.2                       | 0.51                  | 0.128             | 1.429                                      | 1.438           | 1.468            | 1.480          |
| 4        | -32.6<br>(-32.0)            | -7.5<br>(-7.4)             | 0.99<br>(0.99)        | 0.412             | 1.454<br>(1.454)                           |                 | 1.462<br>(1.462) |                |
| 5        | 0.0<br>(0.0)                | 96.7<br>(96.3)             | 0.00<br>(0.00)        | 0.069             | 1.474 <sup>z</sup><br>(1.474) <sup>z</sup> |                 | 1.465<br>(1.466) |                |

The results for **4** and **5** obtained at the B3LYP/6-311G++(d,p) level of theory are given in the brackets

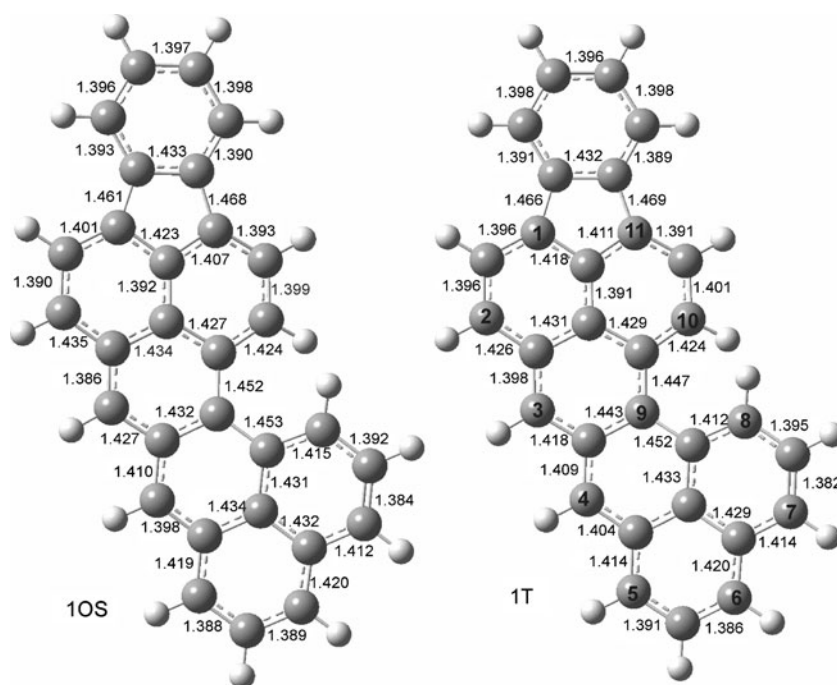
<sup>x</sup> Open shell singlet energy minus RB3LYP singlet energy. <sup>y</sup> Triplet energy minus open shell singlet energy. <sup>z</sup> The value is identical to that obtained by close shell calculation

As expected, the application of the symmetry-broken method to **5** resulted neither in energy lowering, nor invoked structural changes, in comparison to the close shell calculation (Table 1). This finding is in accord with the well-known fact that **5** is a singlet Kekulé hydrocarbon. In addition, the positive singlet – triplet gap for **5**, and negative singlet – triplet gap for **4** confirm the applicability of the unrestricted symmetry-broken method to the hydrocarbons under investigation. It is worth pointing out that the calculated value of the singlet - triplet gap for **4** ( $-7.5 \text{ kJ mol}^{-1}$ ) agrees well with the experimental estimation ( $-3.3 - -5.4 \text{ kJ mol}^{-1}$ ) [13, 35]. Taking into account the size of the investigated molecules, the spin contamination values are not very large.

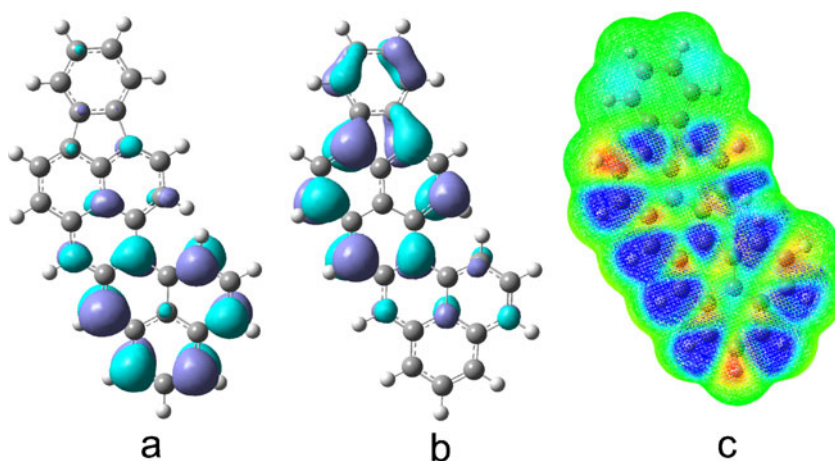
According to the values for  $\Delta E_{\text{T-OS}}$  and  $\Delta E_{\text{OS-CS}}$  in Table 1, hydrocarbons **1** – **4** are pure diradicals whose less favorable singlet states are best described with the unrestricted symmetry-broken method, and show pronounced diradical character. The values of diradical index  $y$  for the hydrocarbons **1** - **5** are calculated in this work, and they are equal to 50, 43, 13, 41, and 7 %, respectively. The very low  $y$  value for **5** is in agreement with its singlet nature. In the case of **3**, the low  $y$  value is in accord with the weak energetic stabilization expressed with the  $\Delta E_{\text{OS-CS}}$  and  $\Delta E_{\text{T-OS}}$  values (Table 1).

A striking feature of **1** – **4** (Fig. 1) is a large number of fixed double and single bonds, where the bonds marked by a and b are double in all Kekulé structures. Note that bond a

**Fig. 2** Optimized structures with indicated bond lengths ( $\text{\AA}$ ) for **1** as singlet diradical (**1OS**) and triplet diradical (**1T**)



**Fig. 3** SOMO (a), SOMO-1 (b), and spin density map (c) for **1 T**. In the spin density maps the blue and red regions indicate the highest and lowest spin density values, respectively. In the grayscale presentation the dark regions indicate the highest spin density values



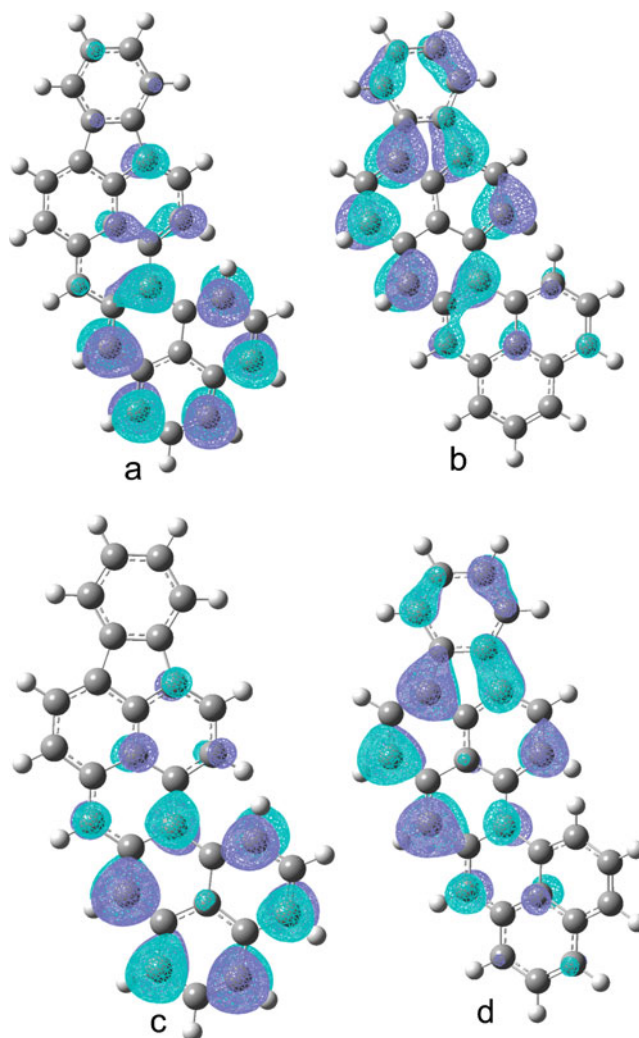
is single in all Kekulé structures for the singlet fluoranthene **5**. Table 1 shows that the bonds a and b, for both singlet and triplet state of **1–4**, lie in the range of single bonds, and are similar in length to  $a_{CS}$  for **5**. The only exception is **3**, where  $a_{OS}$  and  $b_{OS}$  have lengths characteristic to aromatic bonds. A careful examination of bond lengths for **1–4**, in both singlet and triplet state, reveal that very few bonds can be recognized as double and single, and the majority of bonds lie in the range of aromatic bonds [40]. Here we present the bond lengths for **1** in its singlet and triplet states, calculated in our study (Fig. 2), whereas the data for other diradicals are provided in Online Resource 1.

On the basis of the bond lengths one concludes that **1–4** are molecules with delocalized  $\pi$ -electrons, in both singlet and triplet states. This delocalization leads to aromatic stabilization, which is stronger than the destabilization due to unpaired electrons. Even in the singlet state these molecules show diradical character, because a singlet diradical structure provides a possibility for an electron pair to occupy different parts of space. Such a structure resembles a pure diradical structure, and allows for achieving aromatic stabilization.

**Table 2** Distribution of spin density, obtained by NBO analysis, in **1 T** (see Fig. 2 for atom labeling)

| C atom | Spin density |
|--------|--------------|
| 1      | 0.239        |
| 2      | 0.257        |
| 3      | 0.355        |
| 4      | 0.379        |
| 5      | 0.271        |
| 6      | 0.269        |
| 7      | 0.204        |
| 8      | 0.215        |
| 9      | 0.283        |
| 10     | 0.204        |
| 11     | 0.178        |

As for fluoranthenes examined in this work, aromatic stabilization for **1** and **2** is significantly stronger in comparison to **3** (Table 1). This finding can be explained with the fact that **3** possesses two large domains where



**Fig. 4**  $\alpha$ -HOMO (a),  $\beta$ -HOMO (b),  $\beta$ -LUMO (c), and  $\alpha$ -LUMO (d) of **1OS**

electron delocalization can be achieved (Fig. 1), no matter whether the compound is in singlet or triplet state.

The unpaired electrons in each diradical reside in the delocalized SOMOs. As an illustration, we present the SOMO, SOMO-1, and spin density map for **1 T** (Fig. 3), whereas the same results for other diradicals are provided in Online Resource 1. SOMO and SOMO-1 are almost degenerate (-0.171 and -0.179 eV). Obviously, SOMO and SOMO-1 occupy different parts of space with small sharing region, resulting in a spin density distribution over the entire molecule. The results of NBO analysis for spin density values in **1 T** (Table 2) are in perfect accord with the spin density map (Fig. 3).

The spatial diradical distribution in the singlet diradical structures was examined by inspecting HOMOs and LUMOs for  $\alpha$  and  $\beta$  spin electrons (Fig. 4). A remarkable feature of Fig. 4 is that  $\alpha$ -HOMO and  $\beta$ -LUMO of **1 OS** occupy practically the same part of space, involving approximately 0.75+0.25 electrons (according to the CASSCF(6,6) calculation). The same situation is found in the case of  $\beta$ -HOMO and  $\alpha$ -LUMO. In this way there are no unpaired electrons in **1 OS**, yet two of them occupy different parts of space, thus allowing the  $\pi$ -electrons to delocalize. The figures presenting HOMOs and LUMOs for  $\alpha$  and  $\beta$  spin electrons of other singlet diradicals are provided in Online Resource 1.

## Summary

The unrestricted symmetry-broken method was applied on a singlet indeno[1,2,3-*fg*]naphthacene (**5**) and 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene (**4**), whose triplet ground state has been verified experimentally [13, 35]. An excellent agreement with the experimental results confirms the applicability of the symmetry-broken method to the Kekuléan fluoranthenes **1–3**.

Our investigations reveal that the majority of bond lengths in the hydrocarbons **1–4** lie in the range of aromatic bonds, with very few bonds that can be recognized as single or double. This situation is a result of a tendency of **1–4** to delocalize their  $\pi$ -electrons, thus taking up diradical structures, and achieving aromatic stabilization. This implies that aromatic stabilization is stronger than destabilization due to unpaired electrons.

Even in the singlet state, these Kekuléan hydrocarbons show a pronounced diradical character, and their structures are best presented with that of singlet diradicals. Such structures provide a possibility for an electron pair to occupy different parts of space, and allows for achieving aromatic stabilization.

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