Search for singlet-triplet bistabilities in conjugated hydrocarbons

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The purpose of this paper is to search for bistable hydrocarbons for which the lowest singlet and triplet states are nearly degenerate in their substantially different equilibrium geometries, the two wells being separated by a significant energy barrier. For non-alternant hydrocarbons with fused odd-membered rings, two different ways to anticipate the spin multiplicity are in contradiction. A series of such molecules accepts a Kékulé structure, which suggests that the ground state is a singlet, while extended use of the Ovchinnikov rule predicts a triplet ground state. Calculations using both a geometry-dependent Heisenberg Hamiltonian and *ab initio* methods indicate that most of these hydrocarbons actually have a singlet ground state and a low-lying excited triplet state. Different ways to stabilize the diradical structure are studied. It is found that the presence of external fused six-membered rings on the non-alternant skeleton stabilizes the triplet state, leading to a bistability phenomenon. Such compounds should have interesting magnetic properties.

The bistability phenomenon has many technological implications. One can cite computers' Random Access Memory, which uses electronically bistable devices[1] or information storage, which is ensured by magnetic bistables. Indeed, one may expect that the extension of these applications to the molecular scale would be particularly interesting. Numerous studies have been devoted to this subject.[2–6] Here, we will concentrate on bistability involving states of different spin multiplicity. While this property has been observed in spin-transition compounds,[7–10] it seems to be more difficult to obtain such a bistability in a single organic molecule. In most compounds, the energy difference between the lowest states of different spin multiplicity is quite substantial and their respective equilibrium geometries are close, so that only one corresponds to a minimum on the lowest potential energy surface, which is unique once the spin–orbit interaction is considered. As a counterexample one might cite the CHCl diradical, which, according to previous work,[11] exhibits a singlet-triplet bistability, but the well-known reactivity of carbenes makes them irrelevant for any practical purpose.

The aim of the present work is to propose bistable hydrocarbons presenting both singlet and triplet ground states. This property corresponds to the presence of two wells relative to those two spin states, which are sufficiently separated on the potential energy surface, so that each state is the ground state in its own equilibrium geometry.

In the first section, we review the conditions that molecules should fulfill to present a bistability phenomenon[12–14] and identify a paradigm to look for bistable molecules involving singlet and triplet states. The idea is to find molecular structures satisfying two contradictory rules for the assessment of the ground state spin nature.

A theoretical description is developed in the second section, showing the ability of a geometry-dependent Heisenberg Hamiltonian[15,16] to give reliable results for the compounds studied here by comparing them to accurate *ab initio* calculations.

The third section is devoted to the search for suitable candidates. It is shown that some non-alternant hydrocarbons presenting two fused odd-membered rings accept a Kékulé structure, suggesting a singlet ground state, while the minimum number of spin frustrations is obtained for a triplet state. Since most of the unsubstituted systems that follow these ideas appear to have a unique singlet minimum in the lowest potential energy surface, several ways are investigated to stabilize the triplet one. Some factors such as the delocalization of the unpaired electrons are discussed and the key role of the aromaticity of lateral fused six-membered rings is shown. Finally, an interesting candidate is proposed on the basis of the geometry-dependent Heisenberg Hamiltonian, which is confirmed by *ab initio* calculations.

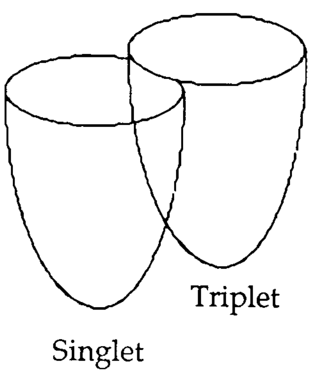
A further qualitative discussion suggests multistable molecules involving states of higher spin multiplicity.

Principle

Bistability conditions

The bistability phenomenon can be analysed in terms of two distinct wells on the potential energy surface as shown in Scheme 1. The ground state is of singlet (or triplet) nature in its equilibrium geometry, while it becomes an excited state in the equilibrium geometry of the triplet (the singlet).

Let us call ϕ_1 and ϕ_2 the singlet and the triplet states, respectively. It is unfortunately difficult to explore the complete potential energy surface but one can obtain a qualitative picture of the problem by defining a geometrical parameter k that describes a linear change of the geometry G between the equilibrium geometries G_1 and G_2 of the two spin states ϕ_1



Scheme 1

and ϕ_2. The geometry G can be expressed as a function of k:

$$G(k) = \frac{G_1 + G_2}{2} + \left(\frac{G_2 - G_1}{2}\right)k$$

such that: $k = 1$, $G = G_2$; $k = 0$, $G = (G_1 + G_2)/_2$; and $k = -1, G = G_1$.

It has been shown in previous works[12–14] that the bistability phenomenon can be treated through a two-state analytic model. The bistability conditions can be summarized as a near degeneracy between two weakly coupled states corresponding to quite different equilibrium geometries. In the case considered here, the coupling is due only to spin–orbit interactions, which are very weak in hydrocarbons. Therefore, one may expect that this effect should not lower appreciably the potential energy barrier between the two states. So, the main difficulty resides in finding molecules for which the two spin states are nearly degenerate but with very different geometries. Of course, the optimal situation is obtained when the two spin states are degenerate or quasi-degenerate and separated by a high potential energy barrier.

A paradigm to suggest singlet-triplet bistable hydrocarbons

When a conjugated hydrocarbon adopts a unique Kékulé structure with alternating single and double bonds, the experimental geometry of that molecule is usually in agreement with the Kékulé structure, presenting short and long C—C bonds and having a singlet ground state.

When several electronic structures are possible (including at least one Kékulé form), the resonance between these different structures can lead to an intermediate conformation as occurs in Chichibabin's hydrocarbon,[17] the equilibrium geometry of which is halfway between those of quinoidal and diradical limiting forms.[18,19] Nevertheless, such compounds also have a singlet ground state.[20] Therefore, the existence of a Kékulé structure is generally taken as an empirical indication that the ground state is of singlet nature since it is based on strong local pairing of α, β electrons.

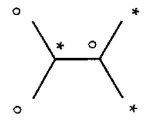
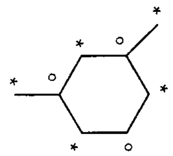
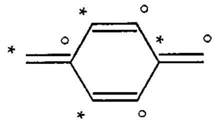
Another way to anticipate the spin multiplicity is obtained from the Ovchinnikov rule.[21] For alternant (*i.e.* spin non-frustrated) hydrocarbons, the spin nature of the ground state is determined by the spin multiplicity of the most alternant spin distribution. This rule has been confirmed by studies on numerous polyradical hydrocarbons,[15,22] without any counterexamples. In the present case, we shall refer to an extension of the Ovchinnikov rule, applying it to non-alternant skeletons considering that again the S_z value of the most alternant spin distribution defines the spin multiplicity of the ground state (*i.e.* if the optimal S_z value is equal to 1, the state will be a triplet). Within the molecular orbital (MO) picture, one may use the rules concerning the nonbonding orbitals (NBMO) proposed by Borden and Davidson[23] for polyradicals (*cf.* Appendix).

According to these two rules, hydrocarbons can be divided into three classes. Examples of hydrocarbons belonging to these different classes are itemized in Table 1.

In the first class are the non-Kékulé hydrocarbons. For them, the only way to anticipate the spin multiplicity of the ground state is to use Ovchinnikov's rule. As examples, let us consider the following two molecules (see Table 1). In dimethylene-2,3-butadiene the Ovchinnikov rule pleads in favour of a singlet ground state, while it indicates a triplet ground state in *m*-dimethylenebenzene whose most alternant spin configuration possesses five (*, alpha) and three (○, beta) spins.

In a second class, we will consider hydrocarbons for which both rules apply and converge to predict a singlet ground state, *i.e.*, they present at least one Kékulé form and their most alternant spin distribution has the same number of α and β spins. To illustrate this case, we may consider *p*-dimethylenebenzene, which is known to have a singlet quinoidal ground state. The unique Kékulé form of this molecule, as well as its fully alternant spin distribution ($S_z = 0$), are represented in Table 1.

Table 1 Examples of hydrocarbons belonging to the three classes

	$S_z = 0$	$S_z \geqslant 1$
non-Kékulé hydrocarbons		
Kékulé hydrocarbons		This work

The last class appears as the most interesting one for our study. It contains hydrocarbons for which both rules may be applied but are in contradiction, *i.e.*, it is possible to find at least one Kékulé form while the most alternant spin distribution does not satisfy $\langle S_z \rangle = 0$. One should expect that such molecules could be interesting candidates for bistability. Of course, since we will be more interested in bistables involving a singlet and a triplet state, we will concentrate here on systems whose most alternant spin distribution is of a triplet nature. The two states should have substantially different equilibrium geometries, but could perhaps be close in energy. Moreover, at variance with Chichibabin's compound, no mixing can lead to a single adiabatic state corresponding to an intermediate conformation. Therefore, for near-degenerate states, one may expect the coexistence of both the singlet and the triplet minima in the lowest potential energy surface, *i.e.* a bistability phenomenon.

In the following, we will study systems that belong to the third class.

Theoretical Description

It is quite difficult to describe the electronic structures of singlet-triplet bistable hydrocarbons. A recent work[24] on the subject of bistability or mixing between a quinoidal and a diradical structure has revealed the difficulty in treating such a problem with *ab initio* quantum chemical approaches. Surprisingly enough, computations carried out using a magnetic treatment of such systems give results[19] in good agreement with highly correlated treatments[24] such as very large CASSCF (Complete Active Space Self Consistent Field) or MRSDCI (Multireference Single and Double Configuration Interaction) ones and experimental evidence.[18] This magnetic treatment[15,16] has been proposed ten years ago by our group. It is based on a geometry-dependent Heisenberg Hamiltonian and gives quantitative geometries[25] for conjugated hydrocarbons at rather low cost.

The Hamiltonian may be written as

i.e.
$$H = \sum_{i,j} R_{ij} + g_{ij} | i\bar{j} - \bar{i}j \rangle \langle i\bar{j} - \bar{i}j |$$

where the indices i and j label bonded carbon atoms, bearing the 2_{p_z} $|i\rangle$ and $|j\rangle$ atomic orbitals. The parameters R_{ij} and g_{ij} are functions of the interatomic distances r_{ij}. This Hamiltonian works on the basis of all neutral valence bond (VB) single determinants and treats electronic delocalization through the effective exchange integrals g_{ij}, which incorporate the effect of mixing between neutral and ionic VB configurations. The values of $R(r)$ and $g(r)$ have been extracted from accurate *ab* *initio* calculations on the lowest singlet and triplet states of the ethylene molecule.

The method proceeds through the construction of a rather large-dimension Hamiltonian (C_{2m}^{m} for a system of $2m$ conjugated carbons) and its diagonalization. Its superiority over the traditional molecular orbital approach is that it does not assume any molecular orbital filling and it treats on an equal footing both closed shell and more-or-less diradical wavefunctions. The treatment of the triplet state, for instance, is as accurate as that of the singlet one.

In order to check the efficiency of this Heisenberg Hamiltonian for this type of compound, we have performed large CASSCF calculations in a double zeta (DZ) basis set for the first basic framework. Such calculations have also been performed on the finally proposed bistable molecule.

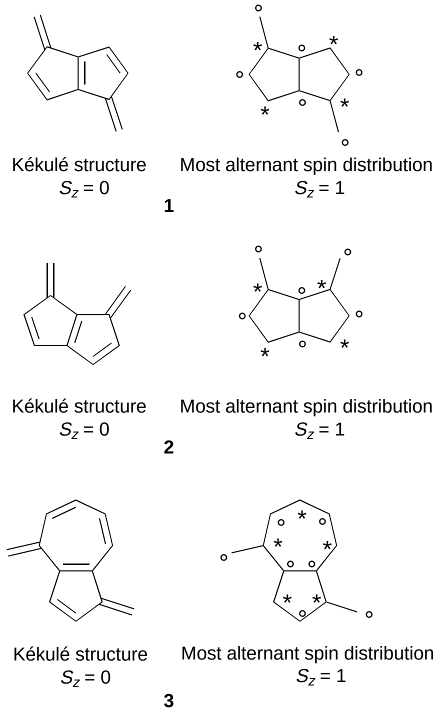
Search for an Appropriate Hydrocarbon

Basic frameworks

We have seen that hydrocarbons for which the rules presented above are in contradiction should be interesting candidates. Such a contradiction may be observed in all properly substituted non-alternant hydrocarbons constituted of fused odd-membered rings. Let us consider the non-alternant hydrocarbon (compound **1**) given in Scheme 2. The Kékulé structure indicates that the ground state should be of singlet nature. Since the system contains odd-membered rings, there is no fully alternating spin distribution. The most alternant spin determinant is obtained when the only spin frustration is on the bond common to the two cycles. It presents four (∗, alpha) and six (○, beta) spins, *i.e.*, it corresponds to a triplet state.

The expected equilibrium geometries are completely different in the two representations. In the Kékulé structure, the central bond is short and bond alternation is pronounced in the rings. On the other hand, the triplet state should present a long central bond (which bears the spin frustration) and one may expect that some bonds in the rings will have intermediate lengths due to the delocalization of the unpaired electrons.

Hence, one may hope that such a molecule will present a bistability phenomenon. The contradiction between the two rules should be observed in all properly substituted fused odd-membered rings, so the following study will concern three quite similar systems (compounds **1**, **2** and **3**) presenting this characteristic. Compounds **1** and **2** contain two five-membered rings and only differ by the position of the methylene end groups, which are *trans* or *cis*, respectively. The third compound contains one five- and one seven-membered ring.



Scheme 2

A first series of calculations have been performed using the Heisenberg Hamiltonian. The geometries of compounds **1**, **2** and **3**, optimized for both the singlet and the triplet states, are represented in Fig. 1. As expected, bond alternation is strong in the singlet states and the bond common to the rings is short (1.36 Å for **1** and **2**; 1.37 Å for **3**). On the other hand, this bond is long in the triplet states (1.48 Å for **1** and **2**; 1.45 Å for **3**) and the two bonds near the unpaired electrons in the rings favour their delocalisation.

The potential energy curves computed for the two spin states as a function of the parameter *k* are quite similar for the three compounds (see Fig. 2*a*). Unfortunately, the singlet states lie below the triplets for all *k* values. Nevertheless, the energy differences (summarized in Table 2) between the two states at the equilibrium geometries of the triplet ones are quite low (about 0.1 eV). The *trans* position of the tails (methylene end groups) is more likely to stabilize the triplet in compound **1**, showing that the *cis* isomer is less suitable than the *trans*.

To confirm these results and to test the predictability of this geometry-dependent Heisenberg Hamiltonian, CASSCF calculations on compound **1** have been performed using the MOLCAS package.[26] The active space contains all π electrons in all valence π molecular orbitals. The potential energy curves for the two competing states are given in Fig. 2*b* and compare remarkably well with those in Fig. 2*a*. At the equi-

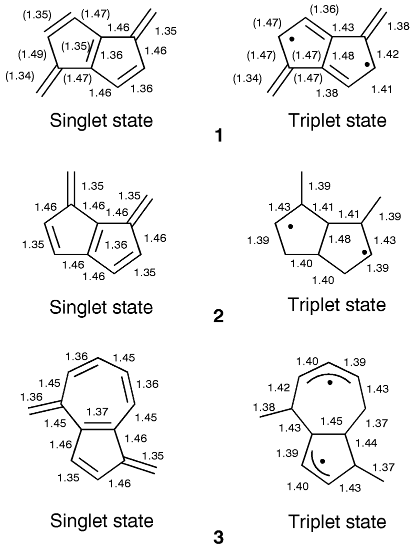


Fig. 1 Geometries of the singlet and the triplet states of compounds **1**, **2** and **3** optimized using the magnetic treatment. For **1**, bond lengths written in parentheses have been optimized at the HF level

Table 2 Energy difference between the lowest singlet and triplet states at the equilibrium geometry of the triplet, computed for compounds **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
ΔE_{ST}/eV	0.11	0.29	0.16	0.03

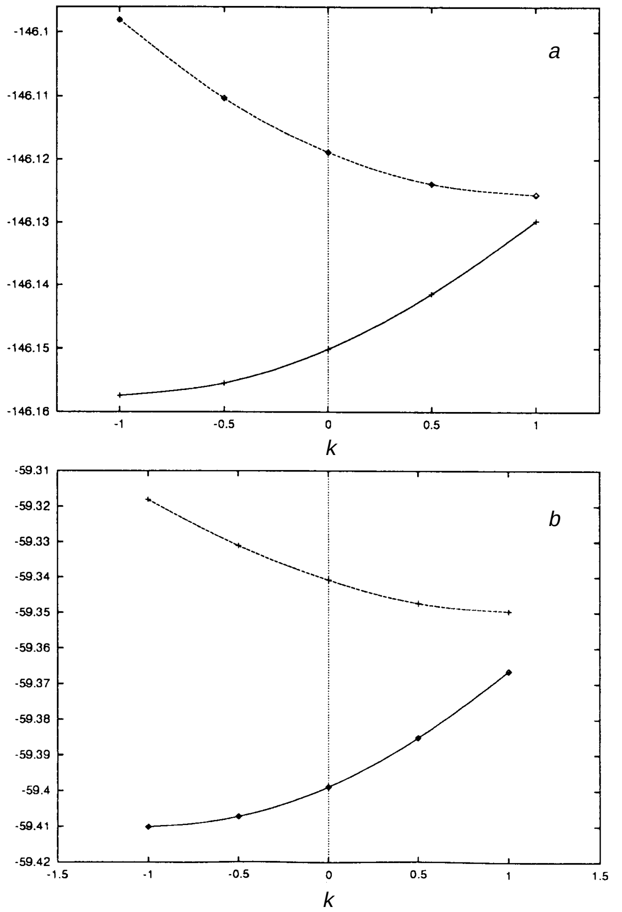


Fig. 2 Singlet (——) and triplet (----) potential energy curves computed for compound **1** using *a* the magnetic treatment and *b* the CASSCF method (all π electrons and orbitals are in the active space), as a function of the geometry change parameter *k*

librium geometry of the triplet state, the singlet state remains slightly below in energy. The geometries of the two spin states have been optimized at the Hartree Fock level (and DZ basis set) using the TURBOMOLE package[27] (see Fig. 1). They are quite similar for the two methods, the bond alternation being somewhat stronger with *ab initio* restricted HF (RHF) calculations, which overestimate this phenomenon. In view of the overall agreement, further explorations have been performed using the Heisenberg Hamiltonian.

In order to improve these architectures, one may think of stabilizing the diradical structure using substituents that delocalize the unpaired electrons.

Effect of delocalizing substituents

To estimate the effect of delocalization on the stability of the triplet state, we will consider only derivatives of compound **1**.

In the first proposition, two molecular tails are fixed on the carbons that bear the unpaired electrons. The resulting compound (**4**) is represented in the optimized geometries of the two spin states in Fig. 3. Looking at the bond lengths in the triplet state, one notices that the unpaired electrons are somewhat delocalized in the tails. The potential energy curves are, unfortunately, quite similar to the previous ones. The singlet remains again the ground state, whatever the geometry. Nevertheless, the energy difference (see Table 2) between the two spin states at the triplet equilibrium geometry is now only 0.03 eV. The effect of delocalization on the stability of the triplet is therefore quite important. Thus, one may suppose that the use of more electron-attracting ligands could change the relative stability of the two spin states at $k = 1$ (triplet equilibrium geometry), leading to a bistability phenomenon.

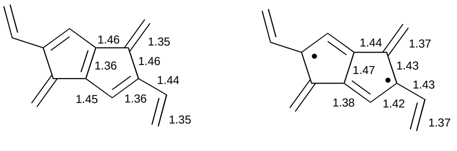


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Fig. 3 Geometries of the singlet and the triplet states of compound **4**, optimized using the magnetic treatment

The second proposition (compound **5**) contains carbon tails localized on peripheral bonds. The two optimized geometries are represented in Fig. 4. The bond lengths in the triplet equilibrium geometry show that delocalization has increased. This result is confirmed by the relative position of the two potential energy curves (see Fig. 5). The triplet state has been stabilized sufficiently to lie below the singlet one at $k = 1$. Therefore, this compound exhibits a bistability phenomenon. Of course, the energy difference between the two spin states in their own equilibrium geometries is quite substantial (0.85 eV) and the potential energy barrier is weak, but this compound constitutes an interesting milestone in the search for singlet-triplet bistable systems. So, let us try another way to stabilize the triplet.

Effect of aromaticity

In the molecules studied thus far, we have only examined the effect of delocalization in order to stabilize the diradical structure. Other phenomena may be considered. The presence of lateral six-membered rings, which would be aromatic only in the diradical structure, could also stabilize the triplet state. Indeed, the aromaticity energy gain is known to be quite high.[28] So the new proposition, compound **6** (see Fig. 6), introduces two six-membered rings fused to the basic non-alternant skeleton. These six-membered rings are aromatic in the triplet state but possess only two double bonds in the

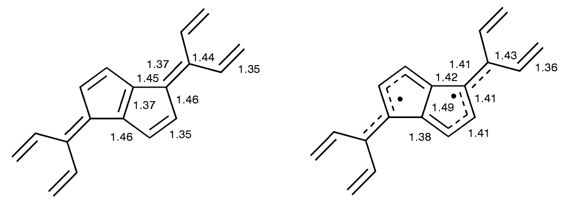

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Fig. 4 Geometries of the singlet and the triplet states of compound **5**, optimized using the magnetic treatment

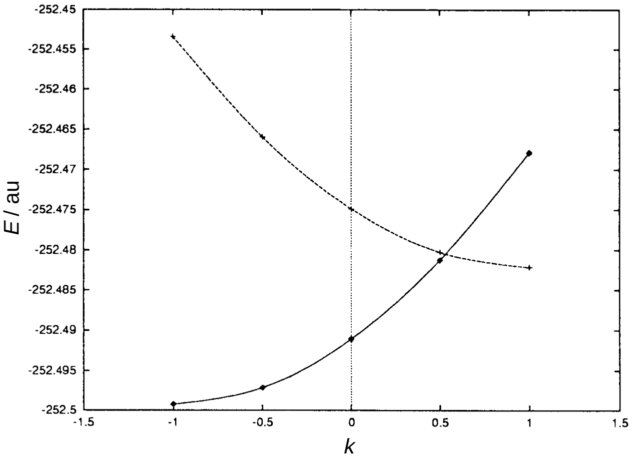
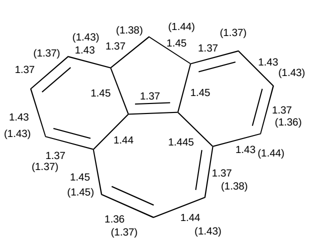
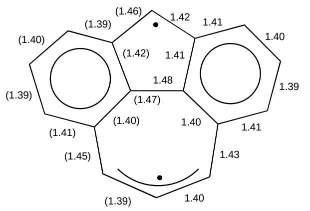


Fig. 5 Singlet (——) and triplet (----) potential energy curves as a function of the geometry change parameter *k* computed for compound **5** using the magnetic treatment



Singlet state



Triplet state

Fig. 6 Optimized geometries of the singlet and the triplet states of compound **6**, optimized using both the magnetic treatment and the HF method (in parentheses)

singlet. This molecule is constructed from compound **3**, which appeared (in the previous computations) to stablize more effectively the triplet state. The resulting architecture may also be represented using a Kékulé form, while its most alternant spin distribution is of triplet nature. The optimized geometries, represented in Fig. 6, share the same features as the previous ones. Bond alternation is strong in the singlet state while delocalization prevails in the triplet. The potential energy curves as functions of k are given in Fig. 7*a*. One finally obtains[29] two quasi-degenerate wells ($\Delta E = 0.046$ eV), separated by a non-negligible potential energy barrier ($E_B = 0.14$ eV).

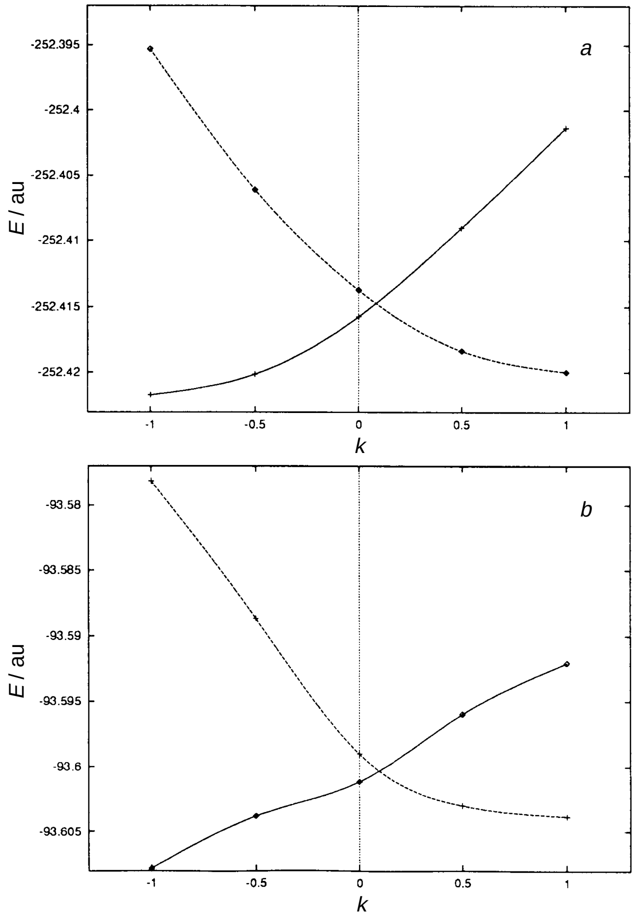


Fig. 7 Singlet (——) and triplet (----) potential energy curves as a function of the geometry change parameter k computed for compound **6** using *a* the magnetic treatment and *b* the CASSCF method (10 electrons in 10 orbitals)

We thought that such an hopeful result deserved to be checked by *ab initio* calculations and CASSCF computations with the largest possible active π space (ten electrons in ten molecular orbitals) have been performed. The potential energy curves given in Fig. 7*b* are quite similar to those of the above reported Heisenberg Hamiltonian calculations and confirm the bistability (the optimized RHF geometries are also in agreement with those predicted by the magnetic treatment, *cf.* Fig. 6).

According to our computations, this bistable compound appears to have all the required qualities. Such a molecule should have quite fascinating magnetic properties since the magnetic susceptibility is different in the two spin states. Assuming that an external perturbation is able to localize the system in the desired local state, one would be able to modify the magnetic property of this molecule. In order to change the localized state, one may, for example, apply an external force. Indeed, the equilibrium geometries in $k = 1$ and $k = -1$ are quite different: the singlet state is longer in the y direction (see Scheme 3) while the triplet is longer in the x direction. A material constituted of these molecules would be either diamagnetic or paramagnetic, according to the environment. We note that, for an appropriate superposition of the molecules and according to the intermolecular interactions, such a material could present a diamagnetic–ferromagnetic transition phase.

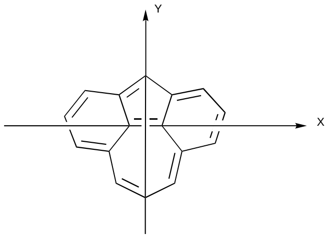
Since this last architecture seems attractive, one may imagine derivatives that would involve states of higher spin multiplicity. By juxtaposing two molecules, one obtains a fused entity, which is represented in Scheme 4. Such a molecule could be a singlet-quintet bistable system. By bridging them through an intermediate bond, one may design a possible singlet-triplet-quintet "tristable" system (see Scheme 5). Many other multistable systems can be pictured, starting from the basic entity. Unfortunately, the size of these molecules prohibits a quantitative study. Nevertheless, such compounds could constitute an exciting starting point in the search for multistable systems involving states of higher spin multiplicity.

Conclusion

This study centered on the search for bistable hydrocarbons for which both the singlet and triplet states correspond to stable (and different) geometrical conformations, each presenting a minimum on the lowest overall (including spin orbit) potential energy surface.

Using both a geometry-dependent Heisenberg Hamiltonian and *ab initio* (CASSCF) calculations, it has been shown that some non-alternant hydrocarbons with properly substituted fused odd-membered rings can exhibit a contradiction between the two rules that allow one to anticipate the spin multiplicity of the ground state. While those compounds all have a Kékulé structure, suggesting a singlet nature for the ground state, the extended use of Ovchinnikov's rule predicts a triplet one.

This contradiction is not sufficient by itself to ensure singlet-triplet bistability, as we have observed for the first set of compounds studied, since even so most of them have a singlet ground state and an low-lying excited triplet state. Different ways to stabilize the diradical structure were tried. Among the possibilities investigated, the addition of fused six-membered rings, which can either be aromatic or present localized double bonds, was very efficient and according to our calculations compound **6** should exhibit the desired bistability. For hydrocarbons the spin–orbit interaction is very weak and should not modify substantially the potential energy barrier separating the two wells.



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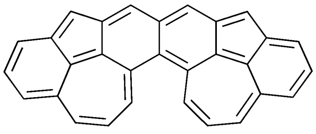
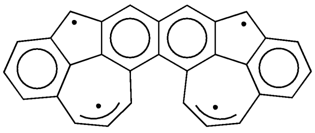
Scheme 3

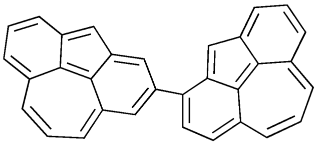


Singlet state

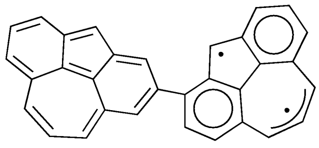


Quintet state

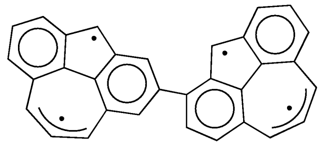
Scheme 4



Singlet state



Triplet state



Quintet state

Scheme 5

Organic compounds presenting a singlet-triplet bistability are certainly rare but are quite fascinating. One could expect that they would have interesting magnetic properties. Finally, this study must be considered as a first step in the search for multistable organic systems involving states of different spin multiplicities. As far as we know, there is no experimental study on the most interesting architecture proposed here. However, its structure does not seem particularly exotic and it could presumably be synthesized.

Appendix

As suggested by a referee, the triplet state stability may be rationalized by invoking the rules concerning the nonbonding molecular orbitals (NBMO) of diradicals, proposed by Borden and Davidson.[23] According to these rules, if one may fragment the diradical into two radicals, with delocalized NBMO, the highest orbitals of the diradical remain nearly degenerate when at least one of the NBMOs has zero amplitude on the atoms connecting the two fragments. These rules cannot apply directly to the proposed compounds, but if one neglects the spin-frustrated internal bond, which is very long in the triplet state, these rules may be applied. One sees that compound **1** may be considered as the interaction of two pentadienyl fragments with zero amplitude on the connecting atoms of at least one NBMO.

The same is true for compound **6**, which may be considered as being built from the interaction of a nonatetraenyl with a heptatrienyl, connected by atoms having zero amplitudes in one of the NBMOs.

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29 We call attention to an interesting characteristic of the potential energy surface. The symmetry of the singlet state is broken. Hence, a mirror-image broken-symmetry structure of singlet nature must exist, corresponding to a third minimum on the potential energy surface (PES). Resonance between these two singlet states is weak and therefore does not induce a sufficient mixing to result in an intermediate symmetrical conformation. The optimized symmetrical conformation is 0.1 eV above the symmetry-broken minima. We note that this symmetrical geometry strongly differs from the geometry of the triplet state (which is also symmetric) by the length of the bond common to the two odd rings and by a deviation from aromaticity in the six-membered rings in the singlet state. In fact, this compound is tristable, presenting three quasi-degenerate wells corresponding to two broken symmetry singlet states and to a symmetrical triplet one.

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