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Bis-periazulene: a simple Kekulé biradical with a triplet ground state*

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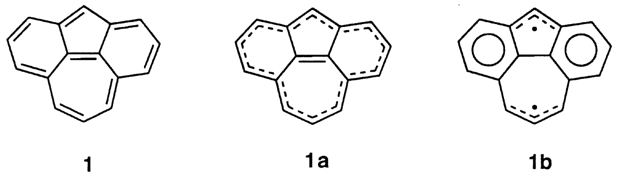
Abstract. B3LYP/6-31G* calculations on bis-periazulene (cyclohepta[*def*]-fluorene) predict a triplet ground state for this molecule. The singlet has an aromatic 14π-electron periphery but is 2 kcal/mol higher in energy. The results agree with earlier predictions by Heilbronner.

Key words: Aromaticity – Pyrene – Nucleus-independent chemical shift – Cyclohepta[*def*]fluorene – Diradical

1 Introduction

"Kekulé hydrocarbons" are unsaturated molecules whose electronic structures can be represented by closed-shell singlet resonance structures with normal single and double bonds. Such molecules normally have singlet ground states and are relatively unreactive. Antiaromatic Kekulé hydrocarbons, such as cyclobutadiene, or large extended conjugated systems such as polyacenes, have low-lying triplet states, but until recently, there were no examples of a Kekulé hydrocarbon with a triplet ground state [1].

Nonetheless, in 1965, Heilbronner predicted on the basis of PPP calculations that bis-periazulene (cyclohepta[*def*]fluorene), **1** (Scheme 1), would have a triplet ground state [2]. Surprisingly, the structure with the aromatic 14π-electron periphery and an ethylene center, **1a**, is expected on this basis to be less stable than the diradical structure, **1b**. Indeed, attempts to synthesize **1** and derivatives [3] have been unsuccessful, even when the precursors contain substituents which are likely to stabilize the diradical.[1] Why is this potentially aromatic compound, a biradical, too reactive to be isolated, and most probably a ground-state triplet hydrocarbon?



We have tested the Heilbronner prediction with density functional theory, using B3LYP/6-31G* calculations [5], which provide excellent singlet-triplet gaps for unsaturated hydrocarbons (Table 1) [6]. In addition, we have explored the electronic structure in detail to understand why the molecule eschews the aromatic 14π-electron periphery.

2 Computational methodology

The structures were optimized using the B3LYP functional and the 6-31G* basis set. All structures were characterized by frequency calculations, and unless otherwise noted, energies are corrected for the zero-point energy (ZPE). All calculations were performed using Gaussian 94 [7].

3 Results and discussion

B3LYP calculations predict that **1** has a triplet ground state and is best represented as **1b**. The lowest singlet state is only 2 kcal/mol higher and is well represented by structure **1a**. The optimized geometries are shown in Fig. 1.

The triplet ground state can be viewed as a biphenyl unit with two benzene rings (r = 1.395–1.429 Å) connected by a longer bond (1.457 Å); additional bridges consist of a benzyl radical center and an allyl radical group. At this geometry, the singlet state is 8.5 kcal/mol higher in energy than the triplet, testimony to the strong diradical character of this π system.

The geometry of the optimized singlet is best described as the expected 14π-electron aromatic periphery (r = 1.396–1.407 Å) joined to the central ethylene

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[1] The cation corresponding to replacement of the 4-CH by a 4-NH$^+$ has been synthesized [4]

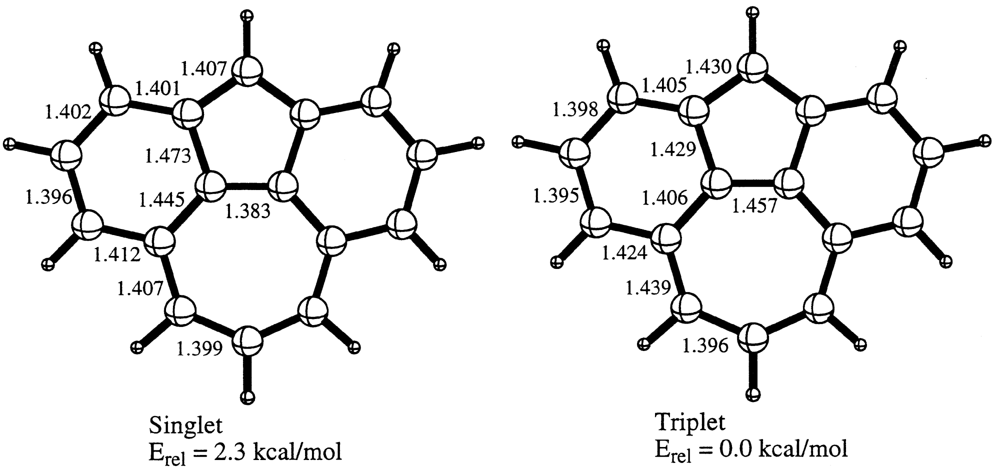

Fig. 1. Bond lengths (Å) and relative energies of singlet and triplet bis-periazulene (B3LYP/6-31G*)

Table 1. Various B3LYP/6-31G* singlet-triplet (*S-T*) gaps, with and without zero-point energy (*ZPE*) correction, and experimental S-T gaps in kcal/mol. Experimental S-T gaps are from Birk JB (1970) Photophysics of aromatic molecules. Wiley, New York

	B3LYP S-T gap		Experimental S-T gap
	incl. ZPE	without ZPE	
Bis-periazulene, **1**	−2.3	−1.7	?
Pyrene	45.8	48.5	48
Benzene	84.3	89.5	85
Naphthalene	59.3	62.6	61
Anthracene	39.5	41.8	42

(r = 1.383 Å) by relatively long bonds (r = 1.45–1.47 Å).[2] This structure is 1.7 kcal/mol above the triplet without ZPE corrections and 2.3 kcal/mol with ZPE corrections. In spite of the similarity in energies, the geometries of the triplet and singlet are significantly different. The triplet-state energy computed at the singlet geometry is 7 kcal/mol higher in energy than the singlet state.

The energy difference is very small, and the calculations could be in error as to the sign of the singlet-triplet gap. However, there is little doubt that the singlet and triplet states are nearly degenerate, and the fact that the singlet HOMO and LUMO share common atoms tends to make the triplet fall below the singlet in energy [9].

The Julg parameter, A, measures the bond length alternation in unsaturated systems [10]. It is defined as follows: $A = 1 - (225/n)\Sigma[1 - (r_i/r)]^2$, where n is the number of delocalized C—C bonds in the system, r_i is the length of an individual C—C bond, and r is the mean C—C bond length. The scaling factor $225/n$ sets A to unity for the structure of benzene which has equal C—C bond lengths and to zero for a hypothetical localized form in which the C—C bond lengths alternate between 1.33 and 1.52 Å. The A parameter of the singlet bis-periazulene is 0.929 if all C—C bonds are included, and it increases to 0.997 for the perimeter C—C bonds only. This confirms the model of the bis-periazulene singlet state as an aromatic [14]annulene linked to an ethylene.

We have compared bis-periazulene to the isomeric pyrene, which contains only six-membered rings. The singlet- and triplet-optimized structures of pyrene are shown in Fig. 2. The lowest electronic state of pyrene is a singlet, and the lowest-lying triplet is predicted to be 45.8 kcal/mol (with ZPE) higher in energy. The singlet of pyrene has significant similarities to the triplet of bis-periazulene, in that pyrene has a biphenyl unit linked by two double bonds which are quite short.

We also calculated the nucleus-independent chemical shift (NICS) values of bis-periazulene and pyrene. The NICS at the center of a ring is a simple aromaticity probe [11]. Negative NICS values denote aromaticity (−11.5 for benzene), and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene). Nonaromatics have negligible NICS values (−2.1 for cyclohexane). The NICS results agree well with magnetic susceptibility exaltation as a criterion of aromaticity. NICS values are less dependent on ring size, and can be used to assess individual rings in polycyclic systems. For example, the NICS values for the five-membered (−21.5) and seven-membered (−8.3) rings of azulene resemble those for the cyclopentadienyl anion (−19.4) and the tropylium ion (−8.2) [11].

The NICS values for singlet states of pyrene and bis-periazulene are shown in Fig. 3. The two benzenoid rings of the biphenyl units have NICS values of −12.7 (pyrene) and −17.3 (bis-periazulene, **1a**), respectively, in the same range as benzene itself (−11.5). In pyrene, the additional benzenoid rings are weakly aromatic as indicated by a NICS value of −5.1. In the bis-periazulene singlet, the five-membered ring is highly aromatic by this criterion (NICS = −25.0), similar to the five-membered ring of azulene (−21.5), while the seven-membered ring is slightly antiaromatic (+3.7) compared to the weakly aromatic seven-membered ring of azulene (−8.3) [11].

To compare the energies of the central double bonds in bis-periazulene and in pyrene, isodesmic equations (Fig. 4) were computed. These hydrogen transfers to central double bonds of bis-periazulene and pyrene result in 14π-electron systems for both species. While the

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[2] The computed structure of [14]annulene has slightly more bond alternation than calculated for the periphery of singlet **1**

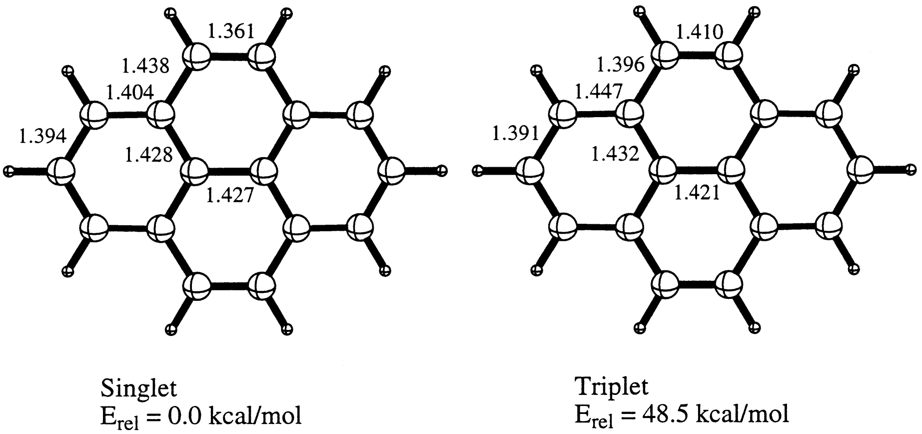

Fig. 2. Bond lengths (Å) and relative energies of singlet and triplet pyrene (B3LYP/6-31G*)

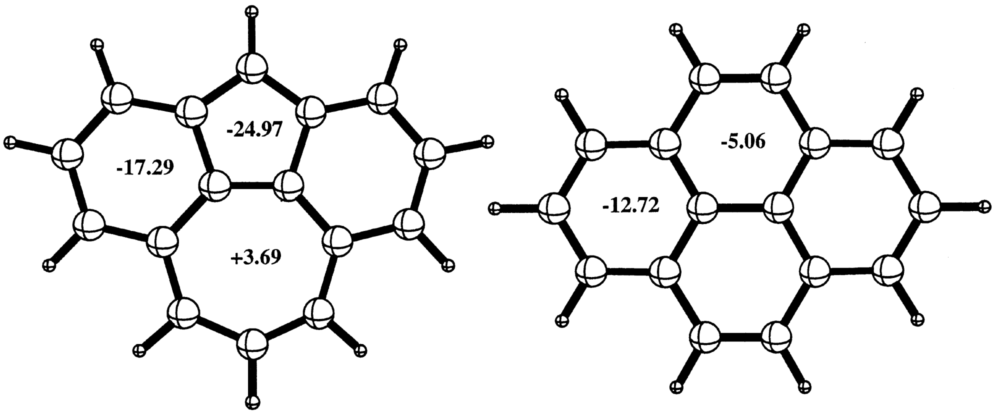

Fig. 3. Nucleus-independent chemical shift values for singlet bis-periazulene (C_{2v}) and pyrene(D_{2h}), (B3LYP/6-31G*)

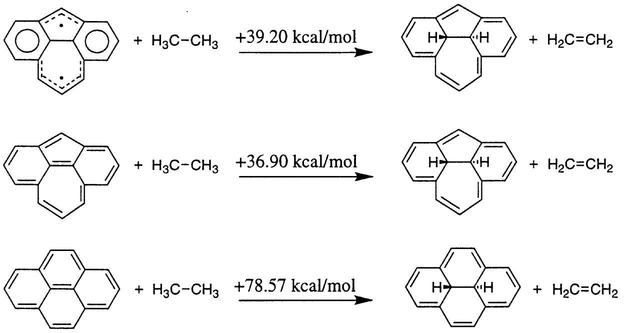

Fig. 4. Isodesmic equations for the hydrogen transfers from ethane to the central double bonds of singlet bis-periazulene (C_{2v}) and pyrene (D_{2h}). (B3LYP/6-31G* and RHF/6-31G* zero-point corrections were scaled by 0.89)

hydrogen transfer to the central double bond of singlet bis-periazulene consumes only 36.9 kcal/mol (39.2 kcal/mol for triplet bis-periazulene), 78.6 kcal/mol is necessary for the central double bond of pyrene (Fig. 4).[3]

The difference between these values provides evidence for the relatively high energy of bis-periazulene. Bis-periazulene is strained somewhat by angle strain, but this strain should be present in both bis-periazulene and its dihydro derivative. Considering pyrene to be a biphenyl bridged by two ethylenes, we would expect the triplet state of **1** to be higher in energy than pyrene by the difference between the sum of the energies of a methyl radical plus an allyl radical and the energy of two ethylenes. This difference is 65 kcal/mol (the π energy of ethylene) minus 15 kcal/mol (the resonance energy of allyl) giving a total of 50 kcal/mol. The difference of 39.4 kcal/mol is smaller than this, presumably because of the stabilizing interactions between the radical centers and the biphenyl unit.

Our calculations provide further support for the diradical nature of bis-periazulene, which arises from the fact that the most stable form is a biphenyl plus secondary and allyl radical units. Stabilization of the molecule might be achieved by stabilization of these radical units. The 14π-electron periphery possible in bis-periazulene provides less stability than the diradical structure with two benzene rings.

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References

1. McMasters DR, Wirz J, Snyder GJ (1997) J Am Chem Soc 119:8568

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[3] For recent calculated and X-ray structures of dimethyldihydropyrene, which has an aromatic bond-delocalized 14π-electron periphery, see Ref. [12]

2. Heilbronner E (1965) Helv Chim Acta 751
3. (a) Grieser U (1994) Ph.D. thesis. Technische Universität Darmstadt; (b) Flach J (1976) Ph.D. thesis. Technische Hochschule Darmstadt
4. Freiermuth B, Wirz J (1988) Angew Chem Int Ed Engl 27:585
5. (a) Becke AD (1993) J Chem Phys 98:5648; (b) Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
6. Davidson ER (1988) Int J Quantum Chem 69:241
7. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith TA, Peterson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94, Revision A.1. Gaussian, Pittsburgh, Pa
8. Choi HC, Kertesz M, Karpfen A (1997) J Am Chem Soc 119:11994
9. Hrovat DA, Borden WT (1997) J Mol Structure (Theochem) 398:211
10. Julg A, François P (1967) Theor Chim Acta 8:249
11. Schleyer PvR, Maerker C, Dransfeld A, Jiao H, Hommes NJRvE (1996) J Am Chem Soc 118:6317
12. Williams RV, Edwards WD, Vij A, Tolbert RW, Mitchell RH (1998) J Org Chem 63:3125