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6,6'-Biindeno[1,2-*b*]anthracene: an Open-Shell Biaryl with High Diradical Character

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ABSTRACT: We report in situ generation of a 6,6'-biindeno[1,2-*b*]anthracene (BIA) derivative as an open-shell biaryl with high diradical character, which could be identified by mass spectrometry, NMR, single-crystal X-ray analysis, UV-vis-NIR absorption, and electron paramagnetic resonance (EPR) spectroscopy. Theoretical calculations by various methods and variable-temperature EPR analyses were performed to tackle the elusive ground state of BIA diradical, suggesting a singlet ground state with a nearly degenerate triplet state. These results provide an insight into the design of unique open-shell biaryls.

Polycyclic conjugated hydrocarbons (PCHs) with diradical character have gained renewed attention in recent years in view of their potential applications in various areas, including spintronics, electronics, optoelectronics, and biology.¹⁻⁵ After the first demonstrations of quinoidal hydrocarbons in the 1900s,⁶⁻⁷ various PCH diradicaloids, such as bisphenalenyls,⁸ quinodimethanes,⁹ zethrenes,¹⁰ anthenes,¹¹⁻¹² higher acenes,¹³ and indenofluorenes,¹⁴⁻¹⁷ have been explored. Particularly, PCH diradicals with high-spin properties have attracted continuous interest due to their potential as molecule-based magnets,^{5, 18-19} but most of the open-shell PCHs synthesized thus far presented singlet ground states with limited diradical characters. Triangulene (**I**) is one of the most representative PCH diradicals (Figure 1),²⁰⁻²¹ which was experimentally revealed to have a triplet ground state by electron paramagnetic resonance (EPR) in 2001.²² Isolation of triangulene is highly challenging due to its instability, but crystallization and comprehensive characterization of a kinetically stabilized derivative substituted with mesityl groups was demonstrated in 2021.²³⁻²⁴ On the other hand, indeno[1,2-*a*]fluorene (**II**)²⁵

and 1,14:11,12-dibenzopentacene²⁶ have also been discussed as triplet PCH diradicals. The ground state of cyclohepta[*def*]fluorene (or bis-periazulene) was highly elusive, different theory predicting triplet ground state²⁷⁻²⁸ or nearly degenerate triplet and singlet states.²⁹ In 2022, aryl-substituted cyclohepta[*def*]fluorene was synthesized, for the first time experimentally revealing its singlet ground state.³⁰ Moreover, benzo-fused cyclohepta[*def*]fluorenes were separately reported in the same year, demonstrating singlet ground states with very low-lying triplet states.³¹ On the other hand, diradical **III** consisting of [2.2]paracyclophane substituted with two fluorenyl radicals was synthesized, and an open-shell triplet ground state via through-space spin-spin coupling was proposed, while an analogous structure with orbital overlaps between fluorenyl radicals displayed a singlet ground state.³² For further development of PCH diradicals, explorations of novel structural motifs is of considerable importance.

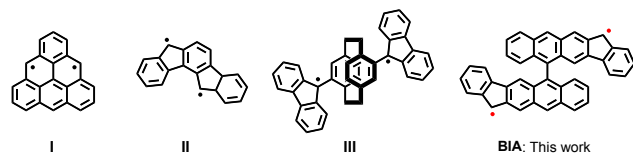


Figure 1. Examples of PCH diradicals. Substituents were omitted for clarity.

After syntheses of indenofluorenes and demonstrations of their intriguing antiaromatic and/or open-shell properties, a variety of diindeno-fused PCHs have been investigated, including those with structures based on naphthalene,³³ anthracene,¹⁶ pyrene,³⁴ perylene,³⁵ bischrycene,³⁶ and corannulene.³⁷ During our attempts to synthesize armchair graphene nanoribbons with indeno-fused edge structures from monomeric precursors based on *o*-tolyl-substituted bianthracene,³⁸ we conceived 6,6'-biindeno[1,2-*b*]anthracene (BIA) as an intriguing indeno-fused PCH dimer possibly exhibiting open-shell properties (Figure 1). According to Clar's aromatic sextet rule,³⁹ BIA has four π -sextets in the open-shell form and only two in the closed-shell form (Scheme 1), which suggests high diradical character, as does the sterically unfavorable conformation of the latter with a central double bond. This is similar to Thiele's and Chichibabin's hydrocarbons,^{7, 40} but distinct from their recently explored π -extended homologs, which lose Clar's sextets in their twisted forms.⁴¹⁻⁴⁴ Herein, we report theoretical studies and in situ generation of BIA **1** (Scheme 1), which was characterized by NMR, mass spectrometry, single-crystal X-ray analysis, and UV-vis-NIR spectroscopy. Notably, its high diradical character was demonstrated by variable-temperature (VT)-EPR experiments, revealing its singlet ground state with a very low-lying triplet state.

We initially calculated the diradical character index (y_0) of BIA **1** using its occupation numbers of spin-unrestricted Hartree-Fock natural orbitals by different DFT methods, namely UB3LYP, UM06-2X, and UCAM-B3LYP (Table 1; see Supporting Information (SI) for details).⁴⁵ A very high y_0 of 0.93–0.96 was estimated in agreement with our assumption, which prompted us to theoretically investigate the ground state of BIA. We next computed the ΔE_{st} of BIA **1** by first-principles calculations, and the UB3LYP/6-311G(d,p) calculation gave a ΔE_{st} of almost zero, indicating that the open-shell singlet (OSS) and open-shell triplet (OST) states are degenerate in **1**. Because the assessment of BIA **1** can be highly challenging for first-principles calculations,⁴⁶ we subsequently employed several other methods (Table 1). Different DFT methods predicted that OSS is slightly more stable with a ΔE_{st} in the range of -0.04–-0.06 kcal/mol (Table 1). Interestingly, we have revealed during our extensive theoretical exploration that CASSCF(12e,12o)/def2-TZVPP methods calculates OST to be more stable than OSS with a ΔE_{st} of 0.43 kcal/mol. This result suggested the possible relevance of static correlation in predicting the ground state of such diradicals (see SI for details), which, to the best of our knowledge, has never been

discussed in the literature. CASSCF(12e,12o)/def2-TZVPP revealed that the orbital occupancies of the two frontier orbitals were close to 1 (0.97), consistent with the diradical character of **1**. The UHF-calculated spin density distribution of **1** showed that the spins were mainly located within the fluorenyl substructures (Figure S1). We also solved a tight-binding Hubbard model approximating BIA with several solvers, including mean-field, CCSD, and CASSCF, which all

predicted a near zero ΔE_{st} . Additionally, we also applied the variational quantum eigensolver (VQE),⁴⁷ an algorithm for quantum chemistry using near-term quantum computers, employing 8 qubits with an emulator of quantum computer, Qamuy⁴⁸ (Figure S2). The VQE gave an ΔE_{st} value similar with that of CASSCF, demonstrating that the efficient estimation of ΔE_{st} would be possible using future quantum computers.

Table 1. Summary of y_0 and ΔE_{st} (kcal/mol) computed by different methods.

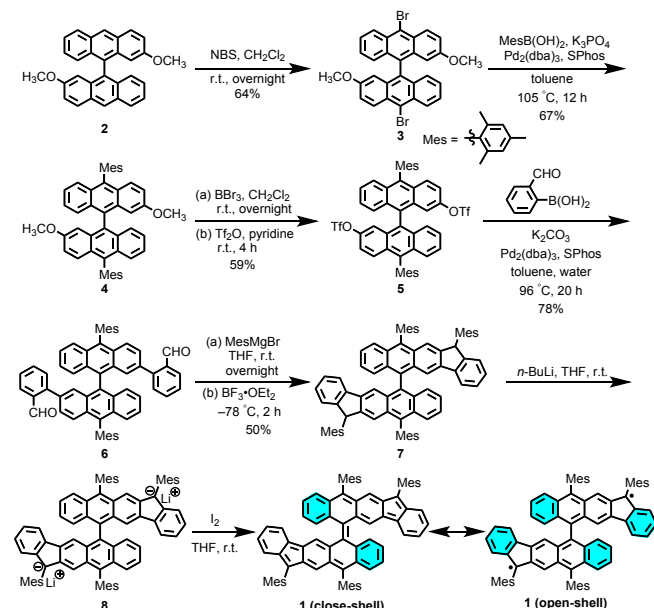
Method	y_0	ΔE_{st}
UB3LYP/6-311G(d,p)	0.93	-0.04
UM06-2X/6-311G(d,p)	0.95	-0.04
UCAM-B3LYP/6-311G(d,p)	0.96	-0.06
CASSCF(12e,12o)/def2-TZVPP	0.97	0.43
Mean Field Hubbard (U=3 eV)	--	-0.0001

To experimentally investigate this highly intriguing diradical, the synthesis of BIA **1** was carried out as displayed in Scheme 1. 2,2'-Dimethoxy-9,9'-bianthracene (**2**) was prepared as reported³⁸ and brominated with *N*-bromosuccinimide (NBS) to provide 10,10'-dibromo-2,2'-dimethoxy-9,9'-bianthracene (**3**) in 64% yield. Suzuki-Miyaura coupling of **3** with mesitylboronic acid gave 10,10'-dimesityl-2,2'-dimethoxy-9,9'-bianthracene (**4**) in 67% yield, which was subjected to demethylation with boron tribromide. The resulting diol was directly reacted with trifluoromethanesulfonic anhydride (Tf₂O) to afford bistriflate **5** in 59% yield. Suzuki-Miyaura coupling of **5** with (2-formylphenyl)boronic acid yielded dialdehyde **6** in 78% yield, which was reacted with mesitylmagnesium bromide (MesMgBr) and then subjected to Friedel-Crafts cyclization mediated by boron trifluoride etherate to obtain precursor **7** in 50% yield over two steps. Dehydrogenation of **7** was initially attempted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or *p*-chloranil as the oxidant, but BIA **1** could not be isolated, indicating the high reactivity resulting from its open-shell character. We thus performed in situ generation and characterization of **1** through deprotonation of **7** with *n*-BuLi to form dianion **8**, followed by oxidation with iodine.⁴⁹

After addition of 2.2 equiv. of *n*-BuLi to a solution of **7** in tetrahydrofuran (THF)-*d*₈ in an NMR tube, the ¹H NMR signals at 5.58 ppm disappeared, indicating quantitative dehydrogenation of **7** to dianion **8** (Figure 2). All proton signals could be assigned using ¹H,¹H-COSY and NOESY techniques (Figures S25-S26). Subsequently, 2.3 equiv. of iodine was added, which led to disappearance of all peaks from **8** and appearance of very weak new signals, suggesting generation of open-shell species **1** (Figures 2). High-resolution electrospray ionization mass spectrometry

analysis of **1** exhibited a peak at $m/z = 1000.4981$, in agreement with the theoretical molecular mass of 1000.5003 (Figure S29). Moreover, the formation of **1** was further supported by single-crystal X-ray analysis (Figures 2 and S5), although anionic iodine species were present in some of the unit cells, implying further oxidation of a part of **1** to radical cation species.

Scheme 1. Synthetic route to BIA **1**.^a



^aAromatic sextets are highlighted in cyan.

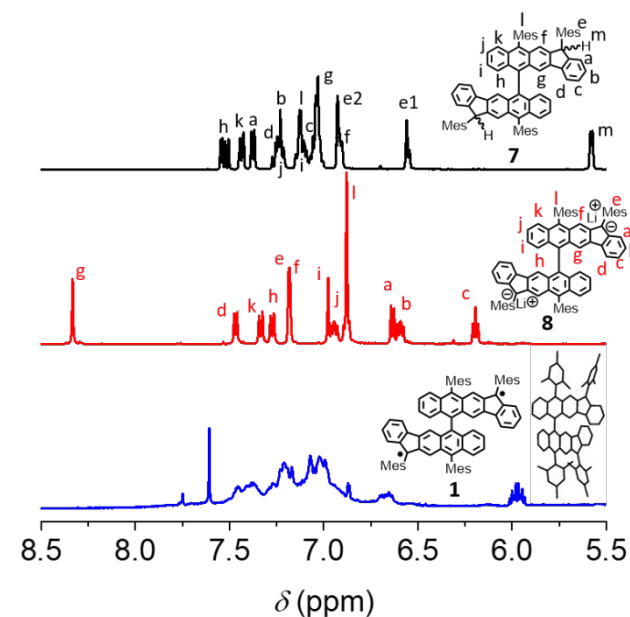


Figure 2. Aromatic region of ^1H NMR spectra (500 MHz) of **7** (CD_2Cl_2 , 298 K, black line) and in situ generated **8** and **1** (THF-d_8 , 298 K, red and blue lines, respectively). Inset: Chemical structures of **7**, **8**, and **1**, and single-crystal structure of **1**.

The aromaticities of **7**, **8**, and **1** were analyzed by calculating the nucleus-independent chemical shift (NICS) with the GIAO-(U)B3LYP/6-31G(d,p) method (Figure 3).⁵⁰

Compared with **7**, dianion **8** displayed high aromaticity ($\text{NICS}(1)_{zz} = -19.20$) in its five-membered rings, as expected for the fluorenyl anion substructure⁵¹ and reflected by the low-field shifts of the NMR signals from protons d and g (Figure 2). In contrast, the five-membered rings of BIA **1** exhibited a positive $\text{NICS}(1)_{zz}$ value (3.97), indicating local antiaromaticity, consistent with the observation of high-field shifted NMR signals at ~ 5.9 ppm.⁵² Similar $\text{NICS}(1)_{zz}$ values were observed for OSS and OST states of BIA.

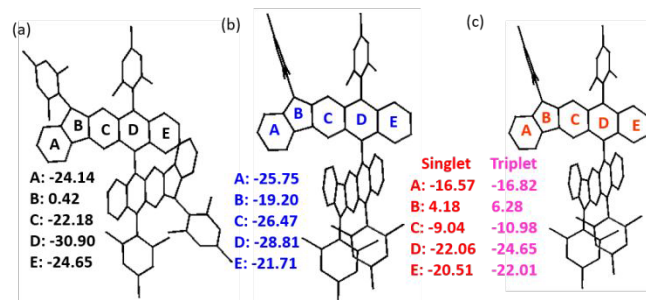


Figure 3. DFT-optimized geometries and $\text{NICS}(1)_{zz}$ values calculated for (a) **7**, (b) **8**, and (c) BIA **1** (singlet and triplet) based on the GIAO-(U)B3LYP/6-31G(d,p) method.

The UV-vis-NIR absorption spectra demonstrated remarkable changes from precursor **7** to dianion **8** and then BIA **1** (Figure 4a). While **7** showed no significant absorption at >450 nm, **8** displayed a very broad absorption extending to almost 1000 nm with a clear peak at 495 nm and featureless maxima at 817 and 925 nm. These observations largely agreed with time-dependent DFT (TD-DFT) results at the B3LYP/6-311(d,p) level, which predicted $\text{HOMO} \rightarrow \text{LUMO}$ and $\text{HOMO}-1 \rightarrow \text{LUMO}+1$ transitions at 837 nm ($f = 0.044$). In contrast, **1** exhibited a more structured spectrum with maxima at 569, 666, 777, and 865 nm, which could be well reproduced by performing TD-DFT calculations for both OSS and OST states at the UB3LYP/6-311G(d,p) level (Figure 4b). The peak at 865 nm corresponded to the $S_0 \rightarrow S_2$ transition of **1** (OSS) calculated at 868 nm ($f = 0.0033$) and contributed by $\text{HOMO} \rightarrow \text{LUMO}$ excitation. A dark $S_0 \rightarrow S_1$ transition assignable to $\text{HOMO} \rightarrow \text{LUMO}$ excitation was additionally seen at 870 nm ($f = 0.0033$), implying the doubly excited electronic configuration.⁵³ The peak at 666 nm could be ascribed to the $S_0 \rightarrow S_5$ transition of OSS, contributed mainly by the $\text{HOMO}-1 \rightarrow \text{LUMO}$ transition (644 nm, $f = 0.0616$), and the $\text{HOMO} \rightarrow \text{LUMO}$ transition of OST (647 nm, $f = 0.0610$). The broad absorption features of **8** and **1** could be due to contributions from optically forbidden states through intensity borrowing from neighboring allowed states (Tables S3–S5).⁵⁴ These results were also consistent with the NEVPT2 calculations (Figure S3). Additionally, the stability of in situ-generated BIA **1** was examined based on decay of its absorption at 666 nm, and its half-life under argon and ambient light was estimated to be 31 h (Figure S8).

EPR measurements were initially performed on in situ-generated dianion **8** and BIA **1** in 1,4-dioxane (Figure S9). While no EPR signal was observed for **8**, **1** displayed an unresolved EPR signal in line with a simulated spectrum

(Figure S4). VT-EPR experiment was next performed from 77 to 260 K by drying and redissolving a crude mixture of **1** in toluene, which showed higher signal intensities at lower temperatures (Figure 3c), indicating the absence of strong antiferromagnetic coupling between the two spin centers. Unfortunately, signals from **1** and monoradical impurities could not be distinguished due to the lack of the zero-field splitting, similar to some other reported PCH diradicals.^{25,55} Nevertheless, a signal corresponding to the forbidden transition of a triplet species could be observed in the $\Delta m_s = \pm 2$ region, when the temperature was further decreased to 4 K in 2-methyltetrahydrofuran (Figure 4d). We thus focused on this half-field signal to address the ground state of BIA **1**. VT-EPR spectra were recorded from 4 to 80 K, exhibiting stronger intensities at lower temperatures. The fitting of the IT - T plot of this data with the Bleaney-Bowers equation⁵⁶ gave a very small ΔE_{st} of approximately -0.03 kcal/mol, which was in line with the UB3LYP/6-311G(d,p) and other DFT calculation results (Table 1), indicating a singlet ground state of **1** with a very low-lying triplet state. We have also attempted superconducting quantum interference device (SQUID) measurements by embedding in situ-generated **1** in a polystyrene matrix, but reliable data could not be obtained due to the instability of **1** and the challenge of preparing a reliable reference sample.

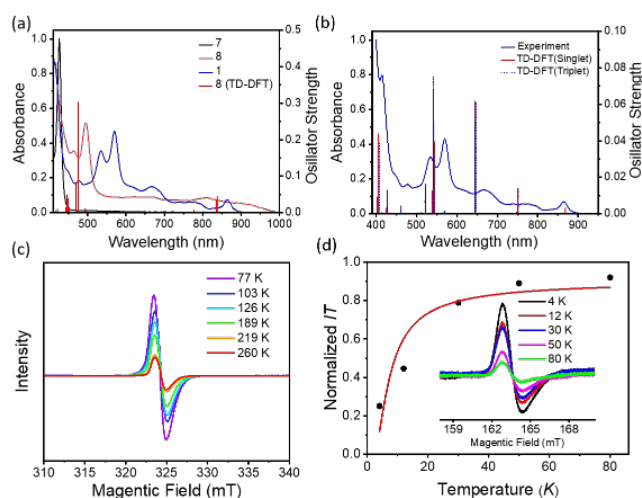


Figure 4. (a,b) UV-vis-NIR absorption spectra of **7** and in situ-generated **8** and BIA **1** (THF, 10^{-5} M), and simulated optical transitions of (a) **8** (B3LYP/6-311G(d,p)) and (b) **1** (singlet and triplet; UB3LYP/6-311G(d,p)). (c) VT-EPR spectra of a crude mixture of **1** in toluene. (d) IT - T plot in $\Delta m_s = \pm 2$ region of **1** in situ generated in 2-methyltetrahydrofuran (VT-EPR spectra shown in inset). Red lines in panels d–e are modified Bleaney-Bowers fits of the data.

In summary, we achieved in situ generation of BIA **1** as unique open-shell biaryl with high diradical character. While CASSCF(12e,12 $^{\circ}$)/def2-TZVPP calculations predicted a triplet ground state of BIA **1**, other theoretical methods pointed to a degenerate or singlet ground state with very small ΔE_{st} . VT-EPR analysis of its half-field signal from 4–80 K indicated the singlet ground state of **1** with a nearly degenerate triplet state, in line with the DFT results. More precise magnetic characterizations and application of BIA

will be further attempted by synthesizing and isolating more stable derivatives through introduction of bulkier substituents. These results may also open up a new avenue toward developments of PCH diradicals with different spatial arrangements of localized radicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental and computational details, synthesis and characterization of new compounds, and additional UV-vis-NIR absorption, EPR, mass, and NMR spectra.

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