Chemical Science





Published on 15 August 2014. Downloaded by Georgia Institute of Technology on 03/11/2014 08:56:28

Cite this: Chem. Sci., 2014, 5, 4944

Indolo[2,3-b]carbazoles with tunable ground states: how Clar's aromatic sextet determines the singlet biradical character*

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Polycyclic hydrocarbons (PHs) with a singlet biradical ground state have recently attracted extensive interest in physical organic chemistry and materials science. Replacing the carbon radical center in the open-shell PHs with a more electronegative nitrogen atom is expected to result in the more stable aminyl radical. In this work, two kinetically blocked stable/persistent derivatives (1 and 2) of indolo[2,3-b]carbazole, an isoelectronic structure of the known indeno[2,1-b]fluorene, were synthesized and showed different ground states. Based on variable-temperature NMR/ESR measurements and density functional theory calculations, it was found that the indolo[2,3-b] carbazole derivative 1 is a persistent singlet biradical in the ground state with a moderate biradical character ($y_0 = 0.269$) and a small singlet-triplet energy gap $(\Delta E_{S-T} \cong -1.78 \text{ kcal mol}^{-1})$, while the more extended dibenzo-indolo[2,3-b]carbazole 2 exhibits a quinoidal closed-shell ground state. The difference can be explained by considering the number of aromatic sextet rings gained from the closed-shell to the open-shell biradical resonance form, that is to say, two for compound 1 and one for compound 2, which determines their different biradical characters. The optical and electronic properties of 2 and the corresponding aromatic precursors were investigated by one-photon absorption, transient absorption and two-photon absorption (TPA) spectroscopies and electrochemistry. Amphoteric redox behaviour, a short excited lifetime and a moderate TPA cross section were observed for 2, which can be correlated to its antiaromaticity and small biradical character. Compound 2 showed high reactivity to protic solvents due to its extremely low-lying LUMO energy level. Unusual oxidative dimerization was also observed for the unblocked dihydro-indolo[2,3-b]carbazole precursors 6 and 11. Our studies shed light on the rational design of persistent aminyl biradicals with tunable properties in the future.

Accepted 14th August 2014 DOI: 10.1039/c4sc01843e

Received 21st June 2014

www.rsc.org/chemicalscience

Introduction

(PHs) in the neutral form have shown a typical closed-shell electronic configuration in the ground state.1 However, recent studies revealed that certain types of PHs with special structures could possess a singlet biradical ground state and exhibit unique optical, electronic and magnetic properties.² Representative examples include Tobe and Haley's indenofluorenes,3 Kubo's bisphenalenyls⁴ and anthenes,⁵ and our zethrenes⁶ and extended p-quinodimethanes.7 In most cases, the fundamental driving force for the appearance of a singlet biradical ground state is the gain of additional aromatic sextet rings in the biradical resonance form in comparison to the closed-shell resonance form. In addition, steric repulsion7a-d and substituents6d,e sometimes also play important roles in stabilizing the biradical form. After appropriate stabilization, this new type of molecular

tronics,11 and energy storage devices.12

To date, most π -conjugated benzenoid polycyclic hydrocarbons

materials have promising applications for organic electro-

nics,3c,4d non-linear optics,6-8 organic photovoltaics,9,10 spin-

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization data of all new compounds, additional spectroscopic data, X-ray crystallographic data, and DFT calculation details. CCDC 1009378-1009380. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4sc01843e



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Although the carbon centered singlet biradicals of pure PHs have been intensively studied in recent years, the nitrogen centered singlet biradicals have rarely been investigated due to the synthetic challenges. Replacing the carbon radical center with a more electronegative nitrogen atom is expected to result in improved stability compared with the unsubstituted carbon centered radicals, which has been demonstrated in phenalenyl monoradicals.^{13,14} In this context, we are interested in developing new nitrogen centered biradicaloids based on a PH framework, and indenofluorene analogues, *i.e.*, indolocarbazoles, were chosen for this study.

Indenofluorenes have five structural isomers based on the fusion mode, and three representative isomers are shown in Fig. 1.15 The parent indenofluorenes are all highly reactive due to the significant contribution of the biradical resonance form to the ground state, therefore, kinetic blocking of the reactive sites (the carbon centers with high spin density, Fig. 1) by aryl or alkyne groups is necessary to obtain stable materials. It was also found that the bulky mesityl blocked indeno[1,2-b]fluorene^{3a} and indeno[2,1-a]fluorene^{3b} both show a closed-shell quinoidal structure in the ground state, while the mesityl derivative of indeno[2,1-b]fluorene^{3f} has a singlet biradical ground state with a moderate biradical character ($y_0 = 0.68$ for the parent compound calculated by the Yamaguchi scheme using the occupation numbers of the spin-unrestricted Hartree-Fock natural orbitals¹⁶). Such a difference can be simply elucidated by the aromaticity change from the closed-shell to open-shell biradical



Fig. 1 Chemical structures of three isomers of indenofluorene and indolocarbazole, and the two new indolo[2,3-*b*]carbazole derivatives reported in this work.

resonance form. We recently demonstrated that Clar's aromatic sextet rule¹⁷ can be further extended to PH-based singlet biradicaloids, that is, for the benzenoid PHs with the same chemical composition, the molecule with more aromatic sextet rings in the biradical resonance form exhibits greater singlet biradical character.6g In the indenofluorene cases, all of the isomers can be drawn with three Clar's aromatic sextet rings (highlighted in blue color) in the biradical form (Fig. 1). In the closed-shell resonance forms, the first two isomers can be regarded as dibenzannulated antiaromatic $12-\pi e$ s-indacene and as-indacene, respectively, with two aromatic sextet rings; the third isomer can be drawn as a benzannulated 16- π e antiaromatic system with only one aromatic sextet. Therefore, from the closed-shell to the openshell biradical resonance form, only one additional aromatic sextet ring is obtained for the first two isomers, while two additional aromatic sextet rings are gained for the third isomer, which can explain its relatively larger singlet biradical character. Based on this analysis, we rationalize that the singlet biradical character is mainly determined by the number of aromatic sextet rings gained from the closed-shell to the singlet biradical form, and an addition to Clar's aromatic sextet rule for singlet biradicaloids can be tentatively described as: for PHs with the same chemical composition, the molecule which can gain more aromatic sextet rings from the closed-shell to the biradical form exhibits the greater singlet biradical character. Similar to the indenofluorenes, the nitrogen centered indolocarbazoles also have five isomers and three of them are shown in Fig. 1. The indo [3,2-b]carbazole was demonstrated to have a quinoidal structure similar to the corresponding indeno[1,2-b]fluorene.18 To the best of our knowledge, the indolo[2,3-a]carbazole¹⁹ and indolo[2,3-b]carbazole20 have never been reported. Given the structural similarity with the indeno[2,1-b]fluorene, the indolo[2,3-b]carbazole is expected to show significant singlet biradical character and thus is the focus of the current research. This type of aminyl biradical should show high reactivity, thus kinetic blocking at the neighbouring sites is necessary for obtaining stable/persistent compounds. For this reason, the bulky tert-butyl or 4-tert-butylphenyl groups are introduced to protect the otherwise highly reactive aminyl radicals in our target compounds such as 1 (Fig. 1). Such a space shielding effect has been demonstrated to be effective at stabilizing triplet aminyl diradicals by Rajca et al.21 A kinetically blocked dibenzannulated indolo[2,3-b]carbazole derivative 2 with more extended π -conjugation was also prepared. Our detailed studies demonstrated that compounds 1 and 2 showed different ground states which could be correlated to the number of aromatic sextet rings gained from the closedshell to the biradical resonance form. Their detailed physical properties were also investigated by various experiments and assisted by DFT calculations, and compared with the corresponding aromatic precursors. A clear structure-biradical character-physical properties relationship was drawn at the end.

Results and discussion

Synthesis and characterization of compound 1

Although the dihydro-indolo[2,3-*b*]carbazole derivatives are known,²⁰ the dehydrogenated products were not reported, likely

due to their high reactivity arising from their biradical character. To block the reactive aminyl radicals, the bulky tert-butyl and 4-tert-butylphenyl groups were introduced into the neighbouring sites by regio-selective chemistry (Scheme 1). The synthesis commenced from the nitration of 1,3-dibromobenzene (3) to give the 1,3-dibromo-4,6-dinitrobenzene (4) in 58% yield. A Suzuki coupling reaction between 4 and 2-(3,5-ditert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded compound 5 in 83% yield, which underwent a ring closing reaction with excess triphenylphosphine in o-dichlorobenzene to give the *tert*-butyl substituted dihydro-indolo[2,3-b]carbazole 6 in 58% yield. The bromination of 6 with N-bromosuccinimide (NBS) selectively introduced a bromo-functional group at the carbon center between the two amine sites (7) due to its high electron density. A subsequent Suzuki coupling reaction gave the precursor 8 in 77% yield and the structure of compound 8 was confirmed by NMR spectroscopy as well as X-ray crystallographic analysis (Fig. 2).²² The bond length analysis of the dihydro-indolo[2,3-b]carbazole core revealed a small bond length alternation for the benzenoid rings and pyrrole rings, which is a typical characteristic for aromatic compounds.

The dehydrogenation of the precursor **8** was first conducted by treatment with PbO_2 in dry ethyl acetate at 70 °C. However, this gave a complicated mixture, which is likely due to the high reactivity of the biradical product. Alternatively, compound **8**



Fig. 2 ORTEP drawings and selected bond length analyses of (a) 8 and (b) 11.

was treated with excess *t*-BuOK (20 equiv.) in anhydrous 2-MeTHF at room temperature to give the corresponding diamino-dianions, with an orange colour. The reaction was conducted in a dry ESR tube under nitrogen atmosphere. Subsequent oxidation (2.5 equiv.) with iodine at -78 °C gave the desired compound **1**, which was a dark brown color.²¹ The VT



Scheme 1 Synthesis of indolo[2,3-*b*]carbazole derivatives 1 and 2. Reagents and conditions: (a) KNO_3 , conc. H_2SO_4 , 130 °C, 2 h; (b) 2-(3,5-ditert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, K_2CO_3 , $Pd(PPh_3)_4$, 1,2-dimethoxyethane, 90 °C, overnight; (c) PPh₃, *o*-dichlorobenzene, 170 °C, 2 days for 6, 1 day for 11; (d) 1 equiv. NBS, dichloromethane, rt, 1 h for 7, 2 h for 14; (e) 4-tert-butyl-phenylboronic acid, Pd(PPh_3)_4, K_2CO_3 , toluene, EtOH, 90 °C, overnight; (f) 5 equiv. t-BuOK, 2-Me-THF, rt, 30 min; (g) I_2 , 2-Me-THF, -78 °C; (h) 3,7-di-tert-butyl-1naphthylboronic acid, Pd(PPh_3)_4, K_2CO_3 , 1,2-dimethoxyethane, 90 °C, overnight; (i) PbO₂, ethyl acetate, 70 °C, 2 days.

ESR spectra of this freshly prepared solution were recorded from 150 K to room temperature and a well-resolved ESR spectrum was observed (Fig. 3). There were no obvious changes to the spectrum shape upon slow warming up to room temperature, indicating the persistence of the obtained radical species under nitrogen protection. So far, the parent indeno-[2,1-b]fluorene has not been synthesized and it is not possible to compare its stability with 1. The simulated ESR spectrum of the open-shell biradical 1 was in good agreement with the observed spectrum (Fig. 3). Therefore, we can assign the observed ESR spectrum to the triplet diradical of 1. The ESR intensity was found to decrease when lowering the temperature (Fig. S1 in ESI[†]), indicating that the compound has a singlet ground state, which is in equilibrium with a higher energy triplet state. Fitting the temperature dependent ESR intensity data (I-T curve) to the Bleaney-Bowers equation²³ gave an antiferromagnetic exchange $J/k_{\rm B} = -895 \text{ K} (-1.78 \text{ kcal mol}^{-1})$, which can be correlated to the singlet-triplet energy gap (ΔE_{S-T}). Such a small ΔE_{S-T} value indicates that the population of the thermally excited triplet state is not negligible at room temperature, which results in an intense ESR signal. So, it is clear that compound 1 has a singlet biradical ground state with a roughly estimated singlet-triplet gap of -1.78 kcal mol⁻¹. The freshly generated biradical sample showed slow decay upon standing at room temperature and fast decay upon contact with air and moisture, giving an unidentified mixture.

Synthesis and characterizations of compound 2

The synthesis of the precursor **15** followed a similar strategy to the synthesis of the precursor to **1** (Scheme 1). A Suzuki coupling between **4** and 3,7-di-*tert*-butyl-1-naphthylboronic acid²⁴ gave the 1,5-dinitro-2,4-bis(3,7-di-*tert*-butylnaphthalenyl) benzene (**10**) in 95% yield. A PPh₃-mediated intramolecular cyclization could in principle form three regio-isomers **11–13**, with 5/5, 5/6, and 6/6 membered ring skeletons, respectively.



Fig. 3 Observed ESR spectrum of **1** (triplet diradical) in 2-MeTHF at 300 K and the simulated ESR spectrum with parameters $g_e = 2.0039$, $A_N = 3.7$ MHz (×2), $A_H = 14.8$ MHz (×2), $A_H = 2.90$ MHz (×2). Since the exchange J/k_B is much larger than the room temperature and the hyperfine coupling, it is not included in the simulation.

However, only one isomer **11** was isolated in 14% yield from the complicated products. The structure of **11** was unambiguously confirmed by X-ray crystallography, showing aromatic character for all of the rings based on the bond length analysis (Fig. 2).²⁵ The regio-selective bromination of **11** using NBS followed by a Suzuki coupling with 4-*tert*-butyl-phenylboronic acid afforded the dihydro-dibenzoindolo[2,3-*b*]carbazole **15** in high yield, which was confirmed by both NMR spectroscopy and X-ray crystallographic analysis (ESI[†]).²⁶

The oxidative dehydrogenation was successfully conducted by the treatment of precursor 15 with excess PbO₂ in dry ethyl acetate at 70 °C for 2 days. After filtration and removal of the solvent, a deep blue solid was obtained in nearly quantitative yield, which has good solubility in chloroform, hexane, and ethyl acetate, moderate solubility in acetonitrile and methanol, and poor solubility in ethanol. The ¹H NMR spectrum of the obtained compound can be clearly assigned to compound 2 (Fig. 4). Compared with the aromatic precursor 15, the resonance for the NH disappeared and all of the other peaks in the aromatic region showed significant shifts to the high field region. In particular, the resonance for proton "a" was shifted from 9.67 ppm in 15 to 6.31 ppm in 2. Such a dramatic change can be explained by the switching from the aromatic 15 to an antiaromatic conjugated quinoidal compound 2. In fact, a 16 π e antiaromatic moiety can by drawn for 2 (Fig. 1 and 4, highlighted in bold form), and the paratropic ring current resulted in a strong shielding effect for the surrounding protons. The reaction was also conducted in other anhydrous solvents such as chloroform, but only incomplete conversion was observed.

A dramatic change of the electronic absorption spectrum was also observed (Fig. 5). Compound **15** displayed an intense absorption band in the UV-visible region with an absorption maximum at 346 nm (log $\varepsilon = 4.53$; ε : molar extinction coefficient in M^{-1} cm⁻¹), along with intense absorptions at 372 and 390 nm. However, compound 2 showed a broad absorption from 450 nm to 760 nm with a maximum at 600 nm (log $\varepsilon = 4.06$), which can be correlated to a combination of electronic



Fig. 4 A comparison of the ${}^{1}H$ NMR spectra of compounds 15 (top) and 2 (bottom) in the aromatic region (in CDCl₃).

transitions from HOMO-1 \rightarrow LUMO (543.6 nm, f = 0.3358), HOMO-2 \rightarrow LUMO (465.8 nm, f = 0.3247), and HOMO-3 \rightarrow LUMO (429.5 nm, f = 0.1177) based on time dependent (TD) DFT calculations (ESI[†]). The singlet excited state lifetime of compound 15 was measured as 4.17 ns by the time correlated single photon counting (TCSPC) technique (Table 1 and Fig. S2 in ESI[†]), but compound 2 exhibited ultrafast excited state dynamics with a singlet excited state lifetime of 4.7 ps according to femtosecond transient absorption measurements (Table 1 and Fig. S3 in ESI[†]). TPA measurements were also conducted by the Z-scan technique and compound 2 showed a TPA cross section ($\sigma^{(2)}$) of 600 GM when excited at 800 nm. Under the same conditions, 15 exhibited a $\sigma^{(2)}$ of 290 GM (Table 1 and Fig. S4 in ESI†).27 The dramatic singlet excited state lifetime changes can be correlated to the change of the electronic structure from an aromatic to an antiaromatic framework.28

The VT ¹H NMR spectra of 2 in CDCl₂CDCl₂ did not show significant broadening upon heating up to 100 °C, indicating that 2 has a closed-shell electronic configuration in the ground state (Fig. S5 in ESI[†]). Compound 2, however, was not stable on silica gel or aluminium oxide columns and the dihydroprecursor 15 was obtained after column chromatography with dichloromethane (DCM)/hexane as an eluent. Further studies on the stability of 2 in different solvents were also conducted and monitored by UV-vis spectroscopy (Fig. S6 in ESI⁺). It was found that in aprotic solvents such as chloroform and THF, the optical intensity at 600 nm (I_{600}) showed minimal changes over 4.5 h. However, when mixing a small amount of water into the THF (H₂O–THF = 1:20), the optical intensity I_{600} decreased slowly to 84% after 4.5 h. In a protic solvent such as methanol, almost all of the samples of 2 were converted into 15 within 1.5 h. Reductive hydrogenation also occurred when conducting MALDI-TOF mass spectroscopic measurements, which gave a peak for the dihydro-precursor 15. In the solid state, it could be stored under an inert atmosphere at room temperature for at least 1 week without obvious decomposition.

The high reactivity of 2 towards protons indicates that it can be easily reduced and hydrogenated to give the more stable aromatic compound 15. To further understand the origin of this, cyclic voltammetry (CV) was performed to investigate its redox behavior and to determine its energy levels. For



Fig. 5 UV-vis absorption spectra of compounds 15 and 2 in CHCl₃.

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comparison, the CV measurements of the aromatic precursors 8 and 15 were also conducted (Fig. 6 and Table 1). Compound 8 only showed three oxidation waves with half-wave potentials $(E_{\rm ox}^{1/2})$ at 0.55, 1.10, and 1.47 V (vs. Fc⁺/Fc) due to its electronrich character. Similarly, compound 15 also exhibited three oxidations with $E_{\text{ox}}^{1/2}$ at 0.51, 1.09, and 1.49 V (vs. Fc⁺/Fc) which are close to those of 8. The most positive oxidation potentials for compounds 8 and 15 are only approximate as they appear chemically irreversible, showing no reverse reductive peaks when the scan direction was reversed following the initial oxidation. Furthermore, the HOMOs of 8 and 15 were also found to be similar, which were determined as -5.29 and -5.26eV, respectively, from the first oxidation onset. In contrast, the dehydrogenated product 2 displayed two oxidation waves $E_{\rm ox}^{1/2}$ at 0.82 and 1.29 V and two reductive waves with $E_{\rm red}^{1/2}$ at -0.42and -1.03 V (vs. Fc⁺/Fc). The HOMO of 2 was determined to be -5.56 eV, which is *ca.* 0.3 eV lower than those of **8** and **15**. The LUMO of 2 was found to be as low as -4.48 eV, and such a lowlying LUMO can explain the vulnerability of 2 towards reductive hydrogenation. On the basis of the HOMO and LUMO energies, a low electrochemical energy band gap $(E_{\rm g}^{\rm EC})$ was calculated as 1.08 eV for 2. In addition, the analyses of the UV-vis spectra (Fig. 5) gave their optical energy gaps (E_g^{Opt}) as 3.22 eV for 8, 2.99 eV for 15, and 1.58 eV for 2. Compared with 8, the two additional fused benzene rings in 15 decreased the energy gap slightly. However, the energy gap in the quinoidal structure of 2 was found to be much lower than those in the other two dihydro-compounds. This is further evidence for the loss of aromaticity in 2.

DFT calculations and discussion on the ground states of 1 and 2

Theoretical calculations (UCAM-B3LYP/6-31G*)30 were conducted to further investigate the ground states of 1 and 2. For 1, the singlet biradical solution with a spin contamination of $\langle S^{**2} \rangle = 0.8912$ is calculated to be 4.4 and 3.6 kcal mol⁻¹ more stable than the closed-shell and the triplet diradical forms, respectively, indicating that the ground state of 1 is a singlet biradical. The calculated small singlet-triplet energy gap $(\Delta E_{\rm S-T} = -3.6 \text{ kcal mol}^{-1})$ and moderate singlet biradical character y_0 of 0.269 imply its intermediate biradical nature between the typical closed-shell state and a pure diradical state. The singly occupied molecular orbital (SOMO) profiles of the α and β spins of **1** show disjoint features and the spins are evenly distributed along the whole π -conjugated framework (Fig. 7a). On the other hand, the ground state of 2 was calculated to be a closed-shell state that is 4.1 kcal mol^{-1} more stable than its open-shell triplet state. The HOMO and LUMO from the closed-shell solution (B3LYP/6-31G*) exhibit an extended delocalization through the dibenzo-indolo[2,3-b]carbazole core, representing the most reactive sites (Fig. 7b). These calculated results are in good agreement with the experimental results.

Nucleus-independent chemical shift (NICS) calculations³¹ were then conducted for the ground state of **1** (singlet biradical) and **2** (closed-shell quinoid) (Fig. 8). Calculations show that both the central diaza-*as*-indacene units have large positive

Table 1 Electrochemical and optical data for 8, 15, and 2^a

Comp.	$E_{\mathrm{red}}^{1/2}$ (V)	$E_{\mathrm{ox}}^{1/2}$ (V)	HOMO (eV)	LUMO (eV)	τ (ps)	$\sigma^{(2)}$ (GM)
8	_	0.55	-5.29	_	4040	<50
		1.10				
		1.47				
15	_	0.51	-5.26	_	4170	290
		1.09				
		1.49				
2	-0.42	0.82	-5.56	-4.48	4.8	600
	-1.03	1.29				

 $^{a}E_{red}^{1/2}$ and $E_{ox}^{1/2}$ are half-wave potentials of the reductive and oxidative waves (vs. Fe⁺/Fc), respectively. The HOMO and LUMO are determined by the equations: HOMO = $-(4.8 + E_{ox}^{onset})$ and LUMO = $-(4.8 + E_{red}^{onset})$, where E_{ox}^{onset} and E_{red}^{onset} are the onset potentials of the first oxidative and reductive waves, respectively.²⁹



Fig. 6 Cyclic voltammograms of 8, 15, and 2 in dry DCM with 0.1 M Bu_4NPF_6 as the supporting electrolyte, Ag/AgCl as a reference electrode, Au disk as a working electrode, Pt wire as a counter electrode, and a scan rate of 50 mV s⁻¹.



Fig. 7 (a) Calculated (UCAM-B3LYP/6-31G*) SOMOs for the α and β electrons and spin densities distribution of the singlet biradical 1. (b) Calculated (B3LYP/6-31G*) HOMO and LUMO of the closed-shell 2.

NICS(1)zz values, indicating that both have a large antiaromatic character. 2 showed more positive values than 1, suggesting that it is less aromatic. The outmost benzene rings in 1 exhibit a nearly zero NICS(1)zz value with a non-aromatic character. The two outmost naphthalene rings in 2 display negative NICS(1)zz values and thus are more aromatic. The calculated bond lengths also showed much larger alternation compared with the aromatic precursors. The difference of their ground states can be elucidated by the number of aromatic sextet rings gained from the closed-shell to the open-shell biradical form. As shown in Fig. 1, two more aromatic sextet rings are gained for 1 but only one aromatic sextet ring is obtained for 2, thus 1 has a greater driving force favouring the biradical form that results in a larger biradical character.

Unexpected oxidative dimerization of 6 and 11

During the synthesis of 1 and 2, we also attempted the oxidative dehydrogenation of the unblocked diamine intermediates 6 and 11 by using an excess of PbO_2 in chloroform. Interestingly, the homo-coupled dimers 16 and 18 were obtained in 65% and 63% yields, respectively (Scheme 2) after overnight refluxing. Extension of reaction time up to 3 days in chloroform or ethyl acetate resulted in partial decomposition of the as-formed products 16 and 18 and did not generate the predicted quinoidal products 17 and 19 or dihydrazine products (*via* intramolecular N–N bond formation). Compounds 16 and 18 showed



Fig. 8 Calculated bond lengths and NICS(1)zz values of 1 (singlet biradical) and 2 (closed-shell quinoid).

long singlet excited state lifetimes (3.13 and 3.72 ns, respectively, Fig. S3 in ESI[†]), similar to those of the corresponding aromatic monomers **8** and **15**. The unusual oxidative dimerization provided evidence of the high reactivity of the central benzene moiety in the dihyro-indolo[2,3-*b*]carbazole molecules and the effectiveness of our regio-selective chemistry.

Conclusions

In summary, the current study provided the first example of systematically investigating the open-shell features of quinoidal indolo[2,3-b]carbazole derivatives. Bulky protecting groups were successfully introduced to kinetically stabilize the two target compounds 1 and 2. It is interesting to observe that compound **1** is a persistent singlet biradical with a moderate biradical character ($y_0 = 0.269$) and a small singlet-triplet energy gap ($\Delta E_{S-T} \cong -1.78 \text{ kcal mol}^{-1}$) while the more π extended compound 2 is a stable closed-shell quinoid in the ground state, which was proved by various experimental measurements and DFT calculations. The origin of this difference can be simply correlated to the number of aromatic sextet rings gained from the closed-shell to the open-shell biradical form, which is an addition to Clar's aromatic sextet rule for singlet biradicaloids. Compared with the aromatic precursors, both compounds 1 and 2 have large non-aromatic character and compound 2 showed ultrafast excited dynamics and a moderate TPA cross section. Compound 2 also showed high reactivity to protic solvents due to its extremely low-lying LUMO energy level. An unexpected dimerization of the unblocked dihydro-indolo[2,3-b]carbazoles was observed due to their unique electronic structure, which also allowed regio-selective introduction of a bulky protecting group. These studies disclose how the aromatic sextet determines the ground-state electronic structures and also provide guidance to design nitrogen centered diradicals and diradical dications³² with tunable biradical character and physical properties in the future.



Scheme 2 Oxidative dimerization of 6 and 11.

J. W. acknowledges the financial support from MOE Tier 2 grants (MOE2011-T2-2-130, MOE2014-T2-1-080), MINDEF-NUS JPP Grant (12-02-05), and A*STAR JCO grant (1431AFG100). The work at Yonsei Univ. was supported by Mid-career Researcher Program (2010-0029668) and Global Research Laboratory (2013K1A1A2A02050183) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT (Information and Communication Technologies) and Future Planning. K.-W. H. acknowledges the financial support from KAUST. We thank Dr Tan Geok-Kheng for crystallographic analysis.

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- 26 Crystallographic data for 15: $C_{66}H_{76}N_2$. M_w : 897.29; monoclinic; space group C2/c; a = 25.799(6) Å, b = 18.171(4) Å, c = 11.441(3) Å, $\alpha = 90^{\circ}$, $\beta = 103.053(4)^{\circ}$, $\gamma = 90^{\circ}$; V = 5225(2) Å³; Z = 4; $\rho_{calcd} = 1.141$ Mg m⁻³; $R_1 = 0.0839$, $wR_2 = 0.2355$ ($I > 2\sigma(I)$); $R_1 = 0.1196$, $wR_2 = 0.2628$ (all data). CCDC number: 1009380. The 4-*tert*-butylphenyl is disordered and had to be refined under PART-1. The solvent toluene has large thermal parameters, suggesting it could be disordered and with a small fraction of other solvent (see ESI[†]).
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