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# Non-Kekulé *meta*-Quinodimethane Singlet Diradicals Based on Classical N-Heterocyclic Carbenes

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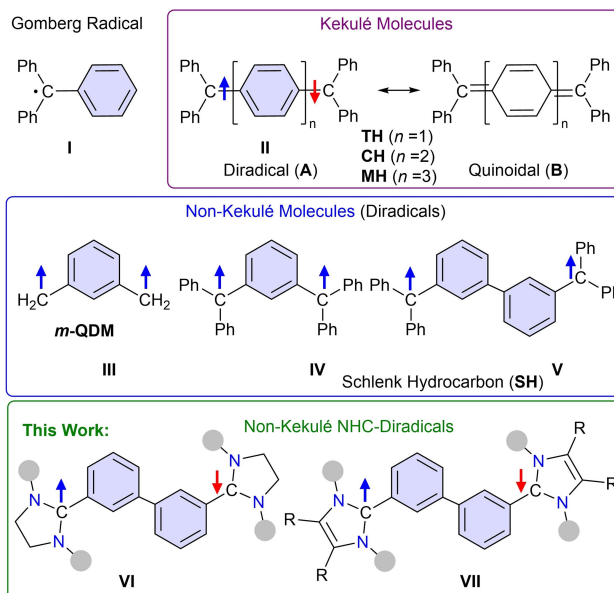
Dedicated to Professor Hansjörg Grützmaier on the occasion of his 65th birthday.

Diradicals based on a *meta*-quinodimethane (*m*-QDM) scaffold generally have a triplet ground state and are rather scarce. Herein, *m*-QDM-based non-Kekulé diradicals [3,3'-(NHC)<sub>2</sub>BP] (3-NHC) (NHC = SIPr = C{N(Dipp)CH<sub>2</sub>}}<sub>2</sub>; IPr = C{N(Dipp)CH<sub>2</sub>}}<sub>2</sub>, Me-IPr = C{N(Dipp)CMe}}<sub>2</sub>; Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; BP = 1,1'-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>) featuring *N*-heterocyclic carbene (NHC) pendants are reported as crystalline solids. The EPR spectra of 3-NHC show both allowed ( $\Delta m_s = 1$ ) and forbidden ( $\Delta m_s = 2$ ; 'half-field')

transitions characteristic for triplet diradicals. Variable temperature EPR studies however reveal a singlet ground state for 3-SIPr. Consistent with the EPR spectra, calculations predict a remarkably small singlet-triplet energy gap ( $\Delta E_{ST} \leq 0.26$  kcal/mol) for the 3-NHC compounds. The calculated singlet diradical character for the ground states of the 3-NHC compounds amounts to ~99%.

## Introduction

Open-shell organic molecules (*i.e.* radicals) with one, two, or more unpaired electrons have emerged as promising molecular building blocks for advanced functional materials.<sup>[1]</sup> The potential of these high-spin organic compounds in magnetics,<sup>[2]</sup> spintronics,<sup>[3]</sup> optoelectronics (singlet fission, light-emitting diodes),<sup>[4]</sup> and electronics (conducting materials, redox-flow batteries)<sup>[5]</sup> is largely attributed to their auspicious electronic structures and physical properties. The intrinsically high reactivity and thermal instability of these subvalent carbon compounds remain, however, a major concern. The first stable radical I (Figure 1) was isolated in 1900 by Gomberg.<sup>[6]</sup> Subsequently, Thiele (TH),<sup>[7]</sup> Tchichibabin (CH),<sup>[8]</sup> and Müller (MH)<sup>[9]</sup> reported the hydrocarbons II in which two (Ph<sub>2</sub>C<sup>•</sup>)-radical moieties are 1,4-bridged by a (C<sub>6</sub>H<sub>4</sub>)<sub>n</sub> linker (*n* = 1, 2, or 3). II are



**Figure 1.** The first stable radical I. Singlet diradical (A) and quinoidal (B) resonance forms of Kekulé hydrocarbons reported by Thiele (TH), Tchichibabin (CH), and Müller (MH). Triplet *m*-QDM (III) and Schlenk hydrocarbon (SH) diradicals IV and V. Non-Kekulé diradicals VI and VII based on *N*-heterocyclic carbenes (NHCs).

archetypical Kekulé molecules, which can be shown with open-shell diradical (A) and closed-shell quinoidal (B) (electron pairs in covalent bonds) resonance forms.<sup>[10]</sup> Diradicals are molecules with two unpaired electrons, typically in two (nearly) degenerate orbitals, and may have (open-shell) singlet or triplet electronic structures.<sup>[11]</sup> Depending on the structural topologies, the triplet state of Kekulé molecules II can be thermally populated as a consequence of a finite singlet-triplet energy gap ( $\Delta E_{ST}$ ).<sup>[12]</sup> Indeed, fine-tuning of the diradical character and

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$\Delta E_{ST}$  are important criteria in the design of new molecular systems with specific properties required for different potential applications.<sup>[13]</sup> Over the past years, a variety of the derivatives of **II** featuring diverse structural and electronic features have been isolated and structurally characterized,<sup>[14]</sup> including the compounds featuring isovalence electronic  $Ar_2N^{*+}$  fragments.<sup>[15]</sup>

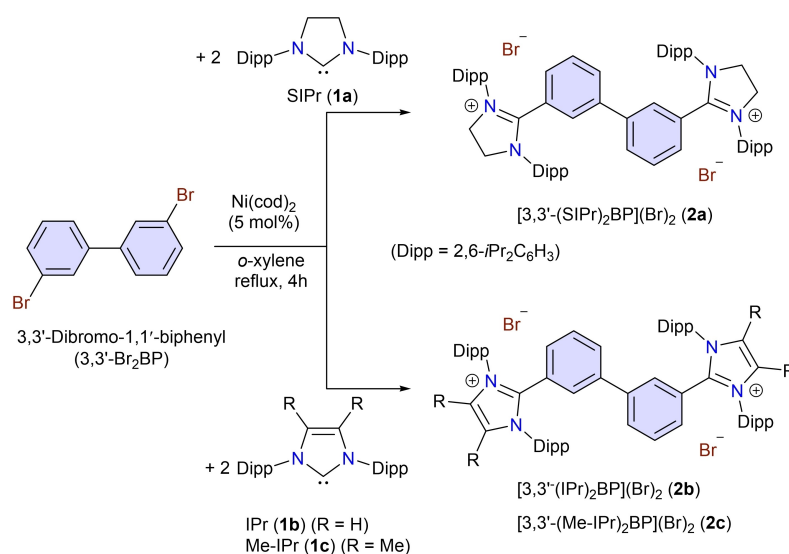
Non-Kekulé diradicals, void of any closed-shell resonance structure such as *meta*-quinodimethane (*m*-QDM) **III** and trimethylene methane (TMM), have two degenerate singly occupied orbitals.<sup>[16]</sup> According to Hückel molecular orbital (HMO) approximations such high-spin molecules generally have a triplet ground state and are extremely reactive.<sup>[17]</sup> A few nitrogen- or oxygen-centered *m*-QDM type singlet diradicals characterized by EPR spectroscopy and calculations have been described.<sup>[18]</sup> In 1915, Schlenk and Braun reported the *m*-QDM-based hydrocarbons (SH)<sup>[19]</sup> **IV** and **V**, which have triplet ground states.<sup>[20]</sup> The molecular structures of **TH** and **CH** were first reported in 1982 by Montgomery *et al.*<sup>[21]</sup> by single crystal X-ray diffraction (sc-XRD). However, the sc-XRD structures of **IV** and **V** remained thus far unknown, apparently due to their high reactivity and thermal instability. In recent years, the use of singlet carbenes as  $Ph_2C$ -surrogates has shown fruitful in accessing remarkably stable analogues of **TH**, **CH**, and **MH**.<sup>[22]</sup> However, the synthesis of stable molecular neutral derivatives of SHs remained thus far a task.<sup>[23]</sup> A cyclic alkyl amino carbene based diradical reported by Jana *et al.* underwent C–H insertion to form a C(IV) compound.<sup>[23a]</sup> Latter, the same group reported bis-olefin derived dicationic diradicals.<sup>[23b]</sup> Herein, we report the synthesis of non-Kekulé diradicals [3,3'-(NHC)<sub>2</sub>BP] (**VI** and **VII**), by combining classical *N*-heterocyclic carbenes (NHCs) with the 1,1'-biphenyl (BP) linker, as crystalline solids and showcase their spectroscopic and structural properties.

## Results and Discussion

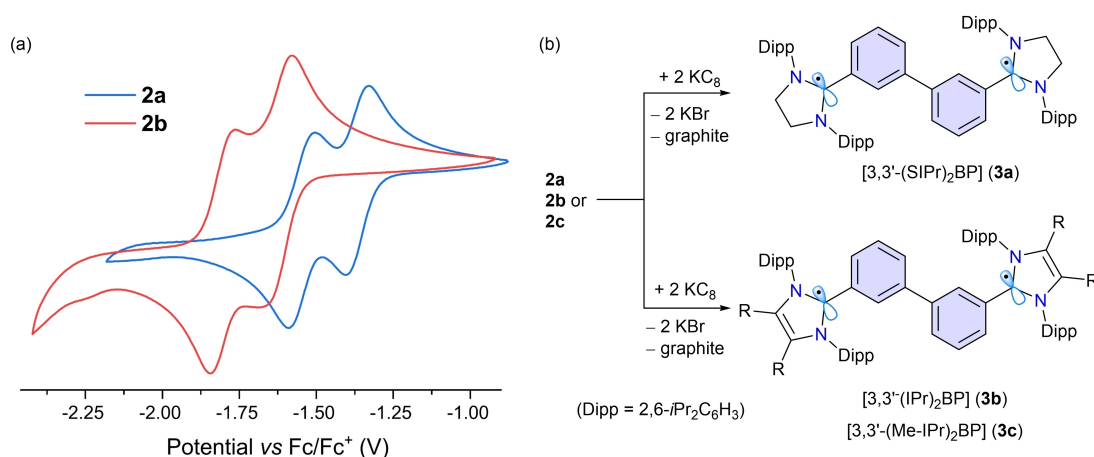
The desired starting materials [3,3'-(NHC)<sub>2</sub>BP](Br)<sub>2</sub> (NHC = SIPr = C{N(Dipp)CH<sub>2</sub>}<sub>2</sub>, **2a**; IPr = C{N(Dipp)CH}<sub>2</sub>, **2b**; Me-IPr = C{N(Dipp)CMe}<sub>2</sub>, **2c**; Dipp = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; BP = biphenyl) were prepared by the C–C coupling of NHCs (*i.e.* SIPr **1a**, IPr **1b**, and Me-IPr **1c**) with 3,3'-dibromo-1,1'-biphenyl under nickel catalysis (Scheme 1).<sup>[24]</sup> Compounds **2a–c** are air stable colorless solids and have been characterized by NMR spectroscopy, mass spectrometry, and sc-XRD. The <sup>1</sup>H NMR spectra of **2a–c** exhibit characteristic doublets and septets for the *H*CMe<sub>2</sub> protons as well as a triplet and a doublet for the C<sub>6</sub>H<sub>3</sub> protons of the Dipp groups. In addition, the <sup>1</sup>H NMR spectra of **2a–c** show four sets of signals for the bridging biphenyl unit, which are fully consistent with their <sup>13</sup>C NMR resonances. The ESI-mass spectra of **2a–c** feature a molecular ion peak that corresponds to the BP-bridged dicationic 1,3-imidazoli(ni)um fragment.

The cyclic voltammograms (CVs) of **2a**, **2b** (Figure 2a), and **2c** (Figure S13) show two distinct ( $\Delta E_{1/2} \sim 0.18$  V) one-electron reversible redox processes at  $-1.36/-1.55$  V (for **2a**),  $-1.62/-1.81$  V (for **2b**), and  $-1.73/-1.89$  V (for **2c**) vs.  $Fc^+/Fc$ . A slightly lower negative reduction potential for **2a** than those of **2b** and **2c** is consistent with the electrophilic nature of the corresponding NHCs (**1a** > **1b** > **1c**).<sup>[25]</sup> The first reduction of **2a–c** may tentatively be assigned to the corresponding radical cations, while the second reduction is likely to result in the neutral diradicals. Indeed, treatments of a colorless THF suspension of **2a**, **2b** or **2c** with two equivalents of  $KC_8$  (Figure 2b) at  $-78^\circ C$  immediately led to the formation of a red-brown suspension. The diradicals **3a–c** were isolated as red-brown crystalline solids in 75–89% yields. They are thermally stable under an inert gas ( $N_2$  or Ar) atmosphere but readily oxidize when exposed to air (*vide infra*). **3a–c** are NMR silent, indicating their paramagnetic property.

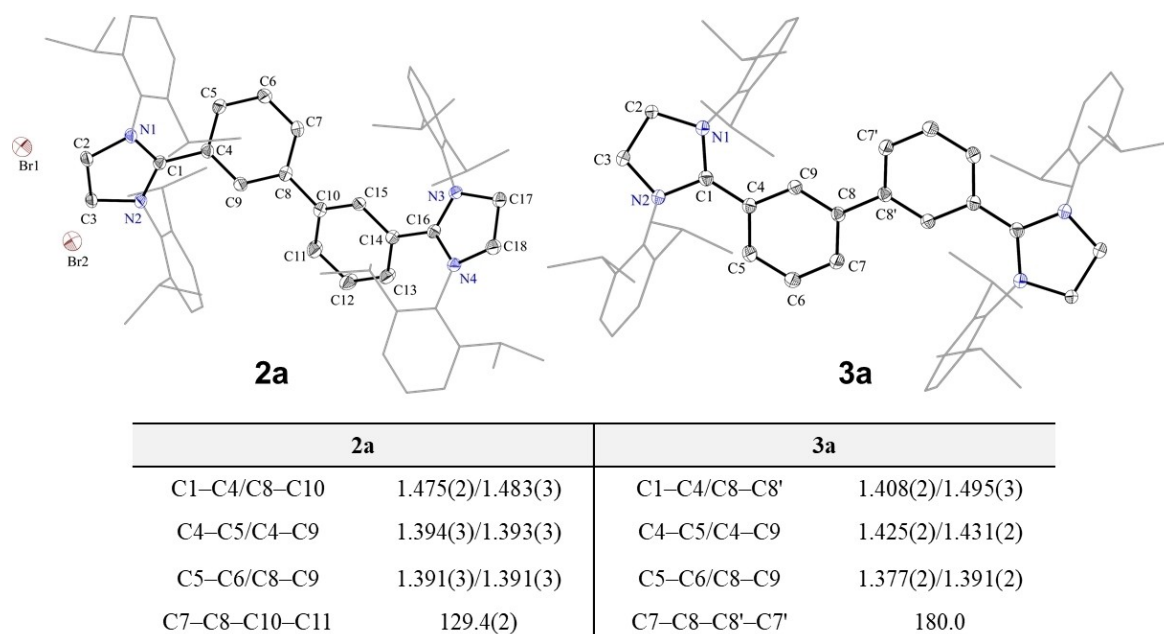
The solid-state molecular structures of **2a** and **3a** (Figure 3) exhibit the expected atom connectivity. The C1–C4/C8–C10



**Scheme 1.** Nickel catalyzed C–C couplings of NHCs (**1a–c**) with 3,3'-Br<sub>2</sub>BP to **2a**, **2b**, and **2c**.



**Figure 2.** (a) Cyclic voltammograms (CVs) of **2a** [ $E_{1/2} = -1.36, -1.55$  V] and **2b** [ $E_{1/2} = -1.62, -1.81$  V] measured in  $\text{CH}_3\text{CN}/0.05$  M  $n\text{-Bu}_4\text{NPF}_6$  at 100 mV/s; vs.  $\text{Fc}^+/\text{Fc}$  (see Supporting Information for **2c**). (b)  $\text{KC}_8$  reductions of **2a**, **2b**, and **2c** to **3a**, **3b**, and **3c**, respectively.

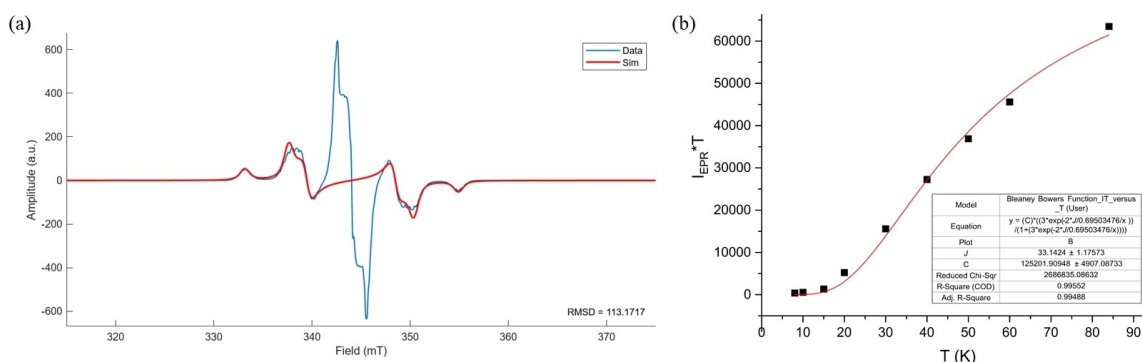


**Figure 3.** Solid state molecular structures of **2a** and **3a**. H atoms are omitted and Dipp groups are shown as wireframes for clarity. Thermal ellipsoids are at 50%. Selected bond lengths (in Å) and angles (in °) for **2a** and **3a**.

bond lengths of **2a** (1.475(2)/1.483(3) Å) are in line with C–C single bonds in the 2-biphenyl-1,3-imidazolium monocation (1.471(2)/1.481(2) Å).<sup>[24a]</sup> The C–C bond lengths of the BP linker in **2a** are comparable with those of 3,3'-dibromo-1,1'-biphenyl derivatives (1.363–1.399 Å).<sup>[26]</sup> The N1/N2–C1 bond lengths (1.329(2)/1.325(3) Å) and N1–C1–N2/N3–C16–N4 bond angles (112.1(2)/111.9(2)°) of **2a** are consistent with related 1,3-imidazolium cations.<sup>[24]</sup> The C1–C4 bond length of **3a** (1.4082 Å) is smaller while the C8–C8' (1.495(3) Å) bond length is comparable with those of **2a** (1.475(2) Å and 1.483(3) Å, respectively). The C–C bond length alteration (BLA) for the  $\text{C}_6\text{H}_4$  rings of the BP linker is marginally larger for **3a** (BLA=0.044 Å) with respect to that of **2a** (BLA=0.003 Å, *i.e.* a perfectly aromatic ring). Notably, the BLA in **3a** is still smaller than those of the *p*-QDM derivatives based on NHCs (BLA~0.10 Å).<sup>[22a–l]</sup> The

bridging  $\text{C}_6\text{H}_4$ -rings of **3a** are essentially coplanar (C7–C8–C8'–C7' torsion angle=180°), while the same in **2a** are tilted (C7–C8–C10–C11 torsion angle=129.4(2)°). A comparison of the sum of the angles at the nitrogen atoms of **2a** (e.g.,  $\Sigma_{\text{N1}} = 357.9(2)^\circ$ ) and **3a** ( $\Sigma_{\text{N1}} = 344.4(3)^\circ$ ) indicates pyramidalization of the nitrogen atoms in the latter. Thus, the structural parameters of **3a** point to the delocalization of the unpaired electrons over the adjacent  $\text{C}_6\text{H}_4$ -rings, largely at the *ortho*- and *para*-positions.

The diradical character of **3a–c** was confirmed by EPR spectroscopy (see the Supporting Information for details). The EPR spectrum of **3a** (Figure 4a) measured in Me-THF at 20 K shows (next to a central line stemming from a doublet ( $S = \frac{1}{2}$ ) impurity) allowed ( $\Delta m_s = 1$ ) and forbidden ( $\Delta m_s = 2$ ; half-field) transitions characteristic for an electronic triplet system. The



**Figure 4.** (a) Experimental and simulated EPR spectra of **3a** in Me-THF at 20 K. (b) Fitting plot according to Bleaney-Bowers equation.

signal can be satisfactorily simulated as an  $S = 1$  system with a  $g$ -value of 2.0025 with a moderate zero-field splitting of 305 MHz (10.9 mT = 108.9 Gauss) and a small rhombicity of the  $D$ -tensor ( $E/D = 0.057$ ). Spectra of **3a–c** for the forbidden transition are shown in the supporting information. The zero-field splitting value translates to an average distance of about 6.35 Å between the two unpaired electrons of **3a**.<sup>[11b]</sup> Variable temperature EPR studies and fitting the intensity of the half-field ( $\Delta m_s = 2$ ) signal as a function of temperature according to the Bleaney-Bowers function reveals an (OS) singlet ground state for **3a** with thermal population of the triplet state (Figure 4b). The Bleaney-Bowers fitting gives  $J = -33.14 \text{ cm}^{-1}$  ( $J = \text{electron exchange integral}$ ) and a corresponding singlet-triplet energy gap ( $\Delta E_{ST} = 2 J$ ) of  $66.28 \text{ cm}^{-1}$  (0.19 kcal/mol).

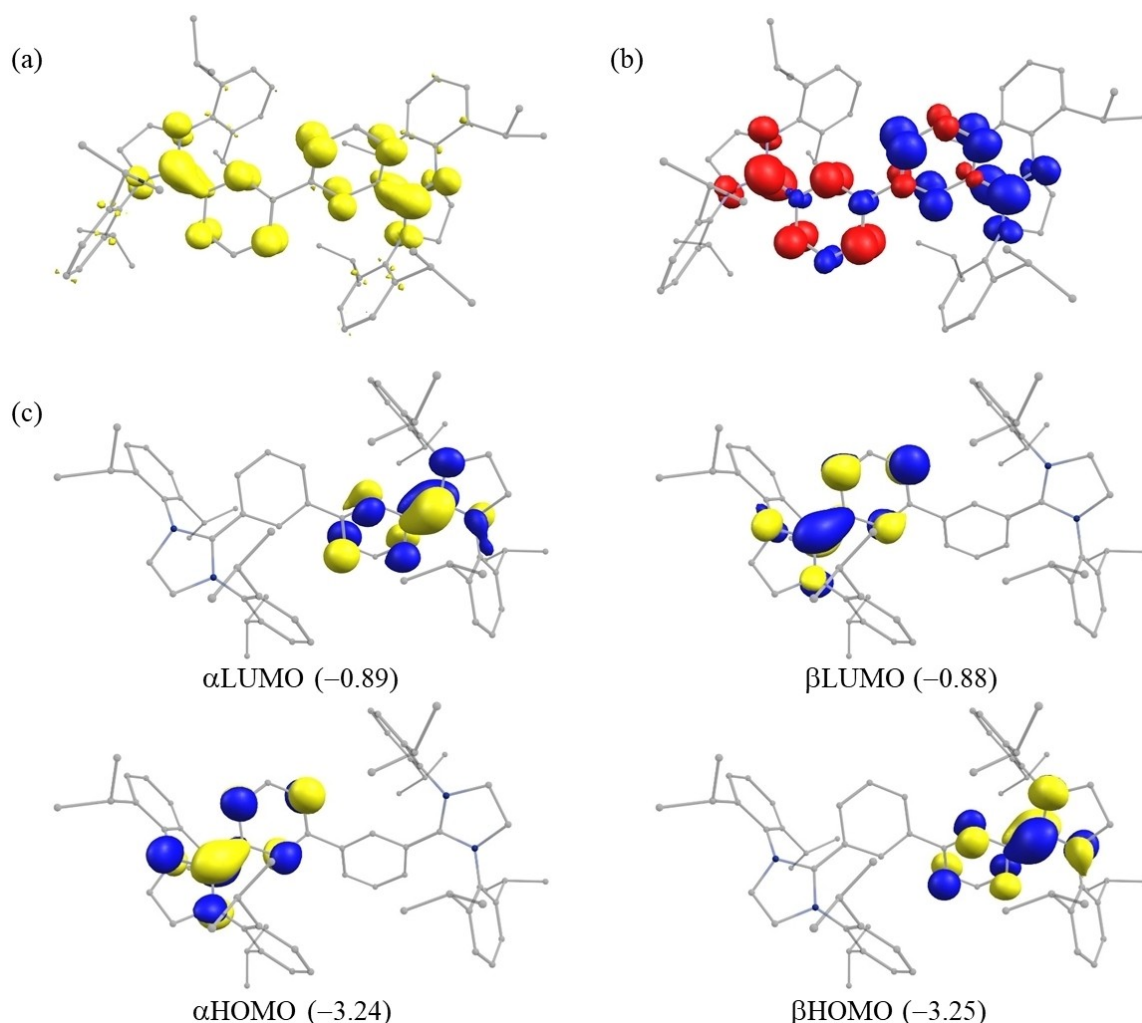
To obtain further insights into the electronic structures of **3a–c**, we performed quantum-chemical calculations at the PBE0-D3BJ/def2-TZVPP level of theory. Closed-shell (CS) singlet, broken-symmetry open-shell (OS) singlet, and triplet (T) solutions were probed for **3a–c**. For comparison, CS singlet dicationic species (**2a–c**)<sup>2+</sup> were also investigated (see the Supporting Information for details). For **3a–c**, CS singlet solutions appeared unstable, while the OS singlet diradical solution was found to be 0.26 (for **3a**), 0.19 (for **3b**), and 0.18 kcal/mol (for **3a**) more stable than the T solution. These values are in good qualitative agreement with the experimentally determined  $\Delta E_{ST}$  of 0.19 kcal/mol for **3a** (Figure 4b). The diradical character ( $y$ ) for **3a–c**, according to the occupation numbers of natural orbitals, amounts to 99%, indicating their almost pure OS singlet diradical structures. This is in contrast to the T ground state observed generally for  $m$ -QMD-based diradicals.<sup>[16,17,23]</sup> We also performed state-specific complete active space self-consistent field (SS-CASSCF) calculations combined with the def2-TZVP basis set. The singlet state  $S_0$  of **3a** for an active space of (2,2) has the occupation pattern "20" (51%) and "02" (49%). This pattern corresponds to 99% diradical character ( $\beta$ ) for **3a**, which is in line with that calculated using UHF method (see above).

To analyze the structures of **3a–c**, we also carried out fractional occupation number weighted density (FOD) calculations as an electron correlation diagnostic.<sup>[27]</sup> FOD studies provide reliable information on the localization of "hot" (strongly correlated and chemically active) electrons in a

molecule. The FOD plot of **3a** (Figure 5a) visualizes the "hot" electrons mainly at the carbene carbon, the  $o$ -,  $p$ - and  $ipso$ -carbon atoms of the  $C_6H_4$  rings. The resulting FOD number ( $N_{FOD}$ ) for **3a** (3.44  $e$ ), **3b** (3.62  $e$ ), and **3c** (3.68  $e$ ) is considerably larger than that of **2a** (1.58  $e$ ), **2b**, (1.50  $e$ ), and **2c** (1.57  $e$ ), respectively. Grimme *et al.* found correlation between the diradical character and the value of  $N_{FOD}$  for organic molecules.<sup>[27a]</sup> Notably, the  $N_{FOD}$  is larger for **3a–c** than that of TH (1.40  $e$ ) and CH (2.04  $e$ ), which exhibit the diradical character ( $y$ ) of 28 and 53% respectively.<sup>[28]</sup> Most of the spin density in **3a** (Figure 5b, Table S13) is found at the carbene carbon atom (40%), while the spin densities at the  $o$ - and  $p$ -carbon atoms of the  $C_6H_4$  rings amount to 21–26%. This suggests that **3a–c** are stabilized by the delocalization of the unpaired electrons over the  $C_6H_4$  rings. The UV-Vis spectra of **3a–c** exhibit a broad absorption band at  $\lambda_{max} = 497, 471, 470 \text{ nm}$ , respectively along with some other weak intensity bands. The UV-Vis spectra of the compounds **3a–c** are in line with the spectroelectrochemistry (SEC) measurements of **2a–c** (see the Supporting Information). The UV-Vis spectrum of **3a** (Figure S17) exhibits a broad absorption band in the 450–750 nm region ( $\lambda_{max} = 449, 497 \text{ nm}$ ). Based on TD-DFT calculations for **3a** (see Table S12), rather weak absorptions in the 548–746 nm region may be assigned to  $\alpha/\beta\text{HOMO} \rightarrow \alpha/\beta\text{LUMO}$ ,  $\alpha/\beta\text{HOMO} \rightarrow \alpha/\beta\text{LUMO} + 1$ , and  $\beta\text{HOMO} \rightarrow \beta\text{LUMO} + 3/4/7$  transitions.

## Conclusions

In conclusion, the first neutral  $m$ -QDM diradicals **3a–c** based on classical NHCs have been isolated as crystalline solids. EPR and computational data suggest OS singlet ground state for **3a–c** with a remarkably small singlet-triplet energy gap ( $\Delta E_{ST} \leq 0.26 \text{ kcal/mol}$ ). The appearance of a triplet and/or half-field EPR signal for **3a–c** is in line with thermal population of the triplet state. Calculations reveals 99% diradical character for **3a–c**. The remarkable stability of **3a–c** may be attributed to the delocalization of unpaired electrons over the  $C_6H_4$  rings. Thermally stable diradicals with accessible singlet and triplet states are considered promising candidates for advanced functional materials.



**Figure 5.** (a) FOD plot of **3a** (isosurface 0.005). (b) Spin density distribution (at UKS-PBE0-D3BJ/def2-TZVPP) in **3a** (isosurfaces 0.005; OS singlet diradical ground state). Selected molecular orbitals (isosurfaces 0.05 a.u.) and respective energies (eV) of **3a** (at PBE0-D3BJ/def2-TZVPP).

## Experimental Section

All syntheses and manipulations were carried out under an inert gas (Ar or N<sub>2</sub>) atmosphere using standard Schlenk techniques or a glove-box (MBraun LABMasterPro). Organic solvents were dried over appropriate drying agents, distilled, and stored over 3 Å molecular sieve. Nano-ESI mass spectra (ESI-MS) were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in THF or dichloromethane and introduced by static nano-ESI using in-house pulled glass emitters. Nitrogen served both as nebulizer as well as dry gas, which was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as a calibration standard. Melting points (MPs) were measured using a Büchi B-545 melting point apparatus. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in  $\delta$ , ppm) are referenced to the residual solvent signal(s): DMSO-*d*<sub>6</sub> (<sup>1</sup>H: 2.50 ppm and <sup>13</sup>C: 39.52 ppm).<sup>[29]</sup> UV-Vis spectra were recorded on a Genesys 50 UV-Vis spectrophotometer (Thermo Fisher Scientific). 3,3'-Dibromo-1,1'-biphenyl (3,3'-Br<sub>2</sub>BP) (Fluorochem) was dried in

vacuum prior to use. IPr (**1a**), SIPr (**1b**), MeIPr(**1c**)<sup>[30]</sup> and KC<sub>8</sub><sup>[31]</sup> were prepared according to literature procedures.

**Synthesis of [3,3'-(SIPr)<sub>2</sub>BP](Br)<sub>2</sub> (**2a**).** To a Schlenk flask containing a mixture of SIPr (**1a**) (3.00 g, 7.68 mmol) and 3,3'-Br<sub>2</sub>BP (1.20 g, 3.84 mmol) in 40 mL *o*-xylene was added Ni(cod)<sub>2</sub> (200 mg, 0.73 mmol) at room temperature (rt). The resulting suspension was stirred under reflux for 4 h, then brought to rt, and filtered through a G4 frit. The insoluble material was washed with toluene (15 mL) and dried under vacuum to obtain **2a** as an off-white solid in 63% (2.65 g) yield. Crystals suitable for single crystal X-ray diffraction analysis (sc-XRD) were obtained by slowly diffusing benzene into a dichloromethane solution of **2a**. **MP**: 368 °C (dec.). Elemental analysis (%) calcd. for C<sub>66</sub>H<sub>84</sub>Br<sub>2</sub>N<sub>4</sub> (1093.23) **2a**: C 72.51, H 7.75, N 5.12; found: C 71.17, H 7.94, N 5.03. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): 7.52–7.46 (m, 6H, *p*-C<sub>6</sub>H<sub>3</sub>, *m*-C<sub>6</sub>H<sub>4</sub>), 7.35 (d, *J* = 7.3 Hz, 8H, *m*-C<sub>6</sub>H<sub>3</sub>), 6.93 (d, *J* = 7.4 Hz, 2H, *p*-C<sub>6</sub>H<sub>4</sub>), 6.80 (s, 2H, *o*'-C<sub>6</sub>H<sub>4</sub>), 6.59 (d, *J* = 7.0 Hz, 2H, *o*-C<sub>6</sub>H<sub>4</sub>), 4.60 (s, 8H, NCH<sub>2</sub>), 3.01 (sept, *J* = 6.4 Hz, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.30 (d, *J* = 5.4 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.78 (d, *J* = 6.6 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K): 164.5 (NCN), 145.2 (*o*-C<sub>6</sub>H<sub>3</sub>), 139.1 (*i*-C<sub>6</sub>H<sub>4</sub>), 131.8 (*m*-C<sub>6</sub>H<sub>4</sub>), 131.3 (*o*-C<sub>6</sub>H<sub>3</sub>), 130.6 (*o*-C<sub>6</sub>H<sub>3</sub>), 130.2 (*m*'-C<sub>6</sub>H<sub>4</sub>), 128.8 (*p*-C<sub>6</sub>H<sub>4</sub>), 128.0 (*o*'-C<sub>6</sub>H<sub>4</sub>), 125.7 (*m*-C<sub>6</sub>H<sub>3</sub>), 121.4 (*p*-C<sub>6</sub>H<sub>4</sub>), 53.6 (NCH<sub>2</sub>); 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.6 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. **ESI-MS** (*m/z*): 466.4 [2a-2Br]<sup>2+</sup>.

**Synthesis of [3,3'-(IPr)<sub>2</sub>BP](Br)<sub>2</sub> (2b).** Compound **2b** was synthesized following a similar protocol as discussed above for **2a** using IPr (**1b**) (1.52 g, 3.91 mmol), 3,3'-Br<sub>2</sub>BP (0.61 g, 1.92 mmol), and Ni(cod)<sub>2</sub> (110 mg, 0.40 mmol) as an off-white solid in 66% (1.40 g) yield. Crystals suitable for sc-XRD were obtained by slowly diffusing benzene into a dichloromethane solution of **2b** over 5 days. **MP**: 355 °C (dec.). Elemental analysis (%) calcd. for C<sub>66</sub>H<sub>80</sub>Br<sub>2</sub>N<sub>4</sub> (1089.20) **2b**: C 72.78, H 7.40, N 5.14; found: C 69.91, H 7.52, N 4.79. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): 8.84 (s, 4H, NCH), 7.66 (t, *J* = 8.5 Hz, 4H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.53 (t, *J* = 7.6 Hz, 2H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.47 (d, *J* = 7.6 Hz, 8H, *m*-C<sub>6</sub>H<sub>3</sub>), 6.88 (d, *J* = 7.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.80 (s, 2H, *o*'-C<sub>6</sub>H<sub>4</sub>), 6.74 (d, *J* = 6.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 2.34 (sept, *J* = 6.5 Hz, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, *J* = 6.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.86 (d, *J* = 6.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K): 144.2 (*o*-C<sub>6</sub>H<sub>3</sub>), 143.4 (NCN), 139.5 (*i*-C<sub>6</sub>H<sub>4</sub>), 132.2 (*p*-C<sub>6</sub>H<sub>3</sub>), 130.5 (*o*'-C<sub>6</sub>H<sub>4</sub>), 129.5 (*i*-C<sub>6</sub>H<sub>3</sub>), 128.2 (*p*-C<sub>6</sub>H<sub>4</sub>), 127.7 (*m*-C<sub>6</sub>H<sub>4</sub>), 126.7 (NCH), 125.2 (*m*-C<sub>6</sub>H<sub>3</sub>), 120.7 (*m*'-C<sub>6</sub>H<sub>4</sub>), 28.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.8 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. **ESI-MS** (*m/z*): 464.4 [2b-2Br]<sup>2+</sup>.

**Synthesis of [3,3'-(Me-IPr)<sub>2</sub>BP](Br)<sub>2</sub> (2c).** Compound **2c** was synthesized following a similar protocol as discussed above for **2a** using Me-IPr (**1c**) (2.50 g, 6.00 mmol), 3,3'-Br<sub>2</sub>BP (0.936 g, 3.00 mmol), and Ni(cod)<sub>2</sub> (166 mg, 0.60 mmol) as an off-white solid in 63% (2.30 g) yield. Crystals suitable for sc-XRD were obtained by slowly diffusing ethyl acetate into a methanol solution of **2c** over 5 days. **MP**: 341 °C (dec.). Elemental analysis (%) calcd. for C<sub>70</sub>H<sub>88</sub>Br<sub>2</sub>N<sub>4</sub> (1145.31) **2c**: C 73.41, H 7.74, N 4.89; found: C 71.96, H 7.97, N 4.35. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): 7.69 (t, *J* = 7.7 Hz, 4H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.54 (d, *J* = 7.7 Hz, 8H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.36 (t, *J* = 7.8 Hz, 2H, *m*-C<sub>6</sub>H<sub>4</sub>), 6.82 (d, *J* = 8.2 Hz, 2H, *p*-C<sub>6</sub>H<sub>4</sub>), 6.77 (s, 2H, *o*'-C<sub>6</sub>H<sub>4</sub>), 6.43 (d, *J* = 7.6 Hz, 2H, *o*-C<sub>6</sub>H<sub>4</sub>), 2.37 (sept, *J* = 6.3 Hz, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.21 (s, 12H, CH<sub>3</sub>), 1.21 (d, *J* = 6.4 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.75 (d, *J* = 6.5 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>, 298 K): 144.7 (*o*-C<sub>6</sub>H<sub>3</sub>), 140.9 (NCN), 139.3 (*i*-C<sub>6</sub>H<sub>4</sub>), 132.6 (*p*-C<sub>6</sub>H<sub>3</sub>), 130.3 (NCCH<sub>3</sub>), 129.9(C<sub>6</sub>H<sub>4</sub>), 129.8 (C<sub>6</sub>H<sub>4</sub>), 128.0 (C<sub>6</sub>H<sub>4</sub>), 127.5 (*i*-C<sub>6</sub>H<sub>3</sub>), 126.1 (*m*-C<sub>6</sub>H<sub>3</sub>), 121.6 (*m*'-C<sub>6</sub>H<sub>4</sub>), 28.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.26 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 9.3 (NCCH<sub>3</sub>) ppm. **ESI-MS** (*m/z*): 568.4 [2c-2Br]<sup>2+</sup>.

**Synthesis of [3,3'-(SIPr)<sub>2</sub>BP] (3a).** To a Schlenk flask containing **2a** (1.18 g, 1.08 mmol) and KC<sub>8</sub> (332 mg, 2.38 mmol) was added pre-cooled (-78 °C) THF (50 mL). The resulting brown suspension was stirred for 2 h at rt, filtered through a plug of Celite, and the volatiles were removed *in vacuo* to afford compound **3a** as dark red solid in 89% (896 mg) yield. Crystals suitable for sc-XRD were obtained by storing a *n*-hexane solution of **3a** at rt for 3 days. Crystals for sc-XRD studies were prepared under a cooling nitrogen stream. **MP**: 112 °C (dec.). **UV-Vis** (THF, λ<sub>max</sub> (nm) (ε (M<sup>-1</sup> cm<sup>-1</sup>)): 284 (9208), 318 (13208), 449 (2542), 497 (2667).

**Synthesis of [3,3'-(IPr)<sub>2</sub>BP] (3b).** Compound **3b** was synthesized following a similar protocol as described above for **3a** using **2b** (0.52 g, 0.48 mmol) and KC<sub>8</sub> (195 mg, 1.44 mmol) as a red-brown solid in 75% (330 mg) yield. **MP**: 85 °C (dec.). **UV-Vis** (THF, λ<sub>max</sub> (nm) (ε (M<sup>-1</sup> cm<sup>-1</sup>)): 285 (13846), 358 (9423), 471 (3615), 559 (2038), 650 (1538).

**Synthesis of [3,3'-(Me-IPr)<sub>2</sub>BP] (3c).** Compound **3c** was synthesized following a similar protocol as described above for **3a** using **2c** (0.50 g, 0.44 mmol) and KC<sub>8</sub> (177 mg, 1.31 mmol) as a red-brown solid in 80% (551 mg) yield. **MP**: 86 °C (dec.). **UV-Vis** (THF, λ<sub>max</sub> (nm) (ε (M<sup>-1</sup> cm<sup>-1</sup>)): 285 (13480), 363 (8720), 470 (5040), 494 (4840), 642 (1000).

## Supporting Information Summary

The plots of NMR, CV, SEC, EPR, and UV-Vis spectra as well as the detail of X-ray crystallography and quantum chemical calculations of the reported compounds are given in the Supporting Information.

Deposition Number(s) 2347224 (for **2a**), 2347225 (for **2b**), 2347226 (for **2c**), and 2347227 (for **3a**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

The authors have cited additional references within the Supporting Information (Ref. [32–51]).

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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- [1] a) C. Shu, Z. Yang, A. Rajca, *Chem. Rev.* **2023**, *123*, 11954–12003; b) K. Kato, A. Osuka, *Angew. Chem. Int. Ed.* **2019**, *58*, 8978–8986; c) Y. Ishigaki, T. Harimoto, T. Shimajiri, T. Suzuki, *Chem. Rev.* **2023**, *123*, 13952–13965; d) Z. X. Chen, Y. Li, F. Huang, *Chem* **2021**, *7*, 288–332; e) I. Ratera, J. Veciana, *Chem. Soc. Rev.* **2012**, *41*, 303–349.
- [2] a) A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503–1505; b) A. Rajca, *Chem. Eur. J.* **2002**, *8*, 4834–4841.
- [3] a) C. Nicolaidis, F. Bazzi, E. Vouros, D. F. Flesariu, N. Chrysoschos, P. A. Koutentis, C. P. Constantinides, T. Trypiniotis, *Nano Lett.* **2023**, *23*, 4579–4586; b) S. Sanvito, *Chem. Soc. Rev.* **2011**, *40*, 3336–3355; c) Y. Zheng, F. Wudl, *J. Mater. Chem. A* **2014**, *2*, 48–57; d) Y. Tan, S.-N. Hsu, H. Tahir, L. Dou, B. M. Savoie, B. W. Boudouris, *J. Am. Chem. Soc.* **2022**, *144*, 626–647.
- [4] a) A. Mizuno, R. Matsuoka, T. Mibu, T. Kusamoto, *Chem. Rev.* **2024**, *124*, 1034–1121; b) P. Murto, B. Li, Y. Fu, L. E. Walker, L. Brown, A. D. Bond, W. Zeng, R. Chowdhury, H.-H. Cho, C. P. Yu, C. P. Grey, R. H. Friend, H. Bronstein, *J. Am. Chem. Soc.* **2024**, *146*, 13133–13141; c) Y. Zhao, A. Abdurahman, Y. Zhang, P. Zheng, M. Zhang, F. Li, *CCS* **2021**, *4*, 722–731;

- d) E. Cho, V. Coropceanu, J.-L. Brédas, *J. Am. Chem. Soc.* **2020**, *142*, 17782–17786; e) Z. Cui, A. Abdurahman, X. Ai, F. Li, *CCS* **2020**, *2*, 1129–1145; f) X. Ai, Y. Chen, Y. Feng, F. Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 2869–2873; g) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki, H. Nishihara, *Angew. Chem. Int. Ed.* **2018**, *57*, 12711–12715; h) T. Ullrich, D. Munz, D. M. Guldi, *Chem. Soc. Rev.* **2021**, *50*, 3485–3518; i) B. S. Basel, I. Papadopoulos, D. Thiel, R. Casillas, J. Zirzmeier, T. Clark, D. M. Guldi, R. R. Tykwinski, *Trends Chem.* **2019**, *1*, 11–21.
- [5] a) K. Hatakeyama-Sato, K. Oyaizu, *Chem. Rev.* **2023**, *123*, 11336–11391; b) H. Maruyama, H. Nakano, M. Nakamoto, A. Sekiguchi, *Angew. Chem. Int. Ed.* **2014**, *53*, 1324–1328; c) T. Suga, H. Nishide, *Rechargeable Batteries Using Robust but Redox Active Organic Radicals*, in *Stable Radicals*, John Wiley & Sons, Ltd, Chichester, West Sussex, PO19 8SQ, United Kingdom, **2010**, pp. 507–519; d) T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397–6409; e) L. Ji, J. Shi, J. Wei, T. Yu, W. Huang, *Adv. Mater.* **2020**, *32*, 1908015.
- [6] a) M. Gomberg, *J. Am. Chem. Soc.* **1902**, *24*, 597–628; b) M. Gomberg, *J. Am. Chem. Soc.* **1901**, *23*, 496–502; c) M. Gomberg, *J. Am. Chem. Soc.* **1900**, *22*, 757–771.
- [7] J. Thiele, H. Balhorn, *Chem. Ber.* **1904**, *37*, 1463–1470.
- [8] A. E. Tschitschibabin, *Chem. Ber.* **1907**, *40*, 1810–1819.
- [9] E. Müller, H. Pfanz, *Ber. Dtsch. Chem. Ges. B* **1941**, *74*, 1051.
- [10] J. Casado, *Top. Curr. Chem.* **2017**, *375*, 73.
- [11] a) T. Stuyver, B. Chen, T. Zeng, P. Geerlings, F. De Proft, R. Hoffmann, *Chem. Rev.* **2019**, *119*, 11291–11351; b) M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088; c) L. Salem, C. Rowland, *Angew. Chem. Int. Ed.* **1972**, *11*, 92–111.
- [12] a) Y. Kanzaki, D. Shiomi, K. Sato, T. Takui, *J. Phys. Chem. B* **2012**, *116*, 1053–1059; b) H. M. McConnell, *J. Chem. Phys.* **1960**, *33*, 1868–1869.
- [13] a) S. Ito, T. Nagami, M. Nakano, *J. Photochem. Photobiol. C* **2018**, *34*, 85–120; b) M. Nakano, K. Fukuda, S. Ito, H. Matsui, T. Nagami, S. Takamuku, Y. Kitagawa, B. Champagne, *J. Phys. Chem. A* **2017**, *121*, 861–873.
- [14] a) T. Y. Gopalakrishna, W. Zeng, X. Lu, J. Wu, *Chem. Commun.* **2018**, *54*, 2186–2199; b) Z. Zeng, X. Shi, C. Chi, J. T. Lopez Navarrete, J. Casado, J. Wu, *Chem. Soc. Rev.* **2015**, *44*, 6578–6596; c) Y. Hayashi, S. Suzuki, T. Suzuki, Y. Ishigaki, *J. Am. Chem. Soc.* **2023**, *145*, 2596–2608; d) T. Nishiuchi, S. Aibara, H. Sato, T. Kubo, *J. Am. Chem. Soc.* **2022**, *144*, 7479–7488.
- [15] G. Tan, X. Wang, *Acc. Chem. Res.* **2017**, *50*, 1997–2006.
- [16] a) K. Kato, K. Furukawa, A. Osuka, *Angew. Chem. Int. Ed.* **2018**, *57*, 9491–9494; b) A. Rajca, K. Shiraishi, M. Vale, H. Han, S. Rajca, *J. Am. Chem. Soc.* **2005**, *127*, 9014–9020; c) D. A. Shultz, R. M. Fico, H. Lee, J. W. Kampf, K. Kirschbaum, A. A. Pinkerton, P. D. Boyle, *J. Am. Chem. Soc.* **2003**, *125*, 15426.
- [17] a) G. R. Luckhurst, G. F. Pedulli, M. Tiecco, *J. Chem. Soc. B Phys. Org.* **1971**, 329–334; b) R. Schmidt, H. D. Brauer, *Angew. Chem. Int. Ed.* **1971**, *10*, 506–507; c) G. Kothe, K.-H. Denkel, W. Sümmerrmann, *Angew. Chem. Int. Ed.* **1970**, *9*, 906–907.
- [18] a) E. Terada, T. Okamoto, M. Kozaki, M. E. Masaki, D. Shiomi, K. Sato, T. Takui, K. Okada, *J. Org. Chem.* **2005**, *70*, 10073–10081; b) K. Okada, T. Imakura, M. Oda, A. Kajiwara, M. Kamachi, M. Yamaguchi, *J. Am. Chem. Soc.* **1997**, *119*, 5740–5741; c) K. Okada, T. Imakura, M. Oda, H. Murai, M. Baumgarten, *J. Am. Chem. Soc.* **1996**, *118*, 3047–3048; d) F. Kanno, K. Inoue, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1993**, *115*, 847–850; e) M. Dvolutzky, R. Chiarelli, A. Rassat, *Angew. Chem. Int. Ed.* **1992**, *31*, 180–181.
- [19] a) W. Schlenk, M. Brauns, *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 661; b) W. Schlenk, M. Brauns, *Chem. Ber.* **1915**, *48*, 716–728.
- [20] a) J. A. Berson, in *Reactive Intermediate Chemistry* (Eds: R. A. Moss, M. S. Platz, M. J. Jr.) John Wiley & Sons, Inc., Hoboken, New Jersey **2004**, pp. 165–203; b) J. L. Goodman, J. A. Berson, *J. Am. Chem. Soc.* **1985**, *107*, 5409–5424.
- [21] L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Grendze, *J. Am. Chem. Soc.* **1986**, *108*, 6004–6011.
- [22] a) H. Steffenfauseweh, Y. V. Vishnevskiy, B. Neumann, H.-G. Stämmler, B. de Bruin, R. S. Ghadwal, *Chem. Eur. J.* **2024**, *30*, e202400879; b) A. Maiti, S. Sobottka, S. Chandra, D. Jana, P. Ravat, B. Sarkar, A. Jana, *J. Org. Chem.* **2021**, *86*, 16464–16472; c) G. Kundu, S. De, S. Tothadi, A. Das, D. Koley, S. S. Sen, *Chem. Eur. J.* **2019**, *25*, 16533–16537; d) D. Rottschäfer, N. K. T. Ho, B. Neumann, H.-G. Stämmler, M. van Gastel, D. M. Andrada, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2018**, *57*, 5838–5842; e) D. Rottschäfer, J. Busch, B. Neumann, H.-G. Stämmler, M. van Gastel, R. Kishi, M. Nakano, R. S. Ghadwal, *Chem. Eur. J.* **2018**, *24*, 16537–16542; f) J.-J. Duan, X.-Q. Yang, R. Li, X. Li, T. Chen, D. Wang, *J. Am. Chem. Soc.* **2024**, *146*, 13025–13033; g) H. Song, E. Pietrasiak, E. Lee, *Acc. Chem. Res.* **2022**, *55*, 2213–2223; h) P. W. Antoni, T. Bruckhoff, M. M. Hansmann, *J. Am. Chem. Soc.* **2019**, *141*, 9701–9711; i) M. M. Hansmann, M. Melaimi, D. Munz, G. Bertrand, *J. Am. Chem. Soc.* **2018**, *140*, 2546–2554; j) D. Rottschäfer, B. Neumann, H.-G. Stämmler, D. M. Andrada, R. S. Ghadwal, *Chem. Sci.* **2018**, *9*, 4970–4976; k) J. Messelberger, A. Grünwald, P. Pinter, M. M. Hansmann, D. Munz, *Chem. Sci.* **2018**, *9*, 6107–6117; l) Y. Kim, E. Lee, *Chem. Eur. J.* **2018**, *24*, 19110–19121; m) R. S. Ghadwal, *Synlett* **2019**, *30*, 1765–1775.
- [23] a) A. Maiti, J. Stubbe, N. I. Neuman, P. Kalita, P. Duari, C. Schulzke, V. Chandrasekhar, B. Sarkar, A. Jana, *Angew. Chem. Int. Ed.* **2020**, *59*, 6729–6734; b) P. Saha, N. Chrysochos, B. J. Elvers, S. Patsch, S. I. Uddin, I. Krummenacher, M. Nandeshwar, A. Mishra, K. V. Raman, G. Rajaraman, G. Prabusankar, H. Braunschweig, P. Ravat, C. Schulzke, A. Jana, *Angew. Chem. Int. Ed.* **2023**, *62*, e202311868.
- [24] a) A. Merschel, D. Rottschäfer, B. Neumann, H.-G. Stämmler, M. Ringenberg, M. van Gastel, T. I. Demirel, D. M. Andrada, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215244; b) N. K. T. Ho, B. Neumann, H.-G. Stämmler, V. H. Menezes da Silva, D. G. Watanabe, A. A. C. Braga, R. S. Ghadwal, *Dalton Trans.* **2017**, *46*, 12027–12031; c) D. Rottschäfer, B. Neumann, H.-G. Stämmler, M. v. Gastel, D. M. Andrada, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2018**, *57*, 4765–4768.
- [25] R. S. Ghadwal, *Acc. Chem. Res.* **2022**, *55*, 457–470.
- [26] A. Sacristán-Martin, D. Miguel, H. Barbero, C. M. Álvarez, *Org. Lett.* **2022**, *24*, 5879–5883.
- [27] a) C. A. Bauer, A. Hansen, S. Grimme, *Chem. Eur. J.* **2017**, *23*, 6150–6164; b) S. Grimme, A. Hansen, *Angew. Chem. Int. Ed.* **2015**, *54*, 12308–12313.
- [28] H. Steffenfauseweh, D. Rottschäfer, Y. V. Vishnevskiy, B. Neumann, H.-G. Stämmler, D. W. Szczepaniak, R. S. Ghadwal, *Angew. Chem. Int. Ed.* **2023**, *62*, e202216003.
- [29] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
- [30] a) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; b) L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49–54.
- [31] H. Podall, W. E. Foster, A. P. Giraitis, *J. Org. Chem.* **1958**, *23*, 82–85.
- [32] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
- [33] M. Krejčík, M. Daněk, F. Hartl, *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179–187.
- [34] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*(1), 42–55.
- [35] *cwEPR-MATLAB Central File Exchange*, <https://www.mathworks.com/matlabcentral/fileexchange/73292-cwepur>.
- [36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [37] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.
- [38] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [39] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- [40] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [41] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [42] F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2022**, *12*, e1606.
- [43] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98–109.
- [44] C. A. Bauer, A. Hansen, S. Grimme, *Chem. Eur. J.* **2017**, *23*, 6150–6164.
- [45] Y. Guo, K. Sivalingam, E. F. Valeev, F. Neese, *J. Chem. Phys.* **2016**, *144*, 094111.
- [46] W. D. Laidig, H. F. Schaefer, *J. Chem. Phys.* **1981**, *74*, 3411–3414.
- [47] E. Miliordos, K. Ruedenberg, S. S. Xantheas, *Angew. Chem. Int. Ed.* **2013**, *52*, 5736–5739.
- [48] D. Doehert, J. Koutecky, *J. Am. Chem. Soc.* **1980**, *102*, 1789–1796.
- [49] K. Yamaguchi, M. Okumura, K. Takada, S. Yamanaka, *Int. J. Quantum Chem.* **1993**, *48*, 501–515.
- [50] F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, New York, USA, **2005**, p. 760.
- [51] E. D. Glendening, J. K. Badenhop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafilloglou, C. R. Landis, F. Weinhold, NBO 7.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI **2018**.

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