

CAAC-Based Thiele and Schlenk Hydrocarbons

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Dedicated to Professor Herbert W. Roesky on the occasion of his 85th birthday

Abstract: Diradicals have been of tremendous interest for over a century ever since the first reports of *p*- and *m*-phenylene-bridged diphenylmethyl radicals in 1904 by Thiele and 1915 by Schlenk. Reported here are the first examples of cyclic(alkyl)-(amino)carbene (CAAC) analogues of Thiele's hydrocarbon, a Kekulé diradical, and Schlenk's hydrocarbon, a non-Kekulé diradical, without using CAAC as a precursor. The CAAC analogue of Thiele's hydrocarbon has a singlet ground state, whereas the CAAC analogue of Schlenk's hydrocarbon contains two unpaired electrons. The latter forms a dimer, by an intermolecular double head-to-tail dimerization. This straightforward synthetic methodology is modular and can be extended for the generation of redox-active organic compounds.

Diradicals are a class of intriguing reactive compounds having two unpaired electrons.^[1] Such compounds have been of considerable interest for several reasons. Firstly, their design and assembly have been a challenge to the synthetic chemists.^[2] Secondly, their structural and spectroscopic properties have been of interest both from a theoretical and an experimental point of view.^[3] And thirdly, open-shell compounds in general, as well as diradicals that fall into this category, have been of significant importance for the design of novel functional materials with applications in a variety of areas including molecular electronics.^[4] Considering their assembly, the two radical centers in reported diradicals have been connected by different types of motifs.^[5] Following the landmark report on the formation of the triphenylmethyl radical in 1900 by Gomberg,^[6] Thiele et al. reported in 1904 the diradical **I** (Scheme 1), that is Thiele's hydrocarbon, in which the two radical centers are connected through a *p*-phenylene bridge.^[7] In 1915, Schlenk et al. reported the diradical **II**, that is Schlenk's hydrocarbon, in which the two

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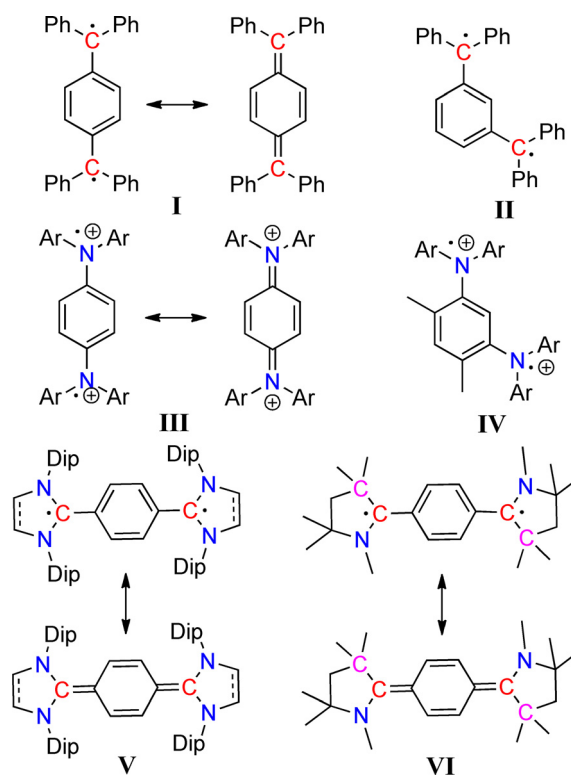
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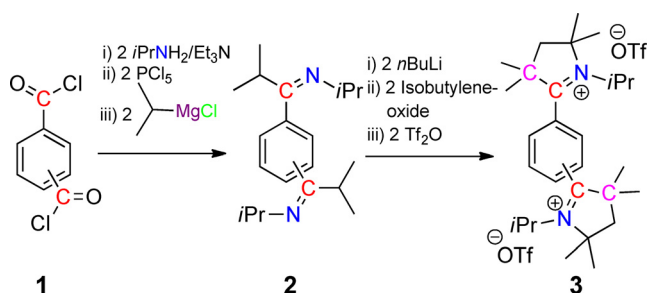
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Scheme 1. The chemical structures I–VI (Ar = 4-MeOC₆H₃, Dip = 2,6-*i*Pr₂C₆H₃).

radical centers are connected through a *m*-phenylene bridge.^[8] This system constitutes an open-shell triplet diradical (non-Kekulé diradical) since a direct communication between the two radical centers of **II** is not possible, in contrast to **I**.

Following the initial syntheses of **I** and **II**, a variety of other derivatives,^[9] including nitrogen analogues such as **III**^[10] and **IV**^[11] (Scheme 1), were prepared and studied.^[12] Ghadwal et al. reported the N-heterocyclic carbene (NHC) analogue (**V**) of Thiele's hydrocarbons.^[13] Recent theoretical studies by Munz et al. and Zeng et al. independently pointed to cyclic-(alkyl)(amino)carbene (CAAC) analogues (**VI**) of Thiele's hydrocarbon (Scheme 1) as excellent candidates for optoelectronic applications.^[14] However, the synthesis and properties of such a system have not been reported yet. It has already been noticed that replacing the Ph₂C/Ph₂C scaffolds in **I** and **II** with isoelectronic Ar₂N⁺/Ar₂N⁺ as in **III** and **IV**, respectively, and with isoelectronic NHC as in **V**, results in distinct changes in their electronic and consequently in their spectroscopic properties. Given this realization, along with the theoretical calculations and, even more importantly, the wide use of CAAC-scaffolds for the isolation of a variety of open-shell compounds,^[15] we were interested in designing diradicals containing CAAC-motifs. Employing the corresponding pyrrolinium salts as precursors constitutes one of the routes toward CAAC-scaffold-based carbon-centered radicals. To get the requisite bis-pyrrolinium salts a strategy based on our recent report^[16] was applied (Scheme 2).^[17] The three sequential reactions of either **1^p** or **1^m** with two equivalents of *i*PrNH₂/Et₃N, PCl₅, and *i*PrMgCl afforded the



Scheme 2. Synthesis of the *p*- and *m*-phenylene-bridged pyrrolinium cations **3^p** and **3^m**, respectively.

bisimines, **2^p** and **2^m**, respectively. The final cyclization step of **2^p** and **2^m** to the corresponding *p*- and *m*-phenylene-bridged pyrrolinium cations, **3^p** and **3^m**, respectively, was accomplished in a one-pot reaction involving two equivalents of *n*BuLi, isobutylene oxide, and Tf₂O (Scheme 2).^[17]

The compounds **3^p** and **3^m** were characterized by multinuclear solution NMR spectroscopy (¹H, ¹³C{¹H}, and ¹⁹F{¹H}) as well as by solid-state single-crystal X-ray diffraction analysis.^[18] The ¹H NMR spectra of **3^p** and **3^m** exhibit only one septet at $\delta = 4.33$ and 4.32 ppm, respectively, indicating the fast rotation of the pyrrolinium-scaffold on the NMR-time scale, even at lower temperature (-35°C). The four aromatic C–H bonds of **3^p** give rise to a singlet at $\delta = 7.69$ while the corresponding aromatic C–H of **3^m** result in three resonances

in a 1:1:2 ratio at $\delta = 7.89$, 7.79, and 7.72 ppm. These results indicate that in solution compounds **3^p** and **3^m** have a symmetric structure with a C₂-axis. This structure has also been reflected in their corresponding solid-state structures as determined by single-crystal X-ray diffraction (see below).

In **3^p** the distance between the connecting carbon centers of the pyrrolinium moiety (C1) and the central phenyl ring (C5) is 1.495(3) Å, indicating single-bond character (Figure 1).^[18] Both C and N centers of the pyrrolinium moieties adopt a planar geometry ($\Sigma\text{C1} = 360.00^\circ$ and $\Sigma\text{N1} = 359.88^\circ$). The angle between the planes involving the N1-C1-C2 moiety of the CAAC-scaffold and the central phenyl ring is 89.006(78)°. Because of the problems of twinning and the presence of disorder, we are not discussing the metrical parameters of **3^m** (Figure 2).^[18]

The cyclic voltammogram of **3^p** showed only a single reversible reduction wave at $E_{1/2} = -1.36$ V in CH₃CN/0.1M

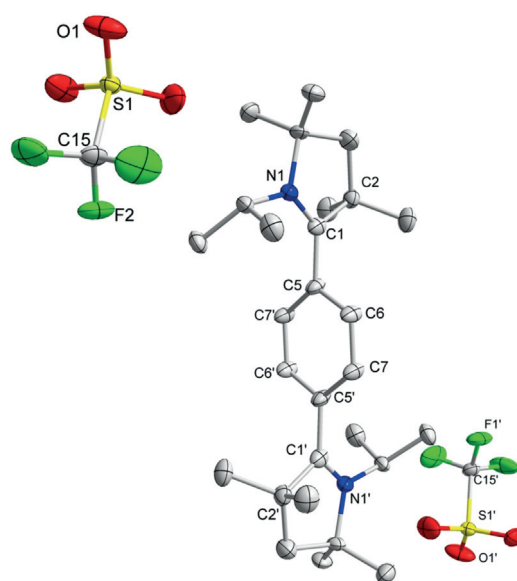


Figure 1. Molecular structure of **3^p** with thermal ellipsoids at 50%. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angle [°]: N1–C1 1.275(3), C1–C5 1.495(3), C5–C6 1.391(3), C6–C7 1.387(3), C7–C5' 1.397(3); N1–C1–C2 113.15(21).

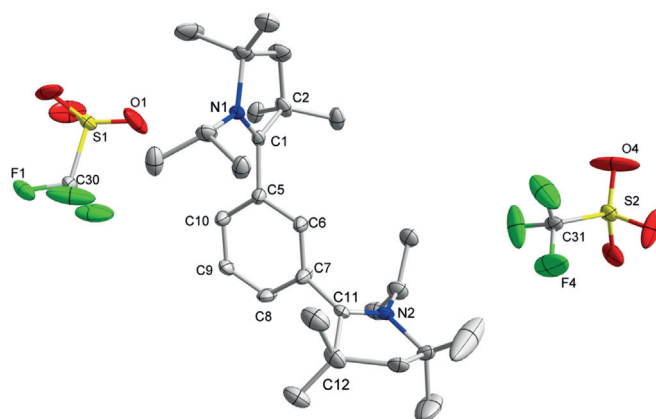


Figure 2. Molecular structure of **3^m** with thermal ellipsoids at 30%. All hydrogen atoms are omitted for clarity.

NBu₄PF₆ or Bu₄NBAR₄^F ([BAR₄^F]⁻ = [3,5-(CF₃)₂-C₆H₃]₄B⁻ (Figure 3)).^[17] No other reduction wave was detected within the solvent/electrolyte window. This result is surprising as the presence of two pyrrolinium substituents is expected to result in two reduction steps, as was observed for the corresponding

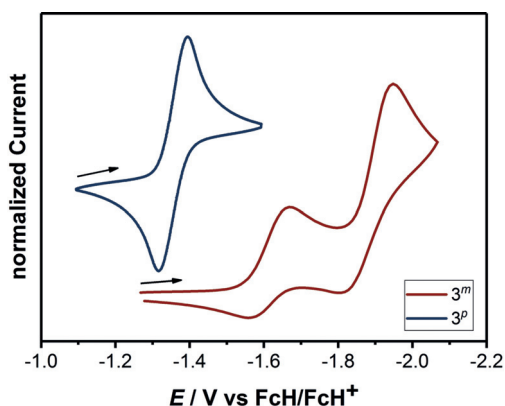


Figure 3. Cyclic voltammograms of **3^p** (blue), with 0.1 M NBu₄BAR₄^F, and **3^m** (red), with 0.1 M NBu₄PF₆, in MeCN at 100 mVs⁻¹.

NHC analogues of Thiele's hydrocarbon, **V**.^[13] A shift of the second reduction wave beyond the solvent/electrolyte window is unlikely as such a shift would lead to a potential difference of more than 1.00 V between the two redox transformations of **3^p**. These data indicate that the reduction wave observed at $E_{1/2} = -1.36$ V should be ascribed to either two close-lying one-electron waves or to one two-electron reduction.

Additionally, proof for the two-electron nature of this wave was generated by performing CV and differential pulse voltammogram (DPV) measurements on an equimolar solution of **3^p** and **3^m** (Figure 4 and see below). The comparative current heights also reinforce the two-electron nature of the reduction wave of **3^p**. This feature implies that the thermodynamic stability of the one-electron reduced mixed-valent species is very small in the case of the CAAC-scaffold and that it is motif dependent. The case of the NHC analogues of Thiele's hydrocarbon, **V** ($\Delta E_{1/2} = 0.25$ V for unsaturated

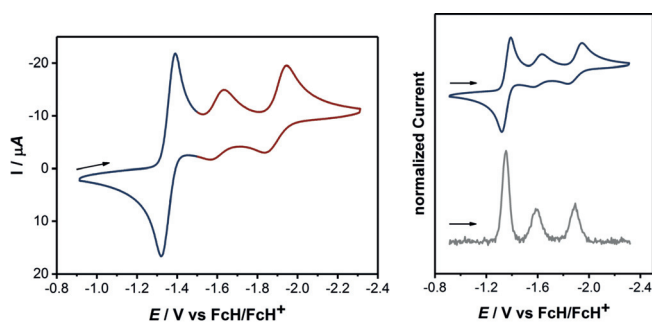
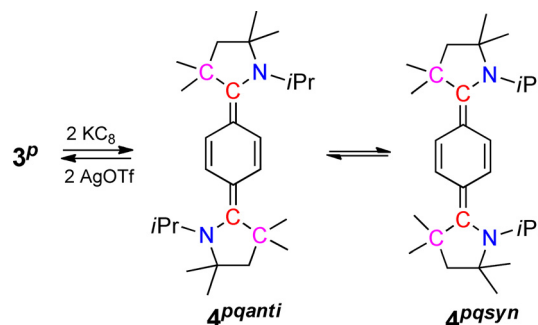


Figure 4. Left: Cyclic Voltammogram of a 0.1 mM solution of **3^p** (blue part) and **3^m** (red part) with 0.05 M NBu₄BAR₄^F in MeCN at 100 mVs⁻¹. Right: Cyclic voltammogram (top) and differential pulse voltammogram (DPV) (bottom) of a 0.1 mM solution of **3^p** and **3^m** in MeCN at 100 mVs⁻¹ (CV) and 20 mVs⁻¹ (dpv) with 0.05 M NBu₄BAR₄^F.

NHC-motif and $\Delta E_{1/2} = 0.15$ V for saturated NHC-motif), supports this reasoning.^[13]

3^p displays a single absorption band at $\lambda_{\max} = 267$ nm consistent with its colorless nature. Vis/NIR spectroelectrochemical measurements showed a clean conversion of this compound into a new species with an absorption maximum at $\lambda_{\max} = 431$ nm (see Figure S41) and this is very similar to the spectrum of the isolated two-electron reduced quinoidal form **4^p** [$\lambda_{\max}(\epsilon) = 429(54062)$ nm (L mol⁻¹ cm⁻¹)].^[17]

In accordance with the cyclic voltammetry experiments, the reduction of **3^p** with two equivalents of KC₈ leads to **4^p** in about 70 % yield as a thermally stable but highly air- and moisture-sensitive yellow solid (Scheme 3).^[17] At room temperature a well-resolved ¹H NMR spectrum was obtained, and is consistent with a diamagnetic singlet ground state. **4^p** consists of a mixture of two isomers (**4^{pqsyn}** and **4^{pqanti}**). Calculations at the TPSSh/def2-TZVP level of theory point to strong antiferromagnetic coupling of the spins, leading to a singlet ground state which is stabilized with respect to the triplet excited state by more than 2000 cm⁻¹.^[17] Accordingly, no EPR signals were observed for the two-electron-reduced compound **4^p**. When a crystalline sample of **4^p** was dissolved in C₆D₆ and a ¹H NMR spectrum immediately recorded, we observed the presence of **4^{pqanti}** as the major isomer as in the solid-state molecular structure (see below). Time-dependent ¹H NMR spectroscopy shows that the **4^{pqanti}** isomer reached an equilibrium with the isomer **4^{pqsyn}** in about 190 minutes (see Figures S16 and S17).^[17]



Scheme 3. Synthesis of **4^p**.

In the solid-state molecular structure only the *anti*-isomer, **4^{pqanti}**, is present (Figure 5).^[18] The C1–C5 distance is 1.381(2) Å, which is similar to that observed in **I** (1.381 Å)^[19] but longer than that found in **V** (1.375 Å for unsaturated NHC and 1.371 Å for saturated NHC).^[13] The C–C bond lengths in the central phenyl ring reveal an alternation of short and long bond lengths consistent with the chemical structure. The sum of the bond angles around C1 and C1' is 359.54°. Both N1 and N1' also adopt an almost planar geometry ($\Sigma N = 358.16^\circ$). **4^p** could be reversibly oxidized to **3^p** by two equivalents of AgOTf in a 78 % yield upon isolation (Scheme 3).

In contrast to **3^p**, the *meta*-substituted compound **3^m** displays two one-electron reduction steps at $E_{1/2} = -1.61$ V and -1.88 V in CH₃CN/0.1 M Bu₄NPF₆ or Bu₄NBAR₄^F ([BAR₄^F]⁻ = [3,5-(CF₃)₂-C₆H₃]₄B⁻), the first of which is com-

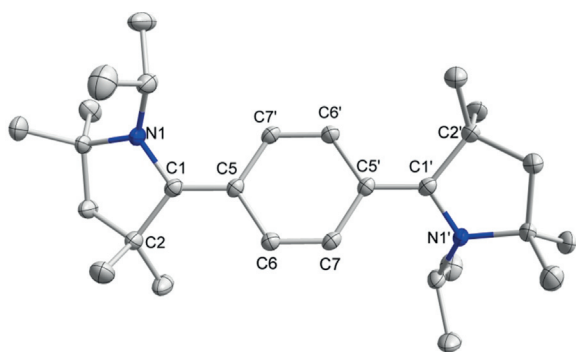


Figure 5. Molecular structure of 4^{paami} with thermal ellipsoids at 50%. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angle [°]: N1–C1 1.395(2), C1–C5 1.381(2), C5–C6 1.452(2), C6–C7 1.352(2), C7–C5' 1.453(2); N1–C1–C2 108.15(10).

pletely reversible (Figure 3; see Figures S34 and S35).^[17] The difference between the two reduction waves of 270 mV points to a reasonable thermodynamic stability for the one-electron-reduced mixed-valence species. However, the second reduction is not reversible in CH_3CN solvent. The native form of 3^m in solution displays absorption bands only in the UV region. Upon one-electron reduction new bands appear in the visible region with maxima at $\lambda_{\text{max}} = 364$ and $\lambda_{\text{max}} = 493$ nm (Figure 6). Reversing the potential to the starting potential led to the quantitative regeneration of the spectrum corresponding to 3^m , thus proving the reversible nature of the first reduction wave on the Vis-NIR spectro-electrochemical timescale. The second reduction turned out to be irreversible in CH_3CN as the starting spectrum of the compound could not be regenerated once two electrons were added. This behavior implies that 4^m , the two-electron-reduced compound, reacts with CH_3CN . This reactivity was confirmed by an independent reaction of 4^m and CH_3CN . This finding is in contrast to the stability of 4^m in *n*-hexane (see Figure S32).^[17] However, the initial changes in the UV/vis spectrum upon the second reduction of 3^m are very similar to those observed for the one-electron-reduced species (Figure 6). This data suggests that there is no electronic coupling between the two reduced centers in the two-electron-reduced form, and the differences in the redox potentials between the two reduction waves should be largely assigned to coulombic interactions. No further bands at longer wavelengths were observed either for the one- or the two-electron-reduced compounds. It was not possible to investigate the one-electron-reduced form of 3^m by

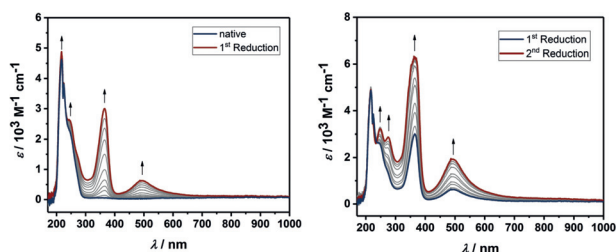
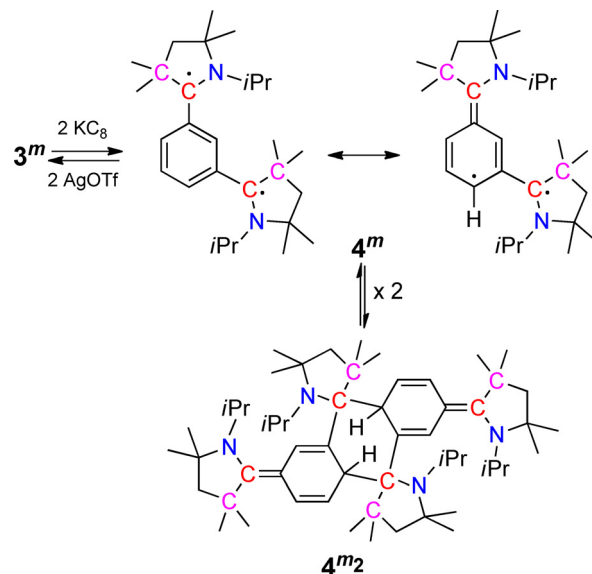


Figure 6. Changes in UV/vis spectrum of 3^m in MeCN with 0.1 M Bu_4NPF_6 during the first reversible (left) and second irreversible (right) reduction.

EPR spectroscopy. Both EPR spectro-electrochemistry (longer electrolysis times compared to Vis-NIR spectroelectrochemistry because of different cell designs) and chemical reduction proved unsuccessful for this purpose.

When the reduction of 3^m was carried out with two equivalents of KC_8 in *n*-hexane, the formation of a deep-red colored solution was observed (Scheme 4). After work up, the



Scheme 4. Syntheses of 4^m and 4^{m_2} .

resulting red and sticky compound was crystallized from a benzene/*n*-hexane solution, and after one week very few yellow crystals of 4^{m_2} could be isolated in a reproducible manner, the molecular structure of which was confirmed by single-crystal X-ray diffraction analysis (Figure 7).^[18] 4^{m_2} is

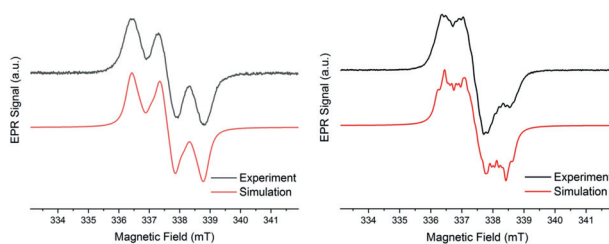


Figure 7. EPR spectra at 25 °C of 4^m as a red oil (left) and 4^m in *n*-hexane solution (by dissolving the red oil) (right).

the dimer of the initially formed diradical 4^m and is possibly formed by an intermolecular double head-to-tail dimerization. 4^m can be reversibly reoxidized to 3^m by two equivalents of AgOTf in *n*-hexane in a 58% yield, indirectly indicating the existence of a diradical center in 4^m (Scheme 4). *m*-Quinodimethane, the parent hydrocarbon of either the *m*-quinonoid or dimethyl-substituted *m*-quinodimethane, is also known to dimerize in an intermolecular double head-to-head fashion under the formation of *m*-cyclophane.^[20] In benzene, 4^{m_2}

dissociates to 4^m , a process that can be followed by a slow color change from light yellow to red.

The chemically isolated two-electron-reduced 4^m was investigated both as the red sticky compound as well as in solution in *n*-hexane by EPR spectroscopy. In both cases, strong EPR responses were observed with signals centered at *g*-values of 2.0032 and 2.0042 respectively (Figure 7).^[17] The spectrum in solution was nicely simulated by considering hyperfine coupling to one ^{14}N and to five different ^1H nuclei (see Table S2).^[17] These findings support a diradical nature of 4^m as required for the subsequent dimerization reaction. Additionally, the EPR data indicate the existence of two uncoupled electron spins in 4^m . This fact is also supported indirectly by the Vis-NIR spectro-electrochemistry data, where the attempted generation of the two-electron-reduced species delivered a spectrum that just displayed a doubling of intensity of the spectrum of the one-electron-reduced form (see above). Calculations at the TPSSh/def2-TZVP level of theory indicate a triplet ground state for 4^m with the excited singlet state lying at least 400 cm^{-1} higher in energy.^[17] A likely explanation for the observation of two uncoupled spins could be the orthogonal twist of the spin-containing peripheral groups with respect to the central phenyl ring. The spin-spin coupling in this case is likely to be highly sensitive to the aforementioned twist, and DFT calculations probably overestimate the coupling because of this sensitivity.

In 4^m_2 , the sum of the bond angles around C1 ($\Sigma\text{C1} = 359.9^\circ$) and C11 ($\Sigma\text{C11} = 325.84^\circ$) indicate that centers adopt a planar and a pyramidal geometry, respectively. The C1–C5 bond distance is $1.370(6)\text{ \AA}$ whereas the C7–C11 bond distance is $1.535(6)\text{ \AA}$. The six-membered ring (C8–C7–C11–C8'–C7'–C11') in the dimer adopts a chair conformation (Figure 8).^[18] Theoretical calculations show that dimerization of 4^m to 4^m_2 is favored, with $\Delta G_{298} = -10.4\text{ kcal mol}^{-1}$.^[17]

In conclusion, we have designed and synthesized the first CAAC-based Thiele and Schlenk hydrocarbons without the use of CAAC as a precursor. The CAAC analogue of the

Thiele hydrocarbon displays a singlet ground state (Kekulé diradical) while the CAAC analogue of the Schlenk hydrocarbon shows two unpaired electrons (non-Kekulé diradical) and undergoes an intermolecular double head-to-tail dimerization. The straightforward synthetic methodology revealed in this study will be instrumental for generating new classes of carbon-center-based di- and polyradical systems^[21] and also for the synthesis of a new class of organic redox systems.

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Conflict of interest

The authors declare no conflict of interest.

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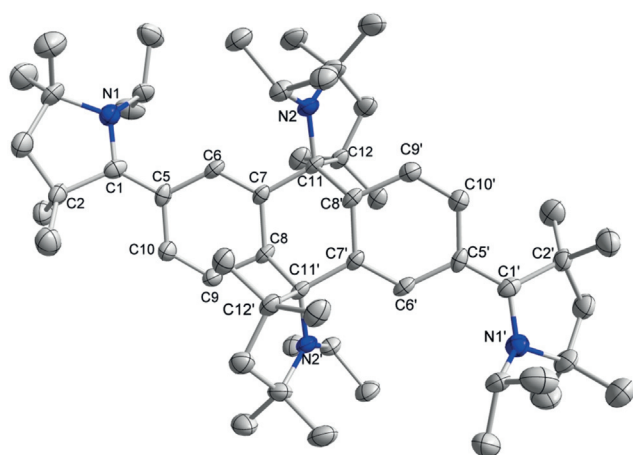


Figure 8. Molecular structure of 4^m_2 with thermal ellipsoids at 50%. All hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and bond angles [$^\circ$]: N1–C1 1.391(5), C1–C5 1.370(6), C5–C6 1.465(6), C6–C7 1.341(5), C7–C8 1.512(6), C8–C9 1.501(6), C9–C10 1.336(6), C10–C5 1.443(6), C7–C11 1.535(6), C8–C11' 1.594(5), C11–N2 1.478(5); N1–C1–C2 109.33(30), N2–C11–C12 103.00(26).

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