Supporting Information

cAAC-Stabilized 9,10-diboraanthracenes—Acenes with Open-Shell Singlet Biradical Ground States

Christian Saalfrank, Felipe Fantuzzi, Thomas Kupfer, Benedikt Ritschel, Kai Hammond, Ivo Krummenacher, Rüdiger Bertermann, Raphael Wirthensohn, Maik Finze, Paul Schmid, Volker Engel, Bernd Engels, and Holger Braunschweig*

anie_202008206_sm_misellaneous_information.pdf
Supporting Information

This PDF file includes:

Materials and Methods
Figs. S1 to S24
Tables S1 to S3
Additional References
S1 Synthetic details and characterization of compounds

General experimental considerations: All reactions were carried out under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. NMR spectra were obtained from Bruker Avance 400 and 500 NMR spectrometers at room temperature. Chemical shifts (δ) are given in ppm and are internally referenced to the carbon nuclei (13C(1H)) or residual protons (1H) of the solvent. NMR spectra were referenced to SiMe4 (1H, 13C), or BF3·OEt2 (11B) as external standards. Solid-state NMR-data were obtained with a Bruker DSX 400 NMR spectrometer. Microanalyses (C, H, N) were performed on an Elementar vario MICRO cube elemental analyzer. HRMS were measured on an Exactive Plus Orbitrap-HRMS manufactured by Thermo Scientific. UV/VIS-measurements were performed at JASCO-V660 and Mettler Toledo UV spectrometers. Absorptions maxima are given in nm with shoulders in brackets, the global maximum being underlined. EPR measurements at X-band (9.4 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using MATLAB 9.6 (2019a) and the EasySpin 5.2.25 toolbox. C6D6 was purchased from Sigma Aldrich, degassed by three freeze-pump-thaw cycles, and dried over molecular sieves. Other solvents were dried by storage over, and distillation from sodium (benzene, toluene), Na/K alloy (hexanes, pentane, THF), 4Å molecular sieves (1,2-difluorobenzene) under an argon atmosphere. Solvents were stored under argon over activated 4Å molecular sieves. cAACMe,[2] cAACCy,[2] 9,10 Dibromo-9,10-dihydro-9,10-diboraanthracene,[3] and Bogdanovic magnesium, [Mg(thf)3][C14H10],[4] were prepared according to literature methods. S8 and CO (Grade 5.0) were purchased from Sigma-Aldrich and Linde, respectively, and used as received.
Synthesis and characterization of 2a

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (1.62 g, 4.86 mmol) in toluene (10 mL) was cooled to –78 °C and reacted dropwise with a solution of cAACMe (2.77 g, 9.72 mmol) in toluene (5 mL). The mixture was allowed to reach 0 °C, and stirred at that temperature for 14 h, during which time a white precipitate formed. The solvent was reduced to approximately half of the volume in vacuo. The off-white solid was collected on a medium porosity frit, washed with toluene and hexanes (3 x 5 mL each), and dried in vacuo. Yield: 1.93 g (2.14 mmol, 44%) of an off-white solid. Note: Due to the low solubility and high lability of 2a, no reliable solution NMR parameter could be obtained. Also, no solid-state 1H NMR data are available.

13C NMR (VACP/MAS, 13.5 kHz): \( \delta = 233.3 \) (C carbene), 210.1 (Cq-aryl), 193.7 (Cq-aryl), 149.3 (Cp-aryl), 145.8 (Cp-aryl), 144.1 (Cp-aryl), 137.5 (Cm-aryl), 136.2 (Cm-aryl), 130.9 (Cp-aryl), 128.9 (C anthracene), 124.5 (C anthracene), 84.8 (C(CH3)2), 83.3 (C(CH3)2), 56.6 (CH2), 53.2 (CH2), 34.9 (CH2), 30.4 (CH3), 29.1 (CH3), 26.7 (CH3).

11B NMR (VACP/MAS, 14.8 kHz): \( \delta = -6.1 \).

Elemental analysis calculated for C72H103B2N2Br4 ((cAACMe)2DBA(cAACMe)(H2Br2)): C 63.97, H 7.68, N 3.11; found: C 63.95, H 7.69, N 3.12.

Synthesis and characterization of 2b

A solution of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene (1.62 g, 4.86 mmol) in toluene (10 mL) was cooled to –78 °C and reacted dropwise with a solution of cAACV (6.32 g, 19.4 mmol) in toluene (20 mL). The mixture was allowed to reach 0 °C, and stirred at that temperature for 14 h, during which time a white precipitate formed. The solvent was reduced to approximately half of the volume in vacuo. The off-white solid was collected on a medium porosity frit, washed with toluene and hexanes (3 x 5 mL each), and dried in vacuo. Yield: 1.10 g (1.12 mmol, 23%) of an off-white solid. Note: Due to the low solubility and high lability of 2b, no reliable solution NMR parameter could be obtained. Also, no solid-state 1H NMR data are available.

13C NMR (VACP/MAS, 13.5 kHz): \( \delta = 231.2 \) (C carbene), 206.2 (Cq-aryl), 192.7 (Cq-aryl), 151.5 (Cp-aryl), 144.6 (Cp-aryl), 143.5 (Cp-aryl), 138.1 (Cm-aryl), 135.6 (Cm-aryl), 133.3 (Cp-aryl), 129.4 (Cp-aryl), 125.3 (C anthracene), 121.6 (C anthracene), 81.6 (C(CH3)2), 61.6 (R2C), 44.6 (CH2), 37.3 (CH2), 31.2 (Cm(CH3)2), 29.3 (C(CH3)2), 26.1 (CH2), 23.2(CH2).

11B NMR (VACP/MAS, 14.8 kHz): \( \delta = -4.3 \).

Elemental analysis calculated for C58H78B2N2Br2(HBr): C 65.37, H 7.47, N 2.63; found: C 65.39, H 7.48, N 2.63.
Synthesis and characterization of 3a

A suspension of 2a (200 mg, 221 µmol) in benzene (3 mL) was reacted with [Mg(thf)₃][C₁₄H₁₀] (46.3 mg, 111 µmol) at room temperature. The mixture was and stirred for 4 h, after which time 2/3 of the solvent were removed under reduced pressure. The mixture was filtrated, and the residue was washed with hexanes (5 x 5 mL), and dried in vacuo. The solid thus obtained was extracted into a minimum amount of 1,2-difluorobenzene, filtered over a medium porosity frit, and dried in vacuo. Yield: 154 mg (188 µmol, 85%) of a green solid that proved NMR silent.

**UV/vis (1,2-C₆H₄F₂):** \( \lambda_{\text{max}} = 321, 403, 471(446) \).

**FTMS/pESI** calculated for C₅₂H₇₀B₂BrN₂: m/z = 823.49; found: m/z = 823.49.

![Fig. S1 | UV/vis spectrum of 3a in 1,2-C₆H₄F₂.](image1)

![Fig. S2 | CW X-Band (9.85 GHz) EPR-spectrum of 3a at room temperature (g = 2.0020).](image2)
Synthesis and characterization of 3b

A suspension of 2b (40.0 mg, 40.6 µmol) in benzene (1 mL) was reacted with [Mg(thf)]_3[C_{14}H_{10}] (8.5 mg, 20.3 µmol) at room temperature. The mixture was and stirred for 4 h, after which time 2/3 of the solvent were removed under reduced pressure. The mixture was filtered, and the residue was washed with hexanes (5 x 1 mL) and dried in vacuo. The solid thus obtained was extracted into a minimum amount of 1,2-difluorobenzene, filtered over a medium porosity frit, and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by slow evaporation of solutions of 3b in 1,2-difluorobenzene into naphthalene. Yield: 26.8 mg (29.7 µmol, 73%) of a green solid that proved NMR silent.

UV/vis (1,2-C_{6}H_{4}F_{2}): \lambda_{\text{max}} = 364, 447, 460, 479, 773(695).

HRMS/LIFDI calculated for C_{58}H_{78}B_{2}BrN_{2}: m/z = 903.55; found: m/z = 903.55.

Fig. S3 | UV/vis spectrum of 3b in 1,2-C_{6}H_{4}F_{2}.

Fig. S4 | CW X-Band (9.85 GHz) EPR-spectrum of 3b at room temperature (g = 2.0023).
Synthesis and characterization of 4a

A suspension of 2a (1.00 g, 1.10 mmol) in toluene (10 mL) was cooled to −78 °C and reacted with [Mg(thf)3][C14H10] (456 mg, 1.21 mmol). After 1 h, the mixture was allowed to warm to room temperature, and stirred for 2 h. All volatiles were removed in vacuo, and the residue was extracted into benzene (3 x 10 mL). All volatiles of the filtrate were removed in vacuo, and anthracene removed by sublimation (10⁻⁶ mbar, 70 °C, 16 h). Crystals suitable for X-ray diffraction were obtained by slow evaporation of solutions of 4a in benzene into anthracene. Yield: 532 mg (715 µmol, 65%) of an orange solid that proved NMR silent.

UV/vis (benzene): \( \lambda_{\text{max}} = 311, 356, 425. \)

FTMS/pESI calculated for C₅₂H₇₀B₂N₂: m/z = 744.57; found: m/z = 744.57.

---

**Fig. S5** | UV/vis spectrum of 4a in benzene.

**Fig. S6** | Experimental and simulated EPR spectra of diradical 4a in frozen toluene solution at 20 K. The inset shows the forbidden \( \Delta m_s = 2 \) half-field transition. The small center peak marked with an asterisk (*) is due to a monoradical impurity. Key parameters for the simulation of the triplet state: \( g_1 = 2.005, g_2 = 2.003, g_3 = 2.002, D = 0.0284 \) cm⁻¹, \( E = 0.0003 \) cm⁻¹.
Fig. S7 | Temperature dependence of the CW X-Band EPR spectra of 4a in frozen toluene. Half-field transition (left) and the $g = 2$ signal (right).

Fig. S8 | Three different representations of the temperature dependence of the double integral EPR intensity ($A$) of 4a in frozen toluene solution. Circles (◯) represent the experimental results and the red line corresponds to the fit with the Bleaney-Bowers equation. Analysis of the variable temperature EPR data gives a singlet-triplet gap of $\Delta E(T-S) = 0.43 \text{ kJ/mol}$. 
Synthesis and characterization of 4b

A suspension of 2b (1.00 g, 1.02 mmol) in toluene (10 mL) was cooled to –78 °C and reacted with [Mg(thf)₃][C₁₄H₁₀] (412 mg, 1.10 mmol). After 1 h, the mixture was allowed to warm to room temperature, and stirred for 2 h. All volatiles were removed in vacuo, and the residue was extracted into benzene (3 x 10 mL). All volatiles of the filtrate were removed in vacuo, and anthracene removed by sublimation (10⁻⁶ mbar, 70 °C, 16 h). Crystals suitable for X-ray diffraction were obtained by slow evaporation of solutions of 4b in benzene into anthracene. Yield: 614 mg (744 µmol, 73%) of an orange brown solid that proved NMR silent.

UV/vis (benzene): $\lambda_{\text{max}} = 298$, 362, 430.

HRMS/LIFDI calculated for C₅₈H₇₈B₂N₂: m/z = 824.64; found: m/z = 824.63.

---

Fig. S9 | UV/vis spectrum of 4b in benzene.

Fig. S10 | Experimental and simulated EPR spectra of diradical 4b in toluene solution. Key parameters for the simulation of the triplet state: $g_{\text{iso}} = 2.003$; $\alpha(\text{N}) = 19$ MHz, with an exchange interaction of $J = 28$ MHz (coupling to boron not considered).
Fig. S11 | Temperature dependence of the CW X-Band EPR spectra of 4b in toluene (left). Experimental and simulated EPR spectrum of 4b after decomposition in solution (right), most likely into a monoradical boryl species. Simulation parameters are: 
\[ g_{iso} = 2.0024, \quad a(B) = 3.9 \text{ and } a(N) = 16 \text{ MHz}. \]

Fig. S12 | Three different representations of the temperature dependence of the double integral EPR intensity (A) of 4b in frozen toluene solution. Circles (◯) represent the experimental results and the red line corresponds to the fit with the Bleaney-Bowers equation. Analysis of the variable temperature EPR data gives a singlet-triplet gap of \( \Delta E(T-S) = 2.3 \text{ kJ/mol}. \)

**Attempted synthesis of 5a**

A solution of 4a (30.0 mg, 40.3 \( \mu \)mol) in benzene (0.5 mL) was degassed by three freeze-pump-thaw cycles, and one atmosphere of CO gas was introduced. The mixture was stirred for two days at room temperature, after which time all volatiles were removed \( \text{in vacuo} \). The residue was extracted into hexanes, filtered and all volatiles were again removed under reduced pressure to afford a red solid. \( ^{11} \text{B} \) NMR spectroscopy indicated the generation of 5a, however, we were not able to isolate this species analytically pure.

\( ^{11} \text{B NMR} \) (128.4 MHz, \( \text{C}_6\text{D}_6 \)): \( \delta = -0.4 \).
Synthesis and characterization of 5b

A solution of 4b (30.0 mg, 36.3 µmol) in benzene (0.5 mL) was degassed by three freeze-pump-thaw cycles, and one atmosphere of CO gas was introduced. The mixture was stirred for two days at room temperature, after which time all volatiles were removed in vacuo. The residue was extracted into hexanes, filtered and all volatiles were again removed under reduced pressure. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of saturated benzene solutions of 5b. Yield: 19.5 mg (22.9 µmol, 63%) of a red solid.

\[ \text{H NMR (400.1 MHz, C}_6\text{D}_6): \delta = 7.68 (dd, 2H, }^3\text{J}_{HH} = 8.4 \text{ Hz, }^4\text{J}_{HH} = 1.4 \text{ Hz, C}_{anthracene-H}), 7.23 (t, 2H, }^3\text{J}_{HH} = 15.2 \text{ Hz, }^4\text{J}_{HH} = 7.9 \text{ Hz, Ar}_{para-H}), 7.12 (m, C}_{anthracene-H}), 7.03 (d, 4H, }^3\text{J}_{HH} = 7.6 \text{ Hz, Ar}_{meta-H}), 6.31 (dd, }^3\text{J}_{HH} = 8.9 \text{ Hz, }^4\text{J}_{HH} = 2.3 \text{ Hz, C}_{anthracene-H}), 4.99 (dd, 2H, }^3\text{J}_{HH} = 10.1 \text{ Hz, }^4\text{J}_{HH} = 1.5 \text{ Hz, C}_{anthracene-H}), 3.42 (m, C}_{iPr-H}), 3.38 (m, C}_{iPr-H}), 3.17 (m, 3H, C}_{Cy-H}), 2.99 (m, 3H, C}_{Cy-H}), 2.02 (m, 6H, C}_{Cy-H}), 1.84 (d, 4H, }^3\text{J}_{HH} = 13.2 \text{ Hz, CH}_2), 1.64 (m, C}_{Cy-H}), 1.26 (s, 12H, C(C}_3\text{H}_3)_2), 1.18 (d, 12H, }^3\text{J}_{HH} = 6.9 \text{ Hz, C}_{iPr(CH}_3)_2), 1.14 (d, 12H, }^3\text{J}_{HH} = 6.7 \text{ Hz, C}_{iPr(CH}_3)_2).

\[ \text{C NMR (100.6 MHz, C}_6\text{D}_6): \delta = 148.2 (C}_{aryl}), 147.4 (C}_{aryl}), 136.8 (C}_{aryl}), 129.7 (C}_{aryl}), 129.4 (C}_{aryl}), 128.6 (C}_{aryl}), 125.4 (C}_{aryl}), 121.1 (C}_{aryl}), 120.6 (C}_{aryl}), 76.8 (C(CH}_3)_2), 45.5 (CH}_2), 38.3 (C}_{Cy-H}), 33.3 (C}_{Cy-H}), 29.5 (C}_{iPr(CH}_3)_2), 28.8 (C}_{iPr(CH}_3)_2), 24.6 (C}_{iPr(CH}_3)_2), 23.6 (C}_{iPr(CH}_3)_2).

\[ \text{B NMR (128.4 MHz, C}_6\text{D}_6): \delta = -2.2.\]

UV/vis (benzene): \( \lambda_{max} = 283, 463 \).

IR (solid): \( \nu(\text{CO}) = 1690 \text{ cm}^{-1} \).

HRMS/LIFDI calculated for C_{59}H_{78}B_{2}N_{2}O: m/z = 852.63; found: m/z = 852.63, 824.63 (7b).
Fig. S15 | $^1$H NMR spectrum of 5b in C$_6$D$_6$. 
S2 X-ray diffraction data

General remarks: The crystal data of 3b and 4a were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated MoKα radiation. The crystal data of 4b was collected on a XTRALAB Synergy Dualflex diffractometer with a Hybrid Pixel Array detector and multi-layer mirror monochromated CuKα radiation. The crystal data of 5b was collected on a BRUKER SMART APEX 1 diffractometer with a CCD area detector and graphite monochromated MoKα radiation. The structures were solved using intrinsic phasing method (SHELXT),[5] refined with the SHELXL program,[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for 3b: C83H80B2F3MgN2O, M_r = 1275.07, green block, 0.589×0.366×0.296 mm³, Monoclinic space group Pc, a = 16.361(4) Å, b = 10.871(3) Å, c = 15.18(5) Å, β = 109.717(12)°, V = 3100.3(13) Å³, Z = 2, ρcalcd = 1.366 g·cm⁻³, µ = 2.012 mm⁻¹, F(000) = 1330, T = 100(2) K, R_f = 0.0316, wR² = 0.0560, 12065 independent reflections [2θ≤52.042°] and 796 parameters. CCDC 2006615.

Crystal data for 4a: C118H148B4N4, M_r = 1581.57, orange block, 0.202×0.122×0.113 mm³, Triclinic space group P 1, a = 13.546(7) Å, b = 17.086(10) Å, c = 23.711(14) Å, α = 69.589(12)°, β = 77.133(11)°, γ = 67.393(15)°, V = 4721(5) Å³, Z = 2, ρcalcd = 1.113 g·cm⁻³, µ = 0.062 mm⁻¹, F(000) = 1724, T = 100(2) K, R_f = 0.0220, wR² = 0.2586, 16588 independent reflections [2θ≤50.046°] and 1106 parameters. CCDC 2006616.

Crystal data for 4b: C85H78B2N2, M_r = 824.84, orange plate, 0.167×0.112×0.032 mm³, Triclinic space group P 1, a = 9.7542(2) Å, b = 12.6657(2) Å, c = 22.2196(4) Å, α = 100.352(2)°, β = 97.137(2)°, γ = 99.894(2)°, V = 2625.95(9) Å³, Z = 2, ρcalcd = 1.043 g·cm⁻³, µ = 0.434 mm⁻¹, F(000) = 900, T = 100(2) K, R_f = 0.0628, wR² = 0.1479, 11044 independent reflections [2θ≤155,102°] and 603 parameters. CCDC 2006614.

Crystal data for 5b: C84H101B2N2O, M_r = 1176.28, violet block, 0.365×0.294×0.274 mm³, Monoclinic space group P21/n, a = 12.509(9) Å, b = 35.90(2) Å, c = 16.214(8) Å, β = 111.65(2)°, V = 6767(7) Å³, Z = 4, ρcalcd = 1.155 g·cm⁻³, µ = 0.066 mm⁻¹, F(000) = 2548, T = 100(2) K, R_f = 0.0848, wR² = 0.1565, 13329 independent reflections [2θ≤52.042°] and 1102 parameters. CCDC 2006613.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2006613-2006616. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Fig. S16 | Molecular structure of 3b in the solid state. Thermal displacement parameters are displayed at the 50%-probability level. Hydrogen atoms, co-crystallized solvent molecules, and some of the thermal ellipsoids of the cAAC\textsuperscript{Cy} ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): B1─Cα: 1.538(5), B1─Cδ: 1.539(5), B1─C9: 1.638(5), B2─Cβ: 1.542(5), B2─C10: 1.632(5), B2─Cγ: 1.548(5), Ca─Cβ: 1.446(4), Cy─C6: 1.444(4), Ca ─C1: 1.416(4), C1 ─C2: 1.370(4), C2 ─C3: 1.400(5), C3 ─C4: 1.377(4), C4 ─C5: 1.409(4), Cy─C5: 1.410(4), C5 ─C6: 1.372(4), C6 ─C7: 1.402(4), C7 ─C8: 1.370(4), C8─C9: 1.419(4), Br1─Mg: 2.4822(1), Br2─Mg: 2.4484(1), Br3─Mg: 2.4601(1), Ca─B1─C9: 120.8(3), Ca ─B1─C6: 118.8(3), B1─C6─Cy: 120.1(3), Cy─B2─Cβ: 118.6(3), Cβ─B2─C10: 120.9(3), B2─Cβ─Ca: 120.6(3), B1─Ca ─Cβ: 120.4(3), Ca─C1─C2: 123.3(3), C1─C2─C3: 119.6(3), C2─C3─C4: 123.2(3), Cy─C5─C6: 123.9(3), C5─C6─C7: 119.0(3), C6─C7─C8: 119.0(3), C7─C8─Cy: 123.4(3), Br1─Mg─Br2: 117.54(5), Br1─Mg─Br3: 112.04(5), Br ─Mg ─O: 103.67(8).

Fig. S17 | Molecular structure of 4a in the solid state. Thermal displacement parameters are displayed at the 50%-probability level. The asymmetric unit contains two independent molecules, only one is displayed. Hydrogen atoms, co-crystallized solvent molecules, and some of the thermal ellipsoids of the cAAC\textsuperscript{Me} ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): B1─C9: 1.527(6), B1─Ca: 1.583(7), B1─Cδ: 1.585(7), B2─C10: 1.52(1), B2─Cβ: 1.569(8), B2─Cγ: 1.587(9), Ca─C6: 1.441(7), Cy─C8: 1.437(9), Ca ─C1:1.394(7), C1─C2: 1.395(6), C2─C3: 1.395(6), C3─C4: 1.390(8), C4─C5: 1.400(5), Cy─C5: 1.393(7), C5─C6: 1.383(7), C6─C7: 1.376(9), C7─C8: 1.390(7), C8─C9: 1.406(7), C9─B1: 123.3(5), Ca─B1─C9: 108.1(5), Cβ─B2─C10: 128.2(5), Cβ─B2─Cy: 108.7(5), Cβ─B2─Cy: 116.2(4), Ca─Cβ─B2: 112.5(4), Cβ─Cγ─B1: 115.8(5), Cy─C5─B1: 112.8(4), B1─Ca─C1: 112.8(4), Ca─C1─C2: 122.1(4), C1─C2─C3: 119.4(5), C2─C3─C4: 120.2(5), C3─C4─C8: 121.7(5), B2─Cy─C5: 125.7(5), Cy─C5─C6: 122.9(5), C5─C6─C7: 119.5(5), C6─C7─C8: 119.6(5), C7─C8─C5: 121.8(5).
**Fig. S18 | Molecular structure of 4b in the solid state.** Thermal displacement parameters are displayed at the 50%-probability level. Hydrogen atoms, co-crystallized solvent molecules, and some of the thermal ellipsoids of the cAAC<sub>Cy</sub> ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): B1─C9: 1.531(2), B1─Ca: 1.589(3), B1─C5: 1.595(2), B2─C10: 1.528(2), B2─C8: 1.593(2), B2─Cy: 1.588(3), Ca─C8: 1.429(2), Cy─C5: 1.431(2), Ca─C1: 1.400(2), C1─C2: 1.391(3), C2─C3: 1.391(3), C3─C4: 1.394(2), C4─C6: 1.401(2), C5─C6: 1.399(2), C5─C6: 1.394(3), C6─C7: 1.384(2), C7─C8: 1.393(2), C8─C8: 1.401(3), C9─B1─Ca: 127.4(1), Ca─B1─C5: 107.2(1), C8─B2─C10: 125.1(1), C8─B2─Cy: 106.8(1), B1─Ca─C8: 113.5(1), Ca─C8─B2: , B2─Cy─C5: 117.0(1), Cy─C5─B1: 117.0(1), B1─Ca─C1: 127.5(1), Ca─C1─C2: 121.6(1), C1─C2─C3: 120.0(2), C2─C3─C4: 119.7(1), C3─C4─C8: 121.6(1), B2─Cy─C5: 127.5(1), Cy─C5─C6: 121.4(1), C5─C6─C7: 120.0(2), C6─C7─C8: 119.7(2), C7─C8─C8: 121.6(2).

**Fig. S19 | Molecular structure of 5b in the solid state.** Thermal displacement parameters are displayed at the 50%-probability level. The asymmetric unit contains two independent molecules, only one is displayed. Hydrogen atoms, co-crystallized solvent molecules, and some of the thermal ellipsoids of the cAAC<sub>Cy</sub> ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): B1─C9: 1.630(3), B1─Ca: 1.637(3), B1─C5: 1.649(3), B2─C10: 1.589(3), B2─C8: 1.609(3), B2─Cy: 1.630(3), Ca─C8: 1.417(3), Cy─C5: 1.433(3), C8─C1: 1.397(3), C1─C2: 1.396(3), C2─C3: 1.384(3), C3─C4: 1.393(3), C4─C8: 1.399(3), Cy─C5: 1.399(3), C5─C6: 1.392(3), C6─C7: 1.377(3), C7─C8: 1.394(3), C8─C8: 1.399(3), B1─C11: 1.695(3), C11─O1: 1.205(2), C11─B1: 1.755(3), C9─B1─Ca: 106.8(2), Ca─B1─C5: 105.5(2), Ca─B1─C11: 98.9(1), C6─B2─C10: 121.9(2), C6─B2─Cy: 104.0(2), C8─B2─C11: 99.3(1), B1─Ca─C8: 109.8(2), C8─B2: 110.7(2), B2─Cy─C8: 110.5(2), C6─B2─Cy: 104.0(2), C8─C8─B1: 109.0(2), B1─Ca─C1: 130.7(2), Ca─C1─C2: 120.9(2), C1─C2─C3: 119.7(2), C2─C3─C4: 120.1(2), C3─C4─C5: 121.2(2), B2─Cy─C5: 130.2(2), Cy─C5─C6: 121.4(2), C5─C6─C7: 121.4(2), C6─C7─C8: 121.4(2), C7─C8─C8: 121.4(2), B1─C11─B2: 94.9(1), B1─C11─O1: 133.1(2), B2─C11─O1: 130.6(2).
S3 Computational details

**General remarks:** Initially, we performed geometry optimization and hessian calculations for the closed-shell singlet (CS), open-shell singlet (OS) and triplet (T) states of 4a and 4b at the (U)B3LYP[7L-D3(BJ)[8]/def2-SVP[10] level of theory. We collected the vertical $\Delta E$ and adiabatic $\Delta E_0$ energy gaps between the states, the former calculated at the equilibrium geometry of the OS states. The DFT calculations pointed the OS states as the ground states of both systems, with the triplet states lying less than 0.15 kcal/mol above. Additionally, we also optimized the geometry of 5b at the B3LYP-D3(BJ)/def2-SVP level of theory. All systems were characterized as minimum energy structures by vibrational frequency calculations, which indicated that all Hessian eigenvalues were positive. In order to confirm the biradical character[11] of the singlet diboraanthracenes studied herein, as well as to validate the computed singlet-triplet gaps obtained by DFT, single-point calculations were performed for 4a using high-level complete active space self-consistent field (CASSCF)[12] and N-electron valence state second-order perturbation theory (NEVPT2)[13] calculations. Due to the large molecular size, these calculations were done using the Resolution of the Identity (RI)[14] approximation. The CASSCF calculations were performed for two distinct active spaces: one composed of 2 electrons and 2 orbitals, CASSCF(2,2); and a second one containing 6 electrons and 6 orbitals, CASSCF(6,6). For an accurate determination of the adiabatic singlet-triplet gaps, RI-NEVPT2 calculations were performed using reference CASSCF(2,2) and CASSCF(6,6) wavefunctions for both the singlet and triplet multiplicities. All DFT calculations were performed with the Gaussian 16, Revision B.01 software.[15] CASSCF and RI-NEVPT2 calculations were performed with the Orca 4.1.1 software.[16] Pictures of molecular structures, orbitals and densities were visualized and generated with Chemcraft, CYLview,[17] and Gaussview.

The biradical character index, $y$

The $y$ index,[18] which can vary from 0 (closed-shell system) to 1 (pure biradical state), was obtained for 4a using the natural orbital occupancy numbers (NOON)[19] of the highest occupied (HONO) and lowest unoccupied (LUNO) natural orbitals from the CASSCF calculations, according to the following expression[18]:

$$y = 1 - \frac{2T}{1 + T^2} \quad (S1)$$

where $T$ is the orbital overlap of HONO and LUNO, and is given by:

$$T = \frac{NOON_{HONO} - NOON_{LUNO}}{2} \quad (S2)$$
Fig. S20 | Mulliken spin density plots of 7a. Blue colors illustrate the alpha spin density, and white colors are used for the beta spin density. Level of theory: B3LYP-D3(BJ)/def2-SVP; isovalues: 0.004 au.

Table S1 | Electronic energies of open-shell singlet (OS), closed-shell singlet (CS) and triplet states of 4a and 4b. The vertical (ΔE(T-OS) and ΔE(OS-CS)) and adiabatic (ΔE₀(T-OS) and ΔE₀(OS-CS)) energy gaps, as well as the average values of <S²> for the OS state before and after (values in parentheses) annihilation of the first spin contaminant, are also shown.

|                   | 4a                      | 4b                      |
|-------------------|-------------------------|-------------------------|
| **Electronic energies, E, at the open-shell singlet optimized structure** |                         |                         |
| OS, Eₙ            | -2181.683400            | -2415.024889            |
| CS, Eₙ            | -2181.655968            | -2414.998135            |
| TS, Eₙ            | -2181.683221            | -2415.024678            |
| <S²> (OS)         | 1.00 (0.05)             | 1.00 (0.05)             |
| Vertical ΔE(T-OS), kcal/mol | 0.11                   | 0.13                   |
| Vertical ΔE(OS-CS), kcal/mol | -17.21                  | -16.79                  |
| **ZPE-corrected energies, E+ZPE** |                         |                         |
| OS, Eₙ            | -2180.575091            | -2413.783645            |
| CS, Eₙ            | -2180.555035            | -2413.764114            |
| TS, Eₙ            | -2180.574861            | -2413.783413            |
| Adiabatic ΔE₀(T-OS), kcal/mol | 0.14                   | 0.15                   |
| Adiabatic ΔE₀(OS-CS), kcal/mol | -12.59                 | -12.26                 |
Table S2 | CASSCF(2,2)/RI-NEVPT2 results of the singlet and triplet states of 4a using the def2-SVP basis set.

| CASSCF(2,2)/def2-SVP |
|----------------------|
| Electronic energy (singlet), $E_h$ | -2166.526832 |
| Electronic energy (triplet), $E_h$ | -2166.527022 |
| Weight of the 2 0 configuration (singlet) | 0.53858 |
| Weight of the 0 2 configuration (singlet) | 0.46142 |
| Occupation of the HONO (ON$^{HONO}$, singlet) | 1.0772 |
| Occupation of the LUNO (ON$^{LUNO}$, singlet) | 0.9228 |
| HONO-LUNO orbital overlap (T, singlet) | 0.0772 |
| Biradical character ($\gamma$, singlet) | 0.847 (84.7%) |

| RI-NEVPT2/CASSCF(2,2)/def2-SVP |
|-------------------------------|
| Electronic energy (singlet), $E_h$ | -2174.430054 |
| Electronic energy (triplet), $E_h$ | -2174.429979 |
| Adiabatic singlet-triplet gap, $\Delta E_d$(T-S), kcal/mol | 0.05 |

Fig. S21 | CASSCF(2,2) active space natural orbitals of 4a. Natural orbital occupation numbers (NOON) are also shown. Level of theory: CASSCF(2,2)/def2-SVP from optimized structures at UB3LYP-D3(BJ)/def2-SVP. CASSCF calculations were performed with the Resolution of the Identity (RI) approximation.
Table S3 | CASSCF(6,6)/RI-NEVPT2 results of the singlet and triplet states of 4a using the def2-SVP basis set.

| CASSCF(6,6)/def2-SVP                                      | RI-NEVPT2/CASSCF(6,6)/def2-SVP |
|----------------------------------------------------------|---------------------------------|
| Electronic energy (singlet), $E_h$                        | -2166.538685                    |
| Electronic energy (triplet), $E_h$                        | -2166.538864                    |
| Weight of the 2 2 2 0 0 0 configuration (singlet)         | 0.53042                         |
| Weight of the 2 2 0 2 0 0 configuration (singlet)         | 0.45298                         |
| Occupation of the HONO (ON$^{TONO}$, singlet)            | 1.0789                          |
| Occupation of the LUNO (ON$LUNO$, singlet)               | 0.9213                          |
| HONO-LUNO orbital overlap (T, singlet)                    | 0.0788                          |
| Biradical character ($\gamma$, singlet)                   | 0.843 (84.3%)                   |
| Electronic energy (singlet), $E_h$                        | -2174.436983                    |
| Electronic energy (triplet), $E_h$                        | -2174.436875                    |
| Adiabatic singlet-triplet gap, $\Delta E_0(T-S)$, kcal/mol | 0.07                            |

Fig. S22 | CASSCF(6,6) active space natural orbitals of 4a. Natural orbital occupation numbers (NOON) are also shown. Level of theory: CASSCF(6,6)/def2-SVP from optimized structures at UB3LYP-D3(BJ)/def2-SVP. CASSCF calculations were performed with the Resolution of the Identity (RI) approximation.
Fig. S23 | 3D image of the optimized structure of 5b. Level of theory: B3LYP-D3(BJ)/def2-SVP.

Fig. S24 | Frontier Kohn-Sham Molecular Orbitals of 5b. Level of theory: B3LYP-D3(BJ)/def2-SVP; isovalue: 0.04 au.
S4 Cartesian Coordinates

4a (closed-shell singlet), B3LYP-D3(BJ)/def2-SVP
E+ZPE = –2180.555035 Eₜₚₜ
Lowest frequency = 39.63 cm⁻¹

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| N       | -2.975739 | -0.508641 | 0.948824  |
| N       | 2.975674  | 0.508598  | 0.948769  |
| C       | 3.952144  | -0.156108 | 0.127115  |
| C       | 2.333747  | -1.242797 | -2.384504 |
| C       | 1.282382  | -0.751360 | -1.602528 |
| C       | 0.059707  | -1.465225 | -1.549463 |
| C       | -0.067127 | -2.665940 | -2.260539 |
| C       | -3.354285 | -0.997709 | 2.323793  |
| C       | 5.214750  | -2.118184 | -0.513585 |
| C       | 4.702950  | 0.626284  | -0.788360 |
| C       | -1.405971 | -2.212895 | 1.402027  |
| C       | 0.066989  | 2.665908  | -2.260224 |
| C       | -1.282557 | 0.751209  | -1.602635 |
| C       | 2.194289  | -2.443904 | -3.092358 |
| C       | 0.998294  | -3.159235 | -3.026288 |
| C       | -1.822100 | -1.063761 | 0.464197  |
| C       | 1.405718  | 2.212620  | 1.402266  |
| C       | -0.998319 | 3.159247  | -3.026100 |
| C       | 5.698747  | -0.002120 | 0.464390  |
| C       | -3.952166 | 0.156230  | 0.127298  |
| C       | 4.204750  | -1.538315 | 0.265040  |
| C       | 5.960765  | -1.363385 | -1.411883 |
| C       | -4.703063 | -0.626037 | -0.788256 |
| C       | -3.404019 | 2.434984  | 1.192463  |
| C       | 1.821881  | 1.063570  | 0.464390  |
| C       | -0.059910 | 1.465100  | -1.549316 |
| C       | -4.204610 | 1.538472  | 0.265247  |
| C       | -5.698814 | 0.002492  | -1.545263 |
| C       | -0.101294 | -1.879583 | 2.142092  |
| C       | 4.291681  | -3.060255 | 2.280072  |
| C       | 3.354232  | 0.997461  | 2.323795  |
| C       | 4.864486  | 1.174061  | 2.476937  |
| C       | -2.333788 | 1.242667  | -2.384784 |
| C       | 3.404468  | -2.434877 | 1.192471  |
| C       | 4.454004  | 2.109962  | -1.020712 |
| C       | 2.848536  | 0.048703  | 3.424341  |
| C       | 2.608135  | 2.338815  | 2.365770  |
| C       | 2.645322  | -3.522845 | 0.420090  |
| C       | 1.207948  | 3.554221  | 0.672210  |
| C       | -2.645211 | 3.523054  | 0.419888  |
| C       | -4.454160 | -2.109702 | -1.020703 |
| C       | -2.608454 | -2.339216 | 2.365418  |
| C       | 0.100945  | 1.879310  | 2.142178  |
H  -3.676320000  3.605160000  3.015237000  
H  -4.879215000  2.302416000  2.820244000  
H  -5.004140000  1.835556000  -2.013420000  
H  -5.074365000  1.589731000  3.474294000  
H  -5.272425000  1.863432000  1.727520000  
H  -3.281919000  -1.332660000  2.006318000  
H  -2.056433000  -3.786776000  0.011904000  
H  -1.130537000  -4.360446000  1.420680000  
H  -0.295710000  -3.558451000  0.069090000  
H  -0.228156000  -1.024829000  2.816574000  
H  0.678976000  -1.622850000  1.417692000  
H  0.236152000  -2.740633000  2.741725000  
H  3.276580000  -0.702204000  3.577413000  
H  3.027063000  -2.819093000  3.693360000  
H  0.886977000  -4.097195000  -3.226111000  
H  -1.004102000  -3.226111000  -2.234869000  

4a (open-shell singlet), UB3LYP-D3(BJ)/def2-SVP  
E+ZPE = -2180.575091 Eₕ  
Lowest frequency = 35.33 cm⁻¹
C  2.159280000  -2.516314000  -2.970423000  
C  0.947443000  -3.204584000  -2.906771000  
C  -1.996953000  -1.137361000  0.382682000  
C  1.576085000  2.274756000  1.333217000  
C  -0.947099000  3.204727000  -2.906777000  
C  5.779914000  -0.177060000  -1.591623000  
C  -4.057767000  0.203468000  0.113581000  
C  4.228709000  -1.597652000  0.268001000  
C  5.964628000  -1.549333000  -1.438799000  
C  -4.837900000  -0.519887000  0.382889000  
C  4.228840000  1.597634000  0.267772000  
C  5.779770000  0.177005000  -1.592058000  
C  -2.311857000  -1.918521000  2.049077000  
C  3.393780000  -2.433112000  1.223925000  
C  4.672535000  2.014588000  -1.066932000  
C  2.923280000  0.083777000  3.390999000  
C  2.769071000  2.370223000  2.310252000  
C  2.604068000  -3.534548000  0.502442000  
C  1.390875000  3.639583000  0.647116000  
C  -2.604347000  -3.534609000  0.502625000  
C  -4.672311000  -2.014592000  -1.067326000  
C  -2.769218000  -2.370399000  2.309880000  
C  0.259190000  1.918595000  2.049074000  
C  -5.193351000  2.245798000  -0.515095000  
C  -5.964576000  1.549264000  -1.439214000  
C  -1.390716000  -3.639524000  0.646888000  
C  -1.203401000  -0.663385000  -0.833023000  
C  -4.264661000  3.041946000  2.335340000  
C  -2.158929000  2.516459000  -2.970592000  
C  -6.002178000  -2.777793000  -0.980364000  
C  -3.978891000  -2.277412000  -2.413473000  
C  6.002460000  2.777693000  -0.980020000  
C  -2.923529000  -0.084033000  3.390839000  
C  3.979070000  2.277460000  -2.413046000  
B  1.203498000  0.663458000  -0.832875000  
C  -4.988550000  -1.142528000  2.466654000  
H  1.942383000  -3.116339000  -0.263994000  
H  1.987662000  -4.090908000  1.226088000  
H  3.273496000  -4.257712000  0.010918000  
H  2.660265000  -1.762068000  1.683717000  
H  4.946661000  -3.804684000  1.927931000  
H  3.635737000  -3.531515000  3.097264000  
H  4.885365000  -2.285005000  2.837572000  
H  5.325516000  -3.324434000  -0.409418000
|         |   X          |   Y          |   Z          |
|---------|--------------|--------------|--------------|
| H       | -2.458797000 | -2.663616000 | 3.323298000  |
| H       | -2.238219000 | -3.878097000 | -0.013445000 |
| H       | -1.331220000 | -1.729259000 | 1.311852000  |
| H       | 0.065225000  | -2.745615000 | 2.701519000  |
| H       | 0.816954000  | -4.145583000 | -3.448018000 |
| H       | 2.990607000  | -2.913233000 | 3.558870000  |
| H       | 0.112289000  | -2.674353000 | -2.155188000 |
| H       | 3.482189000  | -2.520483000 | -2.154946000 |
| H       | 4.843181000  | 0.515251000  | -0.827895000 |
| H       | -0.112792000 | 1.454481000  | -1.470538000 |
| H       | -0.944662000 | 3.207659000  | -2.899869000 |
| H       | 2.158179000  | -2.520483000 | -2.962955000 |
| H       | 5.192916000  | -2.250796000 | 0.513605000  |
| N       | -3.119165000 | -0.522911000 | 0.910914000  |
| N       | 3.119097000  | 0.522963000  | 0.911404000  |
| C       | 4.062193000  | -0.205156000 | 0.113038000  |
| C       | 2.311521000  | -1.313131000 | -2.274500000 |
| C       | 1.262850000  | 0.762211000  | -1.522931000 |
| C       | 0.014765000  | 1.454481000  | -1.470538000 |
| C       | -0.112289000 | 2.674353000  | -2.155188000 |
| C       | -3.482189000 | -1.008990000 | 2.286229000  |
| C       | 5.192916000  | -2.250796000 | -0.513605000 |
| C       | 4.843181000  | 0.515251000  | 0.827895000  |
| C       | -1.583453000 | -2.273950000 | 1.329500000  |
| C       | 0.112792000  | 2.674550000  | -2.154946000 |
| C       | -1.262579000 | 0.762377000  | -1.523264000 |
| C       | 2.158179000  | -2.520483000 | 2.962955000  |
| C       | 0.945436000  | -3.207427000 | -2.899753000 |
| C       | -2.004672000 | -1.140515000 | 0.378613000  |
| C       | 1.583257000  | 2.277283000  | 1.330174000  |
| C       | -0.944662000 | 3.207659000  | -2.899869000 |
| C       | 5.782901000  | -0.184758000 | -1.594002000 |
| C       | -4.062287000 | 0.205195000  | 0.112559000  |
| C       | 4.230247000  | -1.599540000 | 0.268983000  |
| C       | 5.964896000  | -1.557199000 | -1.439313000 |
| C       | -4.843125000 | -0.515267000 | -0.828449000 |
| C       | -3.394836000 | 2.432199000  | 1.226405000  |
| C       | 2.004598000  | 1.140573000  | 0.379141000  |
| C       | -0.114511000 | 1.454650000  | -1.470394000 |
| C       | -4.230521000 | 1.599562000  | 0.268541000  |
| C       | -5.782856000 | 0.184655000  | -1.594622000 |
| C       | -0.266760000 | -1.919661000 | 2.045298000  |
| C       | 4.263940000  | -3.039448000 | 2.339558000  |
| C       | 3.482045000  | 1.008834000  | 2.286806000  |
| C       | 4.994629000  | 1.142957000  | 2.464844000  |
| C       | -2.310967000 | 1.313326000  | -2.275207000 |
| C       | 3.394253000  | -2.432097000 | 1.226647000  

|         | X          | Y          | Z          |
|---------|------------|------------|------------|

4a (triplet), UB3LYP-D3(BJ)/def2-SVP

\(E + ZPE = -2180.574862 \text{ E}_h\)

Lowest frequency = 35.21 \text{ cm}^{-1}
| Atom | X Position | Y Position | Z Position |
|------|------------|------------|------------|
| C    | 4.680914000 | 2.010114000 | -1.071033000 |
| C    | 2.928697000 | 0.086798000 | 3.389721000 |
| C    | 2.776308000 | 2.372390000 | 2.307081000 |
| C    | 2.603425000 | -3.534601000 | 0.507947000 |
| C    | 1.397309000 | 3.643074000 | 0.646265000 |
| C    | -2.603341000 | 3.534293000 | 0.507811000 |
| C    | -4.680640000 | -2.010101000 | -1.071609000 |
| C    | -2.776581000 | -3.389721000 | 2.306292000 |
| C    | 0.266533000 | 1.919372000 | 2.045826000 |
| C    | -5.193169000 | 2.250733000 | -0.514145000 |
| C    | -5.964991000 | 1.557077000 | -1.439939000 |
| C    | -1.397526000 | -3.643074000 | 0.645394000 |
| B    | -1.207927000 | -0.664497000 | -0.834157000 |
| C    | -4.265009000 | 3.040148000 | 2.338611000 |
| C    | -2.157377000 | 2.520711000 | -2.963549000 |
| C    | -6.012323000 | -2.770329000 | -0.986143000 |
| C    | -3.986949000 | -2.372390000 | 2.417578000 |
| C    | 6.012761000 | 2.770091000 | -0.985869000 |
| C    | 3.986980000 | -2.273323000 | 2.416852000 |
| B    | -1.207971000 | 0.664591000 | 2.464205000 |
| C    | -4.994789000 | -1.143009000 | 2.464205000 |
| H    | 1.941653000 | -3.117754000 | -0.259121000 |
| H    | 1.986948000 | -4.088799000 | 1.233196000 |
| H    | 3.272053000 | -4.259455000 | 0.017826000 |
| H    | 2.661278000 | -1.759353000 | 1.684853000 |
| H    | 4.945373000 | -3.804097000 | 1.933442000 |
| H    | 3.635297000 | -3.526282000 | 3.102420000 |
| H    | 4.886562000 | -2.282214000 | 2.839430000 |
| H    | 5.320381000 | -3.329491000 | -0.406830000 |
| H    | 6.704120000 | -2.085488000 | -2.046138000 |
| H    | 6.383627000 | 0.356634000 | -2.327488000 |
| H    | 4.027717000 | 2.409909000 | -0.287276000 |
| H    | 6.698607000 | 2.488793000 | -1.800221000 |
| H    | 6.531331000 | 2.576850000 | -0.034176000 |
| H    | 5.837891000 | 3.854965000 | -1.065899000 |
| H    | 4.606434000 | 1.921250000 | -3.257319000 |
| H    | 3.807220000 | 3.351458000 | -2.557962000 |
| H    | 3.018892000 | 1.756725000 | -2.475471000 |
| H    | 1.878823000 | -0.173802000 | 3.211712000 |
| H    | 2.995101000 | 0.602164000 | 4.360145000 |
| H    | 3.502629000 | -0.842252000 | 3.469125000 |
| H    | 5.432611000 | 1.818059000 | 1.718452000 |
| H    | 5.499926000 | 0.170172000 | 2.383116000 |
| H    | 5.204722000 | 1.554741000 | 3.468325000 |
| H    | 2.466075000 | 2.666694000 | 3.320260000 |
| H    | 3.477750000 | 3.140357000 | 1.945317000 |
| H    | -0.524208000 | 1.732782000 | 1.308523000 |
| H    | -0.057399000 | 2.744708000 | 2.700807000 |
| H    | 0.368454000 | 1.017566000 | 2.661311000 |
| H    | 0.476721000 | 3.683864000 | 0.056194000 |
\[
\begin{align*}
\text{H} & \quad 2.244130000 \quad 3.882421000 \quad -0.014695000 \\
\text{H} & \quad 1.338994000 \quad 4.427211000 \quad 1.419838000 \\
\text{H} & \quad 1.067479000 \quad 3.204186000 \quad -2.143154000 \\
\text{H} & \quad -0.813271000 \quad 4.148882000 \quad -3.440506000 \\
\text{H} & \quad -2.988525000 \quad 2.918843000 \quad -3.551420000 \\
\text{H} & \quad -3.261371000 \quad 0.786080000 \quad -2.354695000 \\
\text{H} & \quad -1.987161000 \quad 4.088580000 \quad 1.233244000 \\
\text{H} & \quad -3.271516000 \quad 4.259148000 \quad 0.017074000 \\
\text{H} & \quad -1.941217000 \quad 3.117052000 \quad -2.143154000 \\
\text{H} & \quad -3.636676000 \quad 3.526941000 \quad 3.101976000 \\
\text{H} & \quad -4.883330000 \quad 2.283280000 \quad 2.838322000 \\
\text{H} & \quad -4.945895000 \quad 3.804974000 \quad 1.931861000 \\
\text{H} & \quad -2.662282000 \quad 1.759414000 \quad 1.685225000 \\
\text{H} & \quad -5.323477000 \quad 3.329407000 \quad -0.407339000 \\
\text{H} & \quad -6.704216000 \quad 2.085302000 \quad -2.046819000 \\
\text{H} & \quad -6.383458000 \quad -0.356784000 \quad -2.328174000 \\
\text{H} & \quad -4.027201000 \quad -2.409763000 \quad -0.287982000 \\
\text{H} & \quad -3.502180000 \quad 0.841834000 \quad 3.468958000 \\
\text{H} & \quad -1.878869000 \quad 0.173313000 \quad 3.211391000 \\
\text{H} & \quad -2.995207000 \quad -0.602817000 \quad 4.359652000 \\
\text{H} & \quad -5.499996000 \quad -0.170163000 \quad 2.382656000 \\
\text{H} & \quad -5.204495000 \quad -1.554972000 \quad 3.463099000 \\
\text{H} & \quad -5.432815000 \quad -1.817924000 \quad 1.717667000 \\
\text{H} & \quad -3.478060000 \quad -3.140444000 \quad 1.944319000 \\
\text{H} & \quad -2.466448000 \quad -2.667139000 \quad 3.319436000 \\
\text{H} & \quad -2.244295000 \quad -3.882268000 \quad -0.015692000 \\
\text{H} & \quad -1.339346000 \quad -4.427351000 \quad 1.418849000 \\
\text{H} & \quad -0.476880000 \quad -3.683846000 \quad 0.055413000 \\
\text{H} & \quad -0.368689000 \quad -1.017964000 \quad 2.660940000 \\
\text{H} & \quad 0.524031000 \quad -1.732960000 \quad 1.308077000 \\
\text{H} & \quad 0.057106000 \quad -2.745128000 \quad 2.700148000 \\
\text{H} & \quad 3.261969000 \quad -0.788425000 \quad -2.353581000 \\
\text{H} & \quad 2.989546000 \quad -2.918598000 \quad -3.550528000 \\
\text{H} & \quad 0.814245000 \quad -4.148630000 \quad -3.440472000 \\
\text{H} & \quad -1.066970000 \quad -3.204007000 \quad -2.143741000 \\
\end{align*}
\]

4b (closed-shell singlet), B3LYP-D3(BJ)/def2-SVP

\[E+ZPE = -2413.764114 \text{ E}_h\]

Lowest frequency = 19.73 cm\(^{-1}\)
H  -2.314169000  4.427880000  0.481109000
H  -3.499651000  4.171303000 -0.806032000
H  -1.996442000  3.230644000 -0.796835000
C   2.774143000 -3.659520000 -0.156473000
H   3.499791000 -4.170774000 -0.806114000
H   1.996329000 -3.230552000 -0.796835000
C   5.989357000 -1.310268000  1.821343000
H   6.774687000 -1.735861000  2.450411000
H   4.334981000 -2.320950000  1.781095000
H   4.892771000 -2.486295000  2.367241000
H   5.075274000 -3.909894000  1.326789000
H   3.722750000 -3.827755000  2.477398000
C   3.781011000  2.421570000 -2.564532000
H   3.519168000  3.489719000 -2.633669000
H   2.862084000  1.835642000 -2.997960000
H   4.455966000  2.185672000 -3.402829000
C   5.717561000  2.959192000 -1.029662000
H   5.464029000  4.031348000 -1.045185000
H   6.449646000  2.784450000 -1.833477000
H   6.217125000  2.741916000 -0.073145000
C  -1.867712000 -1.005702000  0.284060000
N  -3.021926000 -0.386771000  0.690910000
C   2.786122000  2.152462000  2.204270000
H   3.490302000  2.920676000  1.849160000
H   2.554355000  2.392013000  3.249320000
C   2.888880000 -0.200541000  3.126122000
H   3.396333000 -1.170427000  3.091330000
H   1.817692000 -0.369685000  2.978635000
H   3.036792000  0.218820000  4.133074000
C   4.967249000  0.856348000  2.225723000
H   5.410454000  1.553169000  1.503622000
H   5.443607000 -0.124091000  2.087751000
H   5.205968000  1.214219000  3.238779000

4b (open-shell singlet), UB3LYP-D3(BJ)/def2-SVP
E+ZPE = -2413.783645 E_h
Lowest frequency = 18.77 cm^{-1}
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 6.06961000 | -1.52332100 | -1.87742700 |
| H       | 6.74597800 | -2.00071900 | -2.52523900 |
| C       | 4.39047400 | -3.23983200 | 1.84820100  |
| H       | 4.98179100 | -2.48456500 | 2.38684900  |
| H       | 5.10154500 | -3.95623700 | 1.40631900  |
| C       | 3.78067000 | -2.00071900 | 2.52523900  |
| H       | 3.79782400 | 3.42633100  | 1.40631900  |
| H       | 3.04216700 | 1.81395700  | 2.38684900  |
| C       | 6.01309600 | 2.75325000  | 1.10640700  |
| H       | 5.83067400 | 3.83990300  | 1.11647000  |
| H       | 6.71243100 | 2.53071400  | 1.92751400  |
| C       | 6.00696100 | -1.52332100 | -1.87742700 |
| H       | 6.74597800 | -2.00071900 | -2.52523900 |
| C       | 4.39047400 | -3.23983200 | 1.84820100  |
| H       | 4.98179100 | -2.48456500 | 2.38684900  |
| H       | 5.10154500 | -3.95623700 | 1.40631900  |
| C       | 3.78067000 | -2.00071900 | 2.52523900  |
| H       | 3.79782400 | 3.42633100  | 1.40631900  |
| H       | 3.04216700 | 1.81395700  | 2.38684900  |
| C       | 6.01309600 | 2.75325000  | 1.10640700  |
| H       | 5.83067400 | 3.83990300  | 1.11647000  |
| H       | 6.71243100 | 2.53071400  | 1.92751400  |
| C       | 6.00696100 | -1.52332100 | -1.87742700 |
| H       | 6.74597800 | -2.00071900 | -2.52523900 |
| C       | 4.39047400 | -3.23983200 | 1.84820100  |
| H       | 4.98179100 | -2.48456500 | 2.38684900  |
| H       | 5.10154500 | -3.95623700 | 1.40631900  |
| C       | 3.78067000 | -2.00071900 | 2.52523900  |
| H       | 3.79782400 | 3.42633100  | 1.40631900  |
| H       | 3.04216700 | 1.81395700  | 2.38684900  |
| C       | 6.01309600 | 2.75325000  | 1.10640700  |
| H       | 5.83067400 | 3.83990300  | 1.11647000  |
| H       | 6.71243100 | 2.53071400  | 1.92751400  |

4b (triplet), UB3LYP-D3(BJ)/def2-SVP

\[ E + ZPE = -2413.783412 \text{ E}_h \]

Lowest frequency = 18.39 cm\(^{-1}\)
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 0.940090000 | -2.806820000 | 3.371199000 |
| H    | -0.758956000 | -2.922538000 | 3.816241000 |
| C    | -0.129832000 | -4.417144000 | 2.380542000 |
| H    | 0.711503000 | -5.164676000 | 1.684406000 |
| H    | -1.430911000 | -4.670374000 | 1.614330000 |
| H    | -2.280674000 | -4.716382000 | 2.317614000 |
| H    | -1.389974000 | -5.656065000 | 1.121685000 |
| C    | -1.669702000 | -3.581243000 | 0.562217000 |
| H    | -2.587608000 | -3.791970000 | -0.009234000 |
| H    | -0.838521000 | -3.594725000 | -0.152994000 |
| C    | 1.430765000 | 4.670357000 | 2.317630000 |
| H    | 2.280596000 | 4.716441000 | 2.317630000 |
| H    | 1.389679000 | 5.656051000 | 1.121807000 |
| C    | 4.304284000 | 1.704105000 | -0.146045000 |
| C    | 5.267327000 | 2.289927000 | -0.978600000 |
| H    | 5.422057000 | 3.369536000 | -0.933565000 |
| C    | 6.007921000 | 1.533251000 | -1.879581000 |
| H    | 6.744777000 | 2.013289000 | -2.527904000 |
| C    | 5.797557000 | 0.158627000 | -1.952638000 |
| H    | 6.374319000 | -0.436115000 | -2.663782000 |
| C    | 4.866703000 | -0.479476000 | -1.124641000 |
| C    | 0.018470000 | 1.460262000 | -1.620778000 |
| C    | -1.234966000 | 0.780381000 | -1.710149000 |
| C    | 2.079543000 | 1.053280000 | 0.199386000 |
| B    | 1.226948000 | 0.638353000 | -0.997568000 |
| N    | 3.186470000 | 0.360377000 | 0.655336000 |
| C    | 1.669565000 | 3.581268000 | 0.562277000 |
| H    | 2.587405000 | 3.792090000 | -0.009247000 |
| H    | 0.838323000 | 3.594684000 | -0.152866000 |
| C    | 0.129790000 | 4.416994000 | 2.380784000 |
| H    | -0.002733000 | 5.164492000 | 3.180714000 |
| H    | -0.711639000 | 4.551444000 | 1.684753000 |
| C    | -2.047661000 | 2.511428000 | -3.230033000 |
| H    | -2.845480000 | 2.899224000 | -3.868761000 |
| C    | -4.698124000 | -1.985518000 | -1.263492000 |
| H    | -4.040936000 | -2.325089000 | -0.457117000 |
| C    | -2.970371000 | -2.131383000 | 2.168108000 |
| H    | -3.718996000 | -2.869458000 | 1.840619000 |
| H    | -2.714942000 | -2.376760000 | 3.206345000 |
| C    | -3.577631000 | -0.728367000 | 2.055904000 |
| C    | -1.759155000 | -2.176022000 | 1.205035000 |
| C    | -3.500682000 | 2.615093000 | 0.768224000 |
| H    | -2.733819000 | 2.000395000 | 1.255116000 |
| C    | 4.866639000 | 0.479369000 | -1.124693000 |
| C    | 0.179628000 | 2.674176000 | -2.310695000 |
| H    | 1.136455000 | 3.198295000 | -2.267945000 |
| C    | -0.179545000 | -2.674088000 | -2.310693000 |
| H    | -1.136707000 | -3.198209000 | -2.267928000 |
| C    | 0.839102000 | -3.197868000 | -3.114946000 |
| H    | 0.677963000 | -4.130030000 | -3.663150000 |
| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | 2.04771 | -2.51131| -3.23015|
| H    | 2.84551 | -2.89910| -3.86885|
| C    | 2.24285 | -1.32086| -2.52216|
| H    | 3.19126 | -0.79812| -2.63743|
| C    | 1.23504 | -0.78027| -1.71020|
| C    | -0.83903| 3.19795 | 3.11493 |
| H    | -0.67789| 4.13079 | -3.66315|
| C    | 3.57733 | 0.72847 | 2.05591 |
| C    | -4.00780| -2.33873| -2.58977|
| H    | -3.04941| -1.81093| -2.69258|
| C    | -4.63724| -2.06247| -3.45074|
| C    | -3.80973| -3.42122| -2.64953|
| C    | 3.50064 | -2.61508| 0.76833 |
| H    | 2.73373 | -2.00385| 1.25514 |
| C    | 4.69803 | 1.98543 | -1.26363|
| C    | 4.04037 | 2.32505 | -0.45720|
| C    | -2.93951| 0.21857 | 3.08914 |
| H    | -1.87499| 0.37609 | 2.88040 |
| H    | -3.03117| -0.22144| 4.09456 |
| H    | -3.43220| 1.19616 | 3.11019 |
| C    | -4.39558| 3.23789 | 1.85338 |
| H    | -3.78647| 3.78323 | 2.59238 |
| C    | -4.98851| 2.48178 | 2.38928 |
| C    | -5.10525| 3.95616 | 1.41226 |
| C    | -5.09369| -0.74833| 2.24807 |
| C    | -5.32185| -1.09204| 3.26844 |
| C    | -5.58080| -1.43059| 1.53924 |
| C    | -5.53569| 0.24890 | 2.11685 |
| C    | 5.79743 | -0.15876| -1.95273|
| C    | 6.37415 | 0.43594 | -2.66393|
| C    | 5.26724 | -2.29001| -0.97855|
| C    | 5.42194 | -3.36962| -0.93350|
| C    | -6.02502| -2.74395| -1.11406|
| C    | -6.53165| -2.49212| -0.16958|
| C    | -5.84556| -3.83108| -1.12529|
| C    | -6.72296| -2.51853| -1.93557|
| C    | -2.77020| 3.71816 | 0.01115 |
| C    | -2.32971| 4.44274 | 0.68856 |
| C    | -3.45440| 4.27723 | 0.66605 |
| C    | -1.96908| 3.30806 | -0.63541|
| C    | 2.77023 | -3.71824| -0.01100|
| C    | 3.45447| -4.27726| 0.66645 |
| C    | 1.96906| -3.30817| 0.63528 |
| C    | 2.32984| -4.44235| 0.68875 |
| C    | 6.00778| -1.53337| 1.87961 |
| C    | 6.74459| -2.01345| 2.52796 |
| C    | 4.39551| -3.23777| 1.85358 |
| C    | 4.98836| -2.48159| 2.38921 |
| C    | 5.10524| -3.95603| 1.41255 |
| C    | 3.78637| -3.78309| 2.59258 |
| C    | 4.00754| 2.33854 | -2.58965|
|     | X     | Y     | Z     |
|-----|-------|-------|-------|
| C   | 3.809455000 | 3.421022000 | -2.650080000 |
| H   | 3.049142000 | 1.810734000 | -2.692493000 |
| H   | 4.636899000 | 2.062299000 | -3.450882000 |
| C   | 6.024951000 | 2.743855000 | -1.114425000 |
| H   | 5.845330000 | 3.831011000 | -1.125711000 |
| H   | 6.728040000 | 2.518374000 | -1.935985000 |
| H   | 6.531692000 | 2.492141000 | -0.169948000 |
| C   | -2.079478000 | -1.053231000 | 0.199374000  |
| N   | -3.186435000 | -0.360359000 | 0.655300000  |
| C   | 2.970493000 | 2.131495000 | 2.168037000  |
| H   | 3.715166000 | 2.376976000 | 3.206274000  |
| C   | 2.939665000 | -0.218402000 | 3.089823000  |
| H   | 3.432452000 | -1.195935000 | 3.110450000  |
| H   | 1.875163000 | -0.376050000 | 2.880514000  |
| C   | 3.031263000 | 0.221762000 | 4.094610000  |
| C   | 5.093576000 | 0.748438000 | 2.248019000  |
| H   | 5.580891000 | 1.430660000 | 1.539128000  |
| H   | 5.535467000 | -0.248810000 | 2.116171000  |
| H   | 5.322030000 | 1.092213000 | 3.268357000  |

5b, B3LYP-D3(BJ)/def2-SVP

\[ \text{E+ZPE} = -2527.034075 \text{ E}_h \]

Lowest frequency = 20.82 cm\(^{-1}\)
|   |      x         |      y         |      z         |
|---|---------------|---------------|---------------|
| H | -0.566553000  | 2.572484000   | 4.959856000   |
| C | 1.138503000   | 2.415902000   | 3.636611000   |
| H | 1.806025000   | 2.989155000   | 4.286103000   |
| C | 1.619821000   | 1.862849000   | 2.443467000   |
| H | 2.671393000   | 2.018774000   | 2.188423000   |
| C | 0.785805000   | 1.123259000   | 1.599940000   |
| H | -4.553215000  | 2.749769000   | -1.577897000  |
| H | -3.627002000  | -0.179545000  | -3.520899000  |
| C | -4.149305000  | 4.016062000   | 1.344972000   |
| H | -3.434053000  | 5.971934000   | 0.698494000   |
| H | -2.211163000  | 4.953480000   | 1.477345000   |
| H | -1.744116000  | 5.045648000   | -0.948441000  |
| C | -2.138849000  | 2.967123000   | -0.522234000  |
| H | -1.268397000  | 2.893073000   | 0.143888000   |
| H | -1.812048000  | 2.625285000   | -1.512124000  |
S5 Additional References

[1] S. Stoll, A. Schweiger, J. Magn. Reson. 2006, 178, 42.
[2] V. Lavallo, Y. Canac, C. Pråsång, B. Donnadieu, G. Bertrand, Ange. Chem. Int. Ed. 2005, 44, 5705.
[3] S. Bieller, F. Zhang, M. Bolte, J. W. Bats, H.-W. Lerner, M. Wagner, Organometallics 2004, 23, 2107.
[4] B. Bogdanović, K. Schlichte, U. Westeppe, Chem. Ber. 1988, 121, 27.
[5] G. Sheldrick, Acta Cryst. 2015, A71, 3.
[6] G. Sheldrick, Acta Cryst. 2008, A64, 112.
[7] a) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B. 1988, 37, 785; c) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, J. Phys. Chem. 1994, 98, 11623.
[8] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[9] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456.
[10] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.
[11] J. Michl, V. Bonačić-Koutecký, Tetrahedron 1988, 44, 7559.
[12] B. O. Roos, in Advances in Chemical Physics, Wiley, Hoboken, New Jersey, 1987, 399.
[13] a) C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, J. Chem. Phys. 2001, 114, 10252; b) C. Angeli, R. Cimiraglia, J.-P. Malrieu, Chem. Phys. Lett. 2001, 350, 297; c) C. Angeli, R. Cimiraglia, J.-P. Malrieu, J. Chem. Phys. 2002, 117, 9138.
[14] a) E. J. Baerends, D. E. Ellis, P. Ros, Chem. Phys. 1973, 2, 41; b) J. L. Whitten, J. Chem. Phys. 1973, 58, 4496; c) B. I. Dunlap, J. W. D. Connolly, J. R. Sabin, J. Chem. Phys. 1979, 71, 3396; d) C. Van Alsenoy, J. Comput. Chem. 1988, 9, 620; e) K. Eichkorn, O. Treutler, H. Ohm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 1995, 240, 283; f) R. A. Kendall, H. A. Früchtl, Theor. Chem. Acc. 1997, 97, 158; g) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119; h) F. Neese, J. Comput. Chem. 2003, 24, 1740.
[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 16, Revision B.01.
[16] F. Neese, WIREs Comput. Mol. Sci. 2012, 2, 73.
[17] CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009 (http://www.cylview.org).
[18] a) K. Yamaguchi, Chem. Phys. Lett. 1975, 33, 330; b) S. Yamanaka, M. Okumura, M. Nakano, K. Yamaguchi, J. Mol. Struct. 1994, 310, 205; c) M. Nakano, Top. Curr. Chem. 2017, 375, 47.
[19] D. Doehnert, J. Koutecky, J. Am. Chem. Soc. 1980, 102, 1789.