Radicals

Catenation of Two Singlet Diradicals: Synthesis of a Stable Tetraradical (Tetraradicaloid)**

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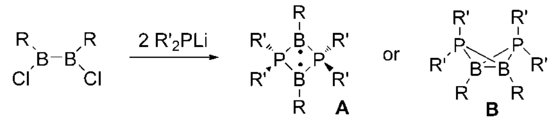
Singlet and triplet diradicals are fascinating as they are even-electron molecules that have one bond less than the number permitted by the standard rules of valency.[1] In localized singlet diradicals the partially filled orbitals reside on two different atoms that are connected by one or more saturated atoms.[1b] These diradicals are also called "nonconjugated". However, the partially filled atomic orbitals that are formally localized on the two radical centers can interact either through space or through the σ bonds of the atoms that connect them. Catenation of singlet diradicals, through appropriate linkers, are predicted to lead to antiferromagnetic low-spin polymers, in which the half-filled electron bands would confer the capability of metallic conduction without doping.[1c,2] However, as noted by Berson,[1c] a vast and largely unmapped terrain must still be explored before these practical objectives can be reached. Not only do we lack knowledge about the solid-state intermolecular interactions between chains, which can be decisive in the ultimate bulk conductivity of a polymer, but it is also necessary to understand the effects induced by the presence of a second diradical site on the first. For this purpose, several carbon-based tetraradical prototypes have already been prepared, but conclusions have been difficult to draw due to the instability of such species.[3]

Similarly to its carbon congeners,[4] 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyls, **A**, feature a trans-annular bonding π-overlap[5,6] that allows for the thermal ring closure to give 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butanes, **B**[7] (Scheme 1). However, we have shown that given the right set of substituents, strongly colored diradicals (or diradicaloids)[8] of type **A** were indefinitely stable both in solution and in the solid state.[9] This very unusual stability gave us the



Scheme 1. Synthesis of type **A** and **B** ring systems.

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opportunity to study whether strong spin coupling can be maintained in extended systems with more than two sites for unpaired electrons.

Herein we report the synthesis of the first stable singlet tetraradical and our first results concerning the influence of the antiferromagnetic and ferromagnetic nature of the linkers[10] on the relative stability of compounds **A**/**B**.

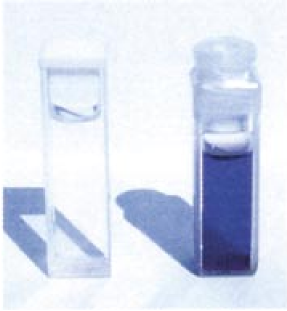
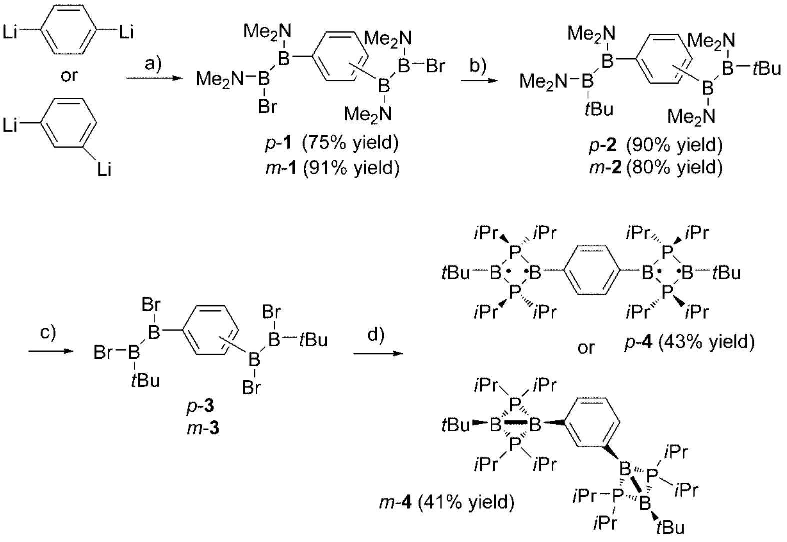


Figure 1. Hexane solutions of *p*-**4** (left) and *m*-**4** (right)

As shown in Scheme 1, the synthesis of derivatives of types **A** and **B** involved the addition of two equivalents of phosphide to the appropriate 1,2-halogenodiborane. Therefore the obvious precursors for derivatives *p*-**4** and *m*-**4** were tetrahalogenotetraboranes *p*-**3** and *m*-**3** (Scheme 2). The latter have been obtained in three steps. The addition of two equivalents of 1,2-bis(dimethylamino)-1,2-dibromodiborane to 1,4- and 1,3-dilithiobenzene afforded derivatives *p*-**1** (75 % yield) and *m*-**1** (91 % yield), respectively. Treatment of *p*-**1** and *p*-**1** with two equivalents of *tert*-butyllithium led to the tetrakis(dimethylamino)tetraboranes *p*-**2** and *m*-**2**, which were isolated in 90 and 80 % yields. An exchange reaction with boron tribromide gave rise to the desired precursors *p*-**3** and *m*-**3** that can only be characterized by ^{1}H NMR spectroscopy due to their high instability.[11] Then, addition of four equivalents of lithium diisopropylphosphide led to *p*-**4** and *m*-**4**, which were isolated in 43 and 41 % yield, respectively, both as oxygen-sensitive but highly thermally stable crystals [m.p.: 261 °C decomp (*p*-**4**); 246 °C decomp (*m*-**4**)]. The similarities between the two isomeric derivatives *p*-**4** and *m*-**4** stop here. As can be seen in Figure 1, compound *p*-**4** is deep violet ($\lambda_{max} = 630$ nm, $\varepsilon = 1374$), whereas *m*-**4** is colorless.[12]



Scheme 2. Synthesis of *m*-**4** and *p*-**4**: a) Me$_2$N(Br)BB(Br)NMe$_2$ (2 equiv), hexane/diethyl ether, −78 °C; b) *t*BuLi (2 equiv), hexane, −78 °C; c) BBr$_3$ (4 equiv), hexane, −78 °C; d) *i*Pr$_2$PLi (4 equiv), hexane/diethyl ether, −78 °C.

The X-ray diffraction analysis[13] of *p*-**4** (Figure 2) revealed that the B atoms are in a planar environment, and the presence of two almost planar PBPB four-membered-ring moieties (interflap angle between the two PBB units 175°) linked by a phenyl ring that is coplanar to the two PBPB skeletons (torsion angle 2°). Another striking feature is the B–B interatomic distance (2.568 Å), which indicates that the B–B bonds have been cleaved. All these geometric parameters are very comparable to those found in the previously reported diradicals of type **A**.[9,14]

In marked contrast, the PBPB cores of *m*-**4** strongly deviate from planarity (interflap angle between the two PBB units 120.7 and 123.6°), and the B–B interatomic distances (1.875 and 1.906 Å) are shortened by more than 25 % compared to *p*-**4** (Figure 3). Moreover, the phenyl ring is perpendicular to the PBPB skeletons. Clearly, the geometric parameters of *m*-**4** are very similar to those observed for bicyclic[1.1.0] derivatives of type **B**.[7]

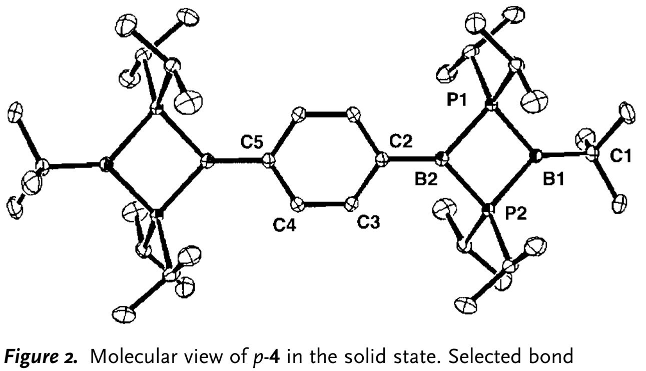


Figure 2. Molecular view of *p*-**4** in the solid state. Selected bond lengths [Å] and angles [°]: B1-B2, 2.568; B1-P1, 1.897 ± 2; P1-B2, 1.894 ± 2; B2-P2, 1.900 ± 2; P2-B1, 1.899 ± 2; B2-C2, 1.547 ± 3; C2-C3, 1.404 ± 3; C3-C4, 1.383 ± 3; C4-C5, 1.411 ± 3; C1-B1-P1, 132.46 ± 16; B1-P1-B2, 85.26 ± 10; P1-B2-C2, 132.50 ± 16; C2-B2-P2, 132.22 ± 17; P1-B2-P2, 94.76 ± 11; B2-P2-B1, 85.06 ± 10; P2-B1-C1, 132.86 ± 16; P2-B1-P1, 94.69 ± 11.

Antiferromagnetic coupling units such as that in *p*-**4** are known to be very effective and to lead to quinoid structures for which the singlet–triplet gap tends to reach zero.[15] A close comparison of the x-ray data of *p*-**4** and *m*-**4** shows that the quinoid character of *p*-**4** is very weak but not non-existent. In particular the B2–C2 bond length is a little shorter in *p*-**4** [1.547(3) Å] compared to *m*-**4** [1.577(2) Å], and there is an alternation between slightly shorter and longer

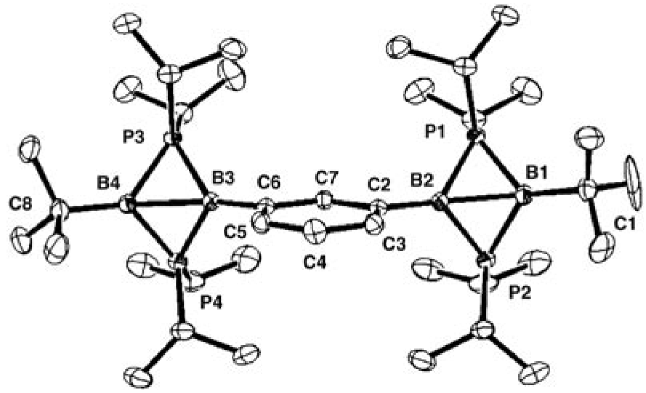
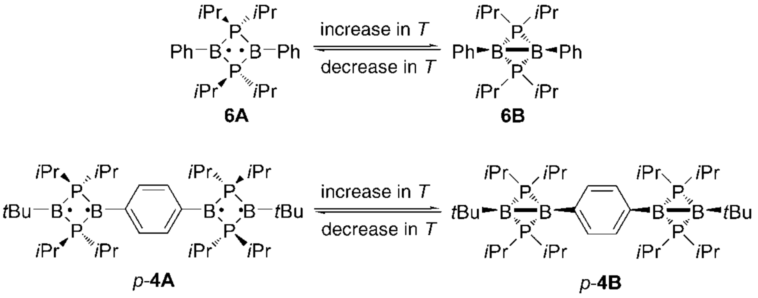


Figure 3. Molecular view of *m*-**4** in the solid state. Selected bond lengths [Å] and angles [°]: B1-B2, 1.909 ± 3; B1-P1, 1.8982 ± 19; P1-B2, 1.8769 ± 19; B2-P2, 1.875 ± 2; P2-B1, 1.898 ± 2; B2-C2, 1.577 ± 2; C2-C3, 1.396 ± 2 A; C3-C4, 1.390 ± 3; C4-C5, 1.385 ± 2; C5-C6, 1.397 ± 2; C6-C7, 1.404 ± 2; C7-C2, 1.401 ± 2; C6-B3, 1.573 ± 2; B3-B4, 1.875 ± 3; B3-P3, 1.8751 ± 18; P3-B4, 1.905 ± 2; B4-P4, 1.903 ± 2; P4-B3, 1.8781 ± 19; C1-B1-P1, 131.99 ± 14; B1-P1-B2, 59.08 ± 8; P1-B2-C2, 132.97 ± 13; P1-B2-P2, 99.73 ± 9; C2-B2-P2, 126.61 ± 13; B2-P2-B1, 60.78 ± 8; P2-B1-C1, 129.01 ± 14; P2-B1-P1, 98.17 ± 9; C6-B3-P3, 130.92 ± 12; B3-P3-B4, 59.48 ± 8; P3-B4-C8, 130.38 ± 14; P3-B4-P4, 97.01 ± 9; C8-B4-P4, 131.65 ± 14; B4-P4-B3, 59.46 ± 8; P4-B3-P3, 98.90 ± 9; P4-B3-C6, 129.05 ± 12.

bonds in the phenyl ring of *p*-**4** [C2−C3: 1.404(3) and C4−C5: 1.411(3) versus C3−C4: 1.383(3) Å]. The coplanarity of the phenyl ring with the PBPB cores also suggests some delocalization between the 2p(B) orbitals and the π ring systems. Lastly, it is worth noting the absence of a signal in both the solution and solid-state electron paramagnetic resonance spectra from −80 °C to room temperature, which indicates that *p*-**4** has a singlet ground state.

To understand why *p*-**4** features a planar structure with long B−B bonds whereas *m*-**4** has a bis(bicyclic[1.1.0]) structure, ab initio calculations at the (U)B3LYP/6-31 g* level[16] were performed for the parent compounds in the planar forms *p*-**5A** (D_{2h} symmetry) and *m*-**5A** (C_{2v} symmetry), and the bis(bicyclic) forms *p*-**5B** and *m*-**5B** (Figure 4). Both open-form species have a singlet ground state, but interestingly the singlet–triplet gap (adiabatic, between two planar forms) for *p*-**5A** ($S^2 = 0.057$; 16.4 kcal mol^{-1}) is 3.9 kcal mol^{-1} smaller than for *m*-**5A** ($S^2 = 0.0$). In addition, *p*-**5A** is 2.2 kcal mol^{-1} more stable than *m*-**5A**, and the energy benefit for the ring closure of *p*-**5A** (16.8 kcal mol^{-1}) is smaller by 2.1 kcal mol^{-1} than for *m*-**5A**.

These small energy differences are in line with the X-ray data for *p*-**4** and *m*-**4** and corroborate the hypothesis that there is only a weak "communication" between both diradical sites of *p*-**4** through the antiferromagnetic linker. One possible reason for this communication is the weakness of B−C double bonds,[17] which hampers the formation of the quinoid structure. However, despite the weakness of the phenomenon, the consequences are of importance since in the solid-state *p*-**4** has an open-form structure whereas *m*-**4** features a bis(bicyclic) structure. In fact, as shown in the preceding paper[14] and in contrast with the parent compounds, the energy difference between the planar form and the bicyclic isomer of substituted PBPB derivatives is only a matter of a very few kcal mol^{-1}. Indeed, as in the case of the "monomeric" derivative **6**, the planar structure of *p*-**4** exists in the solid state but is in equilibrium in solution with the bicyclic structure *p*-**4B** (Scheme 3). Here also the open-structure *p*-**4A** predominates at low temperature (δ^{31}P = +1.0 ppm at 173 K), whereas at room temperature, the bis(bicyclic) system *p*-**4B** is by far the major product (δ^{31}P = −22.4 ppm); this has been confirmed by UV experiments, which show that the absorbtion considerably increases when the temperature decreases.[18] In marked contrast, no dynamic behavior was observed for *m*-**4**: the ^{31}P chemical shift (−28.4 ppm) is not temperature dependent.



Scheme 3. Equilibrium between **6A** and **6B**, and between *p*-**4A** and *p*-**4B**.

We are currently investigating the catenation of diradicals of type **A** with different antiferromagnetic linkers in the hope of quantifying to some extent their efficiency. Moreover, the synthesis of polymers featuring diradical units is underway.

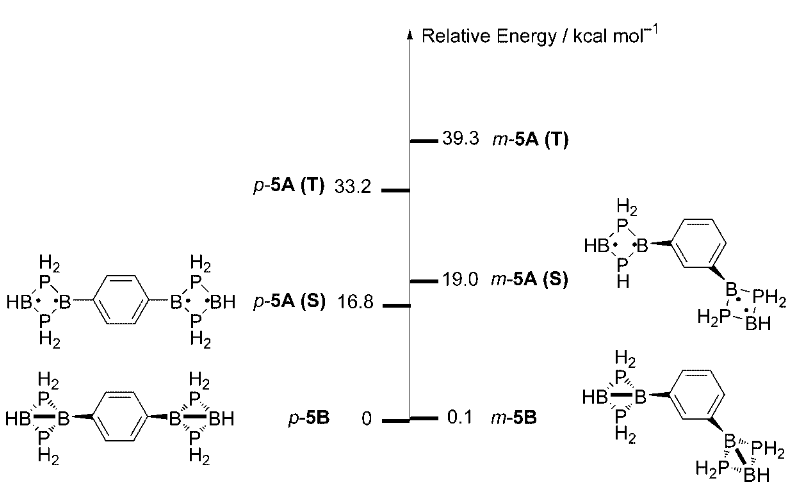


Figure 4. Relative energies of the bis(bicyclic) forms (*p*-**5B** and *m*-**5B**) and planar forms (*p*-**5A** and *m*-**5B**) in their singlet (**S**) and triplet (**T**) configurations.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon by using standard Schlenk techniques.

p-**1** and *m*-**1**: A solution of $[BBr(NMe_2)]_2$ (2.70 g, 10 mmol) in hexane (20 mL) was added to a suspension of 1,4- or 1,3-

dilithiobenzene (1.24 g, 5 mmol) in ether (30 mL) at −78 °C. The mixture was warmed to room temperature and stirred overnight. All the volatiles were removed in vacuo and the residue was extracted with toluene (40 mL). Yield: (*p*-**1**: 1.72 g, 75 %; *m*-**1**: 2.08 g, 91 %;). *p*-**1**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.27$ (s, 4 H, CH_{aro}), 2.95, 2.91, 2.90 and 2.77 ppm (s, 6 H, NMe_2); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta =$ 130.8 (s, CH_{aro}), (*Cipso* not observed), 44.6, 43.2, 40.4 and 29.5 ppm (s, NMe_2); $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = 44.88$, 41.45. *m*-**1**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.21$ (m, 4H, CH_{aro}), 2.89, 2.88, 2.85 and 2.71 ppm (s, 6 H, NMe_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 134.5$, 130.1 and 126.7 (s, CH_{aro}), (*Cipso* not observed), 44.8, 42.3, 40.2 and 37.8 ppm (s, NMe_2); $^{11}B\{^1H\}$ NMR (160.5 MHz, $CDCl_3$): $\delta = 40.3$ ppm (br).

p-**2** and *m*-**2**: 5.01 mL of *t*BuLi (1.5 M, pentane) were added dropwise to a solution of *p*-**1** or *m*-**1** (1.72 g, 3.76 mmol) in hexane (20 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 6 h. All the solvents were then removed in vacuo. Toluene was added and the salts were removed by filtration. Yield: (*p*-**2**: 1.39 g, 90 %; *m*-**2**: 1.23 g, 80 %). *p*-**2**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.25$ (s, 4H, CH_{aro}), 2.97, 2.93, 2.85 and 2.84 (s, 6H, NMe_2), 0.93 ppm (s, 18H, *t*Bu); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 131.3$ (s, CH_{aro}; *Cipso* not observed), 46.8, 45.5, 40.3 and 39.9 (s, NMe_2), 29.6 ppm (s, *t*Bu); $^{11}B\{^1H\}$ NMR (160.5 MHz, $CDCl_3$): $\delta =$ 44 ppm (br). *m*-**2**: ^{1}H NMR ($CDCl_3$) $\delta = 7.10$ (m, 4 H, CH_{aro}), 2.87 and 2.85 (s, 3 H, NMe_2), 2.84 (s, 6 H, NMe_2), 2.79 and 2.78 (s, 3 H, NMe_2), 2.73 (s, 6 H, NMe_2), 0.80 (s, 9 H, *t*Bu), 0.79 ppm (s, 9 H, *t*Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$: $\delta = 136.5$, 130.3 and 126.2 (s, CH_{aro}; *Cipso* not observed), 46.7, 45.5, 40.3 and 39.8 (s, NMe_2), 29.5 ppm (s, *t*Bu); $^{11}B\{^1H\}$ NMR (160.5 MHz, $CDCl_3$): $\delta = 52$ ppm (br).

p-**3** and *m*-**3**: A solution of BBr_3 (1.27 mL, 13.48 mmol) in hexane (20 mL) was added dropwise to a solution of *p*-**2** or *m*-**2** (1.39 g, 3.37 mmol) in hexane (40 mL) at −78 °C. After the solution had been stirred for 30 min, all the volatiles were removed in vacuo and the residue was treated with hexane (20 mL), filtered and used for the next step without further purification. *p*-**3**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.8$ (s, 4 H, CH_{aro}), 1.1 ppm (s, 18 H, *t*Bu). *m*-**3**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.4$ (s, 1H, CH_{aro}), 8.2 (d, $J_{HH} = 7.2$, 2H, CH_{aro}), 7.6 (t, $J_{HH} = 7.2$, 1 H, CH_{aro}), 1.20 ppm (s, 18 H, *t*Bu).

p-**4** and *m*-**4**: A suspension of iPr_2PLi (prepared by adding *n*BuLi (4.80 mL, 2.5 M, pentane) to iPr_2PH (12.04 mmol) in ether (20 mL) at −78 °C and subsequent stirring at room temperature for 1 hour) was added to a solution of *p*-**4** or *m*-**4** (1.66 mL, 3.01 mmol) in hexane (20 mL) at −78 °C. The reaction mixture was warmed to room temperature within 1 hour and the solvents were removed in vacuo. Toluene was added and the salts were filtered off. Violet crystals of *p*-**4** were obtained by cooling a saturated boiling toluene solution to room temperature, Yield: (0.96 g, 43 %). Colorless crystals of *m*-**4** were obtained in THF at −30 °C. Yield: (2.41, 41 %). *p*-**4**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.67$ (s, 4 H, CH_{aro}), 2.06 (m, 8 H, PCH), 1.36 (s, 18 H, *t*Bu), 1.22 (dd, $J_{HH} = 16.5$ Hz, $J_{HP} = 7.2$ Hz, 24 H, $CHCH_3$), 1.13 ppm (dd, $J_{HH} = 15.9$ Hz, $J_{HP} = 7.2$ Hz, 24 H, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): $\delta = 134.9$ (s, CH_{aro}), (*Cipso* not observed), 34.5 (s, *t*Bu), 21.9 (t, $J_{PC} = 22.6$ Hz, PCH), 21.4 ppm (d, $J_{PC} = 14.3$ Hz, $CHCH_3$); $^{11}B\{^1H\}$ NMR (C_6D_6): $\delta = 2.67$, −2.80 ppm; $^{31}P\{^1H\}$ NMR (C_6D_6: $\delta = -22.40$ ppm. *m*-**4**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.88$ (s, 1 H, CH_{aro}), 7.51 (d, $J_{HH} = 7.5$, 2 H, CH_{aro}), 7.30 (t, $J_{HH} = 7.5$, 1 H, CH_{aro}), 2.01 (m, 8 H, PCH), 1.41 (s, 18 H, *t*Bu), 1.22 (dd, $J_{HH} = 16.2$ Hz , $J_{HP} = 6.9$ Hz, 24 H, $CHCH_3$), 1.10 ppm (dd, $J_{HH} =$ 16.0 Hz, $J_{HP} = 7.8$ Hz, 24 H, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): $\delta = 143.9$, 133.3 and 127.0 (s, CH_{aro}), (*Cipso* not observed), 34.7 (s, *t*Bu), 28.8 (t, $J_{PC} = 21.9$ Hz, PCH), 21.4 ppm (d, $J_{PC} = 11.6$ Hz, $CHCH_3$); $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): $\delta = -3.7$, −8.0 ppm; $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -28.4$ ppm.

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[12] As observed for related carbon-based singlet 1,3-diradicals,[4] derivatives of type **A** are strongly colored, whereas the bicyclic[1.1.0] isomers **B** are colorless.

[13] The Bruker SMART-1000[19a] X-ray diffraction instrument with Mo-radiation was used for data collection of compounds *p*-**4** and *m*-**4.** All data frames were collected by using *ω*-scan mode (−0.3° *ω*-scan width, hemisphere of reflections) and integrated by using the Bruker SAINTPLUS program.[19b] The intensity data were corrected for Lorentzian polarization and absorption corrections

were performed by using the SADABS program incorporated in the SAINTPLUS program. The Bruker SHELXTL program[19c] was used for direct methods of phase determination and structure refinement. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of the two compounds were refined by means of a full matrix least-squares procedure on F^2. All H atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. *p*-$\mathbf{4}_{\mathbf{para}}$**:** $C_{38}H_{78}B_4P_4$, $M_r = 702.12$, crystal size $0.35 \times 0.16 \times 0.01$ mm^3, monoclinic, space group $P2_1/n$, $a = 8.2095(19)$, $b = 29.276(7)$, $c = 9.489(2)$ Å, $\beta = 106.524(5)°$, $V = 2186.4(9)$ Å^3, $\rho_{calcd} = 1.067$ g cm^{-3}, $2\theta_{max} = 52.74°$, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), low temperature = 223(2) K, total reflections collected = 12870, independent reflections = 4456 ($R_{int} = 0.0449$, $R_{sig} = 0.$ 0554), 3105 (69.7 %) reflections were greater than $2\sigma(I)$, index ranges $-8 \leq h \leq 10$, $-36 \leq k \leq 31$, $-11 \leq l \leq 11$, absorption coefficient $\mu = 0.197$ mm^{-1}; max/min transmission = 0.9980/0.9343, 258 parameters were refined and converged at $R1 = 0.0442$, $wR2 = 0.1046$, with intensity $I > 2\sigma(I)$, the final difference map was 0.528/−0.204 e Å^{-3}. *m*-**4:** Crystal size $0.46 \times 0.33 \times 0.19$ mm^3, monoclinic, space group $P2_1/c$, $a = 15.197(2)$, $b = 14.183(2)$, $c = 22.454(3)$ Å, $\beta = 107.369(3)°$, $V = 4619.0(12)$ Å^3, $\rho_{calcd} = 1.010$ g cm^{-3}, $2\theta_{max} = 56.56°$, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), low temperature = 223(2) K, total reflections collected = 63660, independent reflections = 11453 ($R_{int} = 0.0540$, $R_{sig} = 0.0372$), 8073 (70.5 %) reflections were greater than $2\sigma(I)$, index ranges $-20 \leq h \leq 20$, $-18 \leq k \leq 18$, $-29 \leq l \leq 29$, absorption coefficient $\mu = 0.186$ mm^{-1}; max/min transmission = 0.9654/0.9192, 569 parameters were refined and converged at $R1 = 0.0464$, $wR2 = 0.1150$, with intensity $I > 2\sigma(I)$, the final difference map was 0.522/−0.241 e Å^{-3}. CCDC-236922 (*p*-**4**) and 236923 (*m*-**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] A. Rodriguez, R. A. Olsen, N. Ghaderi, D. Scheschkewitz, F. S. Tham, L. J. Mueller, G. Bertrand, *Angew. Chem.* **2004**, *116*, DOI: 10.1002/ange.200460475; *Angew. Chem. Int. Ed.* **2004**, *43*, DOI: 10.1002/anie.200460475.

[15] A fully quinoid stucture, in which the unpaired electrons are located far to each other, is expected for the related para-bis(cyclobutanediyl)phenyl system. Consequently, CAS(4,4)/6-31g* calculations result in a singlet–triplet energy separation equal to zero.

[16] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[17] a) A. Berndt, *Angew. Chem.* **1993**, *105*, 1034; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 985; b) R. Boese, P. Paetzold, A. tapper, R. Ziembinski, *Chem. Ber.* **1989**, *122*, 1057.

[18] No evidence for the existence of the unsymmetrical compound featuring a bicyclic and a four-membered-ring unit has been found. Moreover, the equilibrium between *p*-**4A** and *p*-**4B** is not solvent dependent.

[19] a) SMART Software Reference Manual, Version 5.054, Bruker Analytical X-ray System, Inc., Madison, WI **1997–1998**; b) SAINTPLUS Software Reference Manual, Version 6.02A, Bruker Analytical X-Ray System, Inc., Madison, WI **1997–1998**; c) SHELXTL Software Reference Manual, Version 6.10, Dec. 5th, Bruker Analytical X-ray System, Inc., Madison, WI, **2000**.