

Singlet Diradicals: from Transition States to Crystalline Compounds

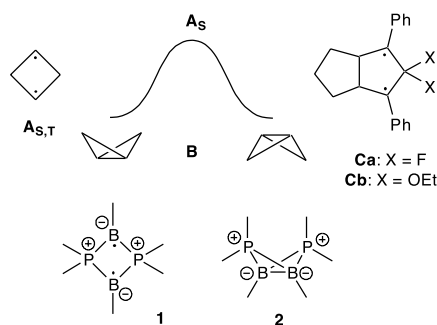
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Singlet diradicals are usually not energy minima. As observed by femtosecond spectroscopy, they readily couple to form σ bonds. Substituent effects allow lifetimes to increase into the microsecond range. Taking advantage of the properties of hetero-elements, a diradical has been prepared that is indefinitely stable at room temperature. The availability of diradicals that can be handled under standard laboratory conditions will lead to further insight into their chemical and physical properties, raising the likelihood of practical applications, especially in the field of molecular materials such as electrical conductors and ferromagnets.

Diradicals are even-electron molecules that have one bond less than the number permitted by the standard rules of valence (1, 2). The two remaining electrons can either be antiparallel (singlet state) or parallel (triplet state). Singlet diradicals are archetypal of chemical bond transformations in many classes of reactions such as ring opening and closure of strained cycloalkanes (3–5), Cope rearrangements (6), and bicyclobutane inversion (7).

Diradicals are even more ephemeral than monoradicals because their bifunctionality permits intermolecular as well as intramolecular coupling reactions. Even the triplet 1,3-cyclobutanediyls A_T (8) can only be observed in matrices at very low temperature, although the combination of the two unpaired electrons, leading to bicyclo[1.1.0]butanes **B**, is impeded by a huge ring strain and a spin barrier. The corresponding singlet diradicals A_S , formally resulting from the homolytic cleavage of the endocyclic σ bond of **B**, are predicted only as transition states for the inversion of **B** (7) (Scheme 1). Optimizing the substituent effects, a few localized singlet diradicals (9–12) have been observed (13), but the half-life in solution at room temperature of the most persistent, **Cb** (14), is only in the microsecond range.

Here we report the synthesis, structural analysis, and reactivity of a localized singlet diradical **1a**, which is indefinitely stable at room temperature both in solution and in the solid state (Scheme 1).



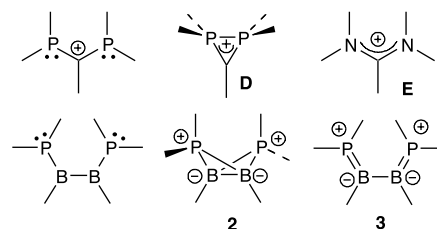
Scheme 1.

The choice of our target molecule **1** was dictated by several factors. (i) The ring strain in the bicyclo[1.1.0] system **2** should favor the diradical structure **1**. (ii) The spin multiplicity and relative stability of **C** were explained by the presence of low-lying $\sigma^*(C-X)$ orbitals allowing through-bond interaction of the two radical sites. Similarly, diradical **1** should benefit from the presence of low-lying σ^* orbitals at the bridging P atoms. (iii) The $\sigma(B-B)$ bond should be weakened by the electrostatic repulsion between the two adjacent negative charges.

Carbon-based 1,3-diradicals are usually prepared via fragmentation reactions with concomitant elimination of a small molecule such as CO or N_2 . Because this approach could not readily be extrapolated to heteroatom analogs, the bicyclic system **2** was envisaged as a possible precursor to **1**. We have recently shown that because P avoids becoming planar and forming π bonds, di(phosphino)carbocations adopt a cyclic form **D** rather than an amidinium-type structure **E** (15). Thus, we believed that 1,2-diphosphino-diboranes should adopt a bicyclo[1.1.0]butane form **2** rather than a butadiene structure **3** (Scheme 2).

The obvious route to the desired 1,2-diphosphinodiboranes is to react 2 equivalents (equiv.) of a lithium phosphide with a

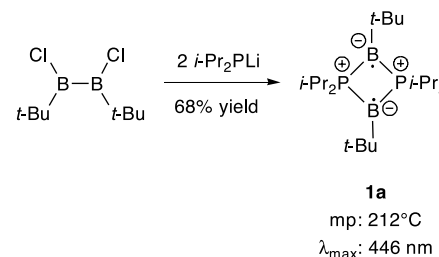
1,2-dichlorodiborane. From the very few available derivatives of this type, we chose 1,2-dichloro-1,2-di(*tert*-butyl)diborane, and, to assure further kinetic protection of the desired diradical moiety, sterically demanding substituents (namely isopropyl groups) were used at P. A clean reaction occurred when the dichlorodiborane was treated with 2 equiv. of lithium diisopropylphosphide in a 1:1 diethylether:tetrahydrofuran mixture at -78°C (all manipulations were performed under argon). After work-up and recrystallization from a toluene solution at room temperature, compound **1a** was isolated in 68%



Scheme 2.

yield as extremely air-sensitive but highly thermally stable yellow crystals (melting point 212°C) (Scheme 3).

The relatively low field ^{11}B and ^{31}P NMR chemical shifts [$\delta_B = +25$ parts per million (ppm) and $\delta_P = +3$ ppm] clearly indicate the absence of four-coordinate B centers and three-membered rings, respectively, ruling out a bicyclic structure of type **2**. The x-ray diffraction analysis (Fig. 1) revealed the PBPB four-membered ring structure of **1a** (16). The ring is perfectly planar; the B atoms are in a planar environment (17, 18) and the P-B bond lengths (1.89 Å) are equal, but a little shorter than expected for single bonds. The most striking feature is the B-B distance (2.57 Å), which indicates that the B-B bond has been cleaved. Indeed, this value is about 38% greater than that of the longest B-B bond reported so far (1.86 Å) (19). All of these data



Scheme 3.

suggest that **1a** is a diradical. Furthermore, the absence of a signal in the electron paramagnetic resonance spectrum, both in solution and in the solid state and from -80°C to room temperature, indicates that **1a** has a singlet ground state.

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Fig. 1. Molecular view of **1a** in the solid state. Selected bond lengths are as follows: P1-B1, 1.8933 \pm 14 Å; P1-B1a, 1.8904 \pm 15 Å; B1-C1, 1.5968 \pm 19 Å; P1-C5, 1.8697 \pm 14 Å; and P1-C8, 1.8753 \pm 13 Å. Selected bond angles are as follows: B1-P1-B1a, 85.13 \pm 7°; P1-B1-P1a, 94.87 \pm 7°; P1-B1-C1, 132.28 \pm 10°; and P1a-B1-C1, 132.83 \pm 10°.

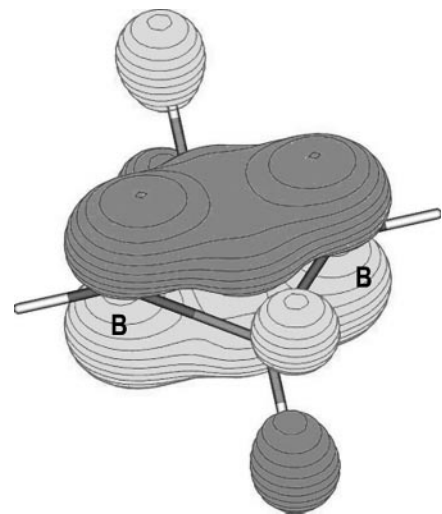
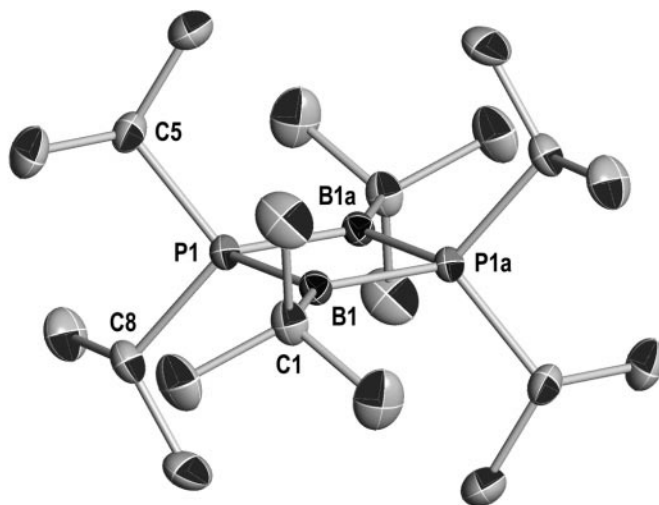


Fig. 2. Highest occupied molecular orbital (HOMO) plot for **1b**.

In order to gain further insight into the electronic structure of **1a**, ab initio calculations (20) were performed for the parent compound **1b** (H atoms at P and B centers) at the B3LYP/6-311++g** level. Compound **1b** is not an energy minimum but only the transition state for the inversion of the bicyclic derivative **2b**. However, the inversion barrier (16.4 kcal/mol) is significantly smaller than that found in the hydrocarbon series for **B** (49.7 kcal/mol) (7), and, thus, it is understandable that the use of substituent effects allowed **1a** to be isolated. Indeed, sterically demanding groups at both P and B favor the less compact planar form **1**, and the σ donor *tert*-butyl groups facilitate the cleavage of the σ bond between the two negatively charged B atoms of **2**. Calculations carried out on the experimentally obtained molecule **1a** at the B3LYP/6-31g* level found it to be an energy minimum whose geometric parameters (B-B, 2.58 Å; P-B, 1.91 Å; interflap angle, 174°) compare well with those found in the solid state by x-ray diffraction. A similar geometry was

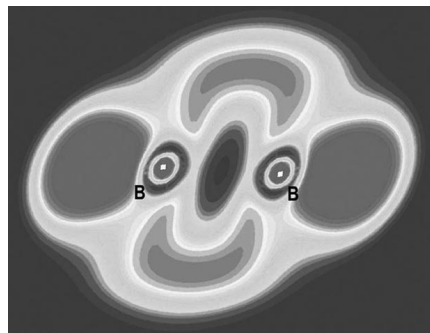


Fig. 3. Two-dimensional electron localization function plot for **1b** (in a plane perpendicular to the four-membered ring).

also predicted for the parent singlet diradical **1b** (B-B, 2.56 Å; P-B, 1.89 Å; interflap angle, 180°), which suggests that the crystalline compound **1a** has a comparable electronic structure to that of the transition state **1b**.

The singlet state of diradical **1b** [$S^2 = 0$ at the (U)B3LYP level] is 17.2 kcal/mol lower in energy than the triplet state, demonstrating a coupling between the two radical sites. Ultraviolet spectroscopy [**1a** (toluene): $\lambda_{\text{max}} = 446$ nm, absorption coefficient $\epsilon = 2200$] indicates that the magnitude of the spin interaction is comparable to that observed for the carbon-based diradicals **Ca** and **Cb** (13, 14). The nature of the coupling is apparent from the highest occupied molecular orbital (HOMO) plot of **1b** (Fig. 2). The participation of the $\sigma^*(\text{P-H})$ orbitals indicates some through-bond interaction, whereas the overlap of the 2p(B) orbitals, despite the long B-B distance, suggests some through-space interaction. The latter is confirmed by the electron localization function (ELF) plot of **1b** (Fig. 3) (21, 22).

Aside from any fundamental curiosity concerning the synthesis and isolation of these species, the availability of diradicals, which can be handled under standard laboratory conditions, opens the way for new developments in various fields. Their chemical behavior will define their

potential use as radical scavengers and initiators, and the study of their physical properties will allow for a better understanding of the factors that control singlet-triplet energy spacing (23) and spin interactions (24) in diradicals. This understanding is decisive for the rational development of new molecular organic materials such as electrical conductors and ferromagnets (25).

References and Notes

1. L. Salem, C. Rowland, *Angew. Chem. Int. Ed. Engl.* **11**, 92 (1972).
2. W. T. Borden, in *Encyclopedia of Computational Chemistry*, P. v. R. Schleyer, Ed. (Wiley-Interscience, New York, 1998), pp. 708-722.
3. S. Pedersen, J. L. Herek, A. H. Zewail, *Science* **266**, 1359 (1994).
4. J. A. Berson, *Science* **266**, 1338 (1994).
5. A. H. Zewail, *Angew. Chem. Int. Ed. Engl.* **39**, 2587 (2000).
6. V. N. Staroverov, E. R. Davidson, *J. Mol. Struct. (Theochem.)* **573**, 81 (2001).
7. K. A. Nguyen, M. S. Gordon, J. A. Boatz, *J. Am. Chem. Soc.* **116**, 9241 (1994).
8. R. Jain, M. B. Sponsler, F. D. Coms, D. A. Dougherty, *J. Am. Chem. Soc.* **110**, 1356 (1988).
9. In comparison with disulfur dinitride (10), 1,3-dihydro-1,3-diboretes (11) and 1,3-diphosphacyclobutane-2,4-diyls (12), localized diradicals contain two well-defined radical substructures that are not in conjugation with one another in a classical π sense.
10. R. D. Harcourt, T. M. Klapötke, A. Schulz, P. Wolyne, *J. Phys. Chem.* **102**, 1850 (1998).
11. M. Pilz, J. Allwohn, M. Buhl, P. v. R. Schleyer, A. Berndt, *Z. Naturforsch. B* **46**, 1085 (1991).
12. E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **34**, 555 (1995).
13. W. Adam et al., *J. Am. Chem. Soc.* **120**, 593 (1998).
14. M. Abe, W. Adam, T. Heidenfelder, W. M. Nau, X. Y. Zhang, *J. Am. Chem. Soc.* **122**, 2019 (2000).
15. T. Kato, H. Gornitzka, A. Baceiredo, W. W. Schoeller, G. Bertrand, *Science* **289**, 754 (2000).
16. Crystal data for **1a** are as follows: Cell constants and an orientation matrix for data collection correspond to the monoclinic space group $P2_1/n$, with $a = 8.9249 \pm 10$ Å, $b = 15.7918 \pm 17$ Å, $c = 9.3721 \pm 10$ Å, $\beta = 116.487 \pm 2^\circ$, and cell volume $V = 1182.3 \pm 2$ Å³. A half molecule of $\text{C}_{20}\text{H}_{46}\text{B}_2\text{P}_2$ per asymmetric unit (number of formula units per cell = 4) has a formula weight of 185.06 and a calculated density D_c of 1.040 Mg m⁻³. The final cycle of full-matrix least square refinement was based on 9788 measured (2921 unique) reflections and 116 variable parameters and converged with the unweighted agreement factor equal to $R1 [I > 2\sigma(I)] = 0.0368$ (I is the observed reflection intensity) and the weighted factor $wR2 = 0.0920$ for all data. Crystallographic details are available on Science Online at www.sciencemag.org/cgi/content/full/295/5561/1880/DC1.
17. A planar environment has also been observed for the only structurally characterized boron-centered radical (18).
18. M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **108**, 4235 (1986).
19. M. Pilz, J. Allwohn, P. Willershausen, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **29**, 1030 (1990).
20. M. J. Frisch et al., *Gaussian 98 (Revision A.1)* (Gaussian, Pittsburgh, PA, 1998).
21. R. F. W. Bader, Ed., *Atoms in Molecules* (Clarendon, Oxford, 1994).
22. A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).
23. J. A. Berson, *Acc. Chem. Res.* **30**, 238 (1997).
24. J. Michl, *J. Am. Chem. Soc.* **118**, 3568 (1996).
25. A. Rajca, *Chem. Rev.* **94**, 871 (1994).
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