Supplementary Materials for

Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond

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Materials and Methods:

Synthesis

General considerations: All manipulations were conducted under an atmosphere of dry argon or in vacuo using standard Schlenk line or glove box techniques. Solvents (pentane, hexane, toluene and THF) were purified by distillation from appropriate drying agents (NaK$_{2.8}$ alloy and sodium/benzophenone) under dry argon immediately prior to use. C$_6$D$_6$ was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer ($^1$H: 500.133 MHz; $^{11}$B: 160.364 MHz; $^{13}$C: 125.697 MHz). $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced to external TMS via the residual protons of the solvent ($^1$H) or the solvent itself ($^{13}$C). $^{11}$B NMR spectra were referenced to external BF$_3$•OEt$_2$. UV-vis spectra were measured on a JASCO V-660 UV-vis spectrometer. Elemental analyses were measured on an Elementar Vario MICRO cube instrument. Starting materials were synthesized according to literature methods (B$_2$Br$_4$ (25), Idip (1,3-bis-{2,6-diisopropylphenyl}imidazol-2-ylidene) (34).

Synthesis of 4: A solution of tetrabromodiborane(4) (2.00 g, 5.86 mmol) in 10 mL pentane at −78 °C was added via a teflon cannula to a stirred suspension of IDip in 100 mL of pentane at −78°C. (6.83 g, 17.5 mmol). The resulting white suspension was warmed to room temperature over 3 h. The reaction mixture was filtered and the white solid was washed three times with 20 mL warm hexane and dried in vacuo. Yield 4.35 g (3.90 mmol, 65%) white solid. M.p.: 257 °C (decomp.). $^1$H NMR (500.1 MHz, C$_6$D$_6$, 293 K): δ = 7.26-7.22 (m, 4 H, CH$_{Aryl}$), 7.16-7.12 (m, 8 H, CH$_{Aryl}$), 6.26 (s, 4 H, CH$_{NC}$), 3.40-3.45 (m, 8 H, CH$_{iPr}$), 1.51 (d, 24 H, CH$_3$), 0.95 (d, 24 H, CH$_3$) ppm. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 293 K): δ = 146.5 (C$_q$), 139.1 (CH), 130.2 (CH$_{Aryl}$), 128.4 (C$_q$), 125.2 (CH$_{NC}$), 124.0 (CH$_{Aryl}$), 29.2 (s, CH$_{iPr}$), 26.1 (CH$_3$), 23.7 (CH$_3$) ppm. $^{11}$B NMR (160.364 MHz, C$_6$D$_6$, 293 K): δ = −4.8 ppm. IR: (solid) n = 2962
(s), 1459 (s), 1411 (s), 948 (s), 755 (s) cm$^{-1}$. Elemental analysis calcd. [%] for C$_{54}$H$_{74}$B$_2$Br$_2$N$_4$: C 57.89, H 6.66, N 5.00; found C 58.14 H 5.69, N 4.55.

Synthesis of 5: A suspension of 4 in 20 mL of tetrahydrofuran (1.15 g, 1.03 mmol) at $-78^\circ$C was charged dropwise with a freshly prepared solution of sodium naphthalenide in tetrahydrofuran (6.60 mL, 2.06 mmol, 0.344 mol/L) over 1 h. The reaction mixture was warmed to room temperature over 3 h at which time the solvent was evaporated in vacuo. The residue was heated to 150°C in high vacuum at 2×10$^{-6}$ mbar for 8 h to remove all volatiles. The resulting green solid was extracted three times with 10 mL toluene. The solvent was removed in vacuo. Yield 480 mg (0.50 mmol, 48%). M.p.: 238 °C (decomp). Single crystals were obtained by slowly evaporating a solution of 5 in benzene in a glovebox. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 293 K): $\delta$ = 7.26-7.23 (m, 4 H, CH$_{Aryl}$), 7.13-7.11 (m, 8 H, CH$_{Aryl}$), 6.38 (s, CH$_{NHC}$), 3.22-3.17 (m, 8 H, CH$_{iPr}$), 1.20 (d, 24 H, CH$_3$), 1.02 (d, 24 H, CH$_3$) ppm. $^{13}$C {$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 293 K): $\delta$ = 146.5 (C$_q$), 139.5 (C$_q$), 129.3 (CH$_{4r}$), 128.3 (C$_q$), 124.2 (s, CH$_{Aryl}$), 122.9 (CH$_{NHC}$), 28.7 (s, CH$_{iPr}$), 26.1 (CH$_3$), 23.5 (CH$_3$) ppm. $^{11}$B NMR (160.364 MHz, C$_6$D$_6$, 293 K): $\delta$ = 20 ppm. IR: (solid) ν = 2962 (s), 1461 (s), cm$^{-1}$. Elemental analysis calcd. [%] for C$_{54}$H$_{74}$B$_2$Br$_2$N$_4$: C 67.52, H 7.76, N 5.83; found: C 68.36, H 7.49, N 5.61.

Synthesis of 6: A suspension of 4 in 10 mL of tetrahydrofuran (512 mg, 0.460 mmol) at $-78^\circ$C was charged dropwise with a freshly prepared solution of sodium naphthalenide in tetrahydrofuran (5.40 mL, 1.84 mmol, 0.344 mol/L) over 1 h. The reaction mixture was warmed to room temperature within 3 h at which point the solvent was evaporated in vacuo. The residue was heated to 150°C in high vacuum at 2×10$^{-6}$ mbar for 8 h to remove all volatiles. The resulting green solid was extracted three times with 10 mL pentane. The solvent was removed in vacuo. Yield: 210 mg (0.26 mmol, 57%). M.p.: 234 °C (decomp.). Single crystals were obtained by slowly evaporating a solution of 6 in benzene in a glovebox. $^1$H
NMR (500.1 MHz, C₆D₆, 293 K): δ = 7.26-7.23 (m, 4 H, CH₄aryl), 7.08-7.07 (m, 8 H, CH₄aryl), 6.04 (s, CH₄NHCe), 3.04-2.99 (m, 8 H, CH₃iPr), 1.17 (d, 24 H, CH₃), 1.10 (d, 24 H CH₃) ppm. 

¹³C{¹H} NMR (125.8 MHz, C₆D₆, 293 K): δ = 147.6 (C₉), 136.8 (C₉), 128.9 (CH₂Ar), 123.9 (CH₄aryl), 118.9 (s, CH₄NHC), 28.9 (CH₃iPr), 24.8 (CH₃), 24.3 (CH₃) ppm. ¹¹B NMR (160.364 MHz, C₆D₆, 293 K) δ = 39 ppm. IR: ν = 1467 (s), 1386 (m), 1363 (m), 1328 (m) cm⁻¹.


Alternative synthesis of 5: 4 (28 mg, 0.025 mmol) and 6 (20 mg, 0.025 mmol) were dissolved in 0.6 mL C₆D₆. Within 2 h the green solution had turned reddish brown. ¹¹B NMR (160.364 MHz) indicated full conversion of both compounds into 5. All volatiles were removed in vacuo and the brown residue was suspended in 1 mL of pentane and filtered. The green solid was washed three times with 1 mL of pentane and dried in vacuo. Yield: 16 mg (0.017 mmol, 33%). NMR spectra of this material are in full agreement with previously synthesized 5.
Crystal structure determination

The crystal data of 5 and 6 were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated MoKα radiation. The structures were solved using direct methods, refined with the Shelx software package (35) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factor calculations.

Crystal data for 5: C₅₄H₇₂B₂Br₂N₄, Mᵣ = 958.60, green block, 0.16×0.13×0.08 mm³, monoclinic space group P2₁/c, a = 20.8472(13) Å, b = 12.2140(10) Å, c = 20.3661(15) Å, β = 100.551(4)°, V = 5098.1(6) Å³, Z = 4, ρ(calcd) = 1.249 g•cm⁻³, μ = 1.629 mm⁻¹, F(000) = 2016, T = 100(2) K, R1 = 0.1069, wR2 = 0.1320, 10525 independent reflections [2θ ≤ 53.62°] and 821 parameters.

Crystal data for 6: C₅₄H₇₂B₂N₄, Mᵣ = 798.78, green plate, 0.19×0.80×0.04 mm³, monoclinic space group P2₁/c, a = 20.967(2) Å, b = 12.1147(12) Å, c = 19.7100(17) Å, β = 94.041(3)°, V = 4994.0(8) Å³, Z = 4, ρ(calcd) = 1.062 g•cm⁻³, μ = 0.061 mm⁻¹, F(000) = 1736, T = 100(2) K, R1 = 0.1183, wR2 = 0.1546, 10192 independent reflections [2θ ≤ 52.74°] and 557 parameters.

Computational methodology

To probe the electronic structure of 6, dipole-allowed electronic excitation calculations were carried out at the B3LYP/6-311G* level. Spectra were simulated by convoluting the oscillator strengths with Gaussian functions taking the half-bandwidths equal to 1000 cm⁻¹. We sought to identify the states that are implicated in the experimentally observed absorption bands. Figure S2 shows the stick plot of the calculated oscillator strengths and the simulated spectra. The overall absorption profile (shape) of the bands is well reproduced. There are however
some small discrepancies, namely, the narrow non-absorbing domain centered at 510 nm observed experimentally, giving the crystal its green color, is shifted some 40 nm lower on an absolute energy scale, and secondly, the relative intensity of the higher energy band is somewhat lower than that observed experimentally. However, these discrepancies do not prohibit us from obtaining the required information as it should be noted that Density Functional Theory (DFT) is known to underestimate HOMO-LUMO gaps, thus its tendency to give excitations far too low in energy. Nevertheless, calculations still predict a green-yellow color for 6. Table S1 gives the various contributions to the observed excitations and the associated oscillator strengths for 6.

The first absorption band obtained experimentally at around 385 nm is not fully symmetrical and there must be a very close absorption peak making it appear steeply cambered in the 410-510 nm region. This is fully explained by calculations. The stronger band hails in fact from an excitation from the HOMO to both the LUMO+5 and the LUMO+7, the neighboring shoulder is a transition from the HOMO to the LUMO+1. Then the calculated spectra predicts a region with no absorption before a rise to a very intense one around 50 nm higher in wavelength. The high intensity is not surprising if one observes the seemingly high overlap between the occupied B-B centered π system and the empty B-C π-like orbitals. These are due to the HOMO-1→LUMO and HOMO→LUMO+9 transitions which are then followed by a long region of low absorption, as confirmed experimentally.

For molecule 6, although we do recall the fact that TDDFT tends to give lower excitation energies, there are additional aspects that should be pointed out. The excitation centered at 600 nm is a very sharp one and there is an exact match between experiment and calculation. Considering the orbitals that are involved for this excitation, these are rather centered "inside" the molecular construct and are thus less susceptible to be affected by any external
perturbation (e.g. through solvents) and most probably not affected by the conformation of the external aryl groups. Inspecting the two other main excitations at higher energies, the orbitals which the electrons are occupying upon excitation are centered on the external aryl rings, which can easily find themselves in diverse conformations when in solution or when in a crystal, without counting on eventual interactions with the surrounding solvent molecules. Hence, a larger broadening and energy shifts may be observed in the experimental spectra with respect to the calculated one. A more accurate way of comparing experimental and calculated spectra would consist of taking into account the vibronic and environmental effects.

Analogous calculations were carried out for 5 at the OLYP/6-311G* level. Figure S3 shows both experimental and the calculated spectra. The experimental absorption profile is nicely reproduced although there is a slight shift of the observed maxima downwards in energy. Table S2 gives the different contributions to the observed excitations and the associated oscillator strengths for 5.

The first absorption that makes up the experimentally observed shoulder is associated to the HOMO→LUMO+4 plus the HOMO→LUMO+5 transitions. The strongest band is made up of contributions from HOMO→LUMO+2 and HOMO→LUMO+4 excitations and an additional HOMO→LUMO+3 excitation. It is interesting to note that the observed absorption bands are solely due to excitations from the the HOMO, which is made up of the B-B π bonding orbitals, in contrast to 6 which has an additional occupied π system.

Furthermore, for 6, we looked at the normal modes and simulated the IR spectra from frequency calculations. The IR spectra were simulated by convoluting the oscillator strengths with a Lorentzian model, the half-bandwidths were taken to be equal to 15 cm⁻¹. At the
B3LYP/6-311G* level, the frequency associated to the B-B-centered stretching mode was found to be 1339 cm\(^{-1}\). Figure S4 depicts this mode. This mode is highly symmetrical and is not IR active. The simulated IR spectra is depicted in Figure S5. As predicted from the high symmetry of the B-B stretch, there is no absorption band centered at 1339 cm\(^{-1}\).

**Computational details**

Geometry optimizations, frequency calculations and electronic excitations calculations were carried out at the B3LYP/6-311G* and OLYP/6-311G* levels (36-39) using the Gaussian03 program (41). Spin-restricted calculations were performed by constraining the projection of the total electronic spin along a reference axis to zero. Frequency calculations were conducted to determine if each stationary point corresponds to a minimum. Dipole-allowed electronic excitation calculations were carried out on gas phase optimized structures within the Adiabatic Local Density Approximation (ALDA) of the Time Dependent Density Functional Theory (TDDFT) (42-43). UV-Vis absorption and IR spectra were simulated using the SWizard program (44). The Jmol (45) program was used for visualisation purposes.
Figure S1. UV-vis spectra of B$_2$Br$_2$(IDip)$_2$ and B$_2$(IDip)$_2$ (5 and 6, both emerald-green) in pentane (at three different concentrations, see box).
Figure S2: Absorption spectra and MO-MO excitations in molecule 6.
Figure S3: Experimental and calculated spectra of 5. For clarity the experimental and calculated intensities are not of the same scale.
Figure S4: The B-B stretching mode in the 6.
Figure S5: Calculated IR spectra of 6 showing the corresponding vibrational modes. The vertical red line indicates the position of 1339 cm$^{-1}$, showing no appreciable absorption at this energy.
**Table S1:** Calculated energy of the excited states of 6 and the associated transitions.

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Table S2: Calculated energy of the excited states of 5 and the associated transitions.

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References


26. See supplementary materials on *Science* Online.


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