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Electronic Supplementary Information

Dimerization of Boryl- and Amino-Substituted Acetylenes by B_2C_2 Four-Membered Ring Formation

Ryo Kitamura, Katsunori Suzuki,* and Makoto Yamashita*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, 112-8551, Japan
Department of Molecular and Macromolecular Chemistry, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

E-mail: katsuno_suzu@oec.chembio.nagoya-u.ac.jp; makoto@oec.chembio.nagoya-u.ac.jp

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Contents

1. Experimental Procedures

General methods

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in glovebox (MIWA and KOREA KIYON) under inert atmosphere of argon. Anhydrous hexane, toluene, and diethylether (Et_2O) were dried by passage through a GrassContour solvent purification system. Deuterated chloroform ($CDCl_3$) was distilled from CaH_2 prior to use. Deuterated benzene (C_6D_6) was distilled from sodium/benzophenone prior to use. Diethylamino- and tributylstannyl-substituted acetylene **2**,[S1] diphenylchloroborane **3a**,[S2] and 9-borabicyclononyl chloride **3b**[S1] were prepared according to the literature procedure. Other chemicals were used as received. The nuclear magnetic resonance (NMR) measurements were carried out by a JEOL ECA-500 spectrometer (500 MHz for ^1H, 160 MHz for ^{11}B and 126 MHz for ^{13}C). Chemical shifts (δ) are given by definition as dimensionless numbers and relative to ^1H and ^{13}C NMR chemical shifts of the residual C_6D_5H for ^1H ($\delta = 7.16$) and C_6D_6 itself for ^{13}C ($\delta = 128.0$). The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), septet (sep), multiplet (m), and broad (br). The ^{11}B cross-polarization magic angle spinning (CP-MAS) NMR spectra were recorded on a JEOL ECA-400 spectrometer (128 MHz for ^{11}B). Chemical shifts are referenced to $NaBH_4$ ($\delta_B = -42.06$). The IR spectra in solution and solid state were recorded on an Agilent Technologies Cary 630 FTIR spectrometer equipped with ATR apparatus in a glovebox filled with argon. High-resolution mass spectroscopy measurements were performed on a Bruker micrOTOF II mass spectrometer with an atmospheric pressure chemical ionization (APCI) probe. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. Melting points were measured on a MPA100 Optimelt Automated Melting Point System and are uncorrected.

Synthesis of diphenylboryl- and diethylamino-substituted acetylene dimer $(\mathbf{1b})_2$

A toluene solution (5 mL) of diphenylchloroborane **3a** (712 mg, 3.55 mmol) was added to a solution of 1-trimethylstannyl-2-diethylaminoacetylene **2** (923 mg, 3.55 mmol) in toluene at –30 ºC. A reaction mixture was allowed to warm to room temperature and stirred for 12 h. After the removal of volatiles, the residue was recrystallized from Et_2O to give pure $(\mathbf{1b})_2$ as pale yellow crystals (1.21 g, 1.10 mmol, 62%). In a solution state, the spectroscopic data indicated the dissociation of $(\mathbf{1b})_2$ to monomer **1b** (Fig. S1): mp (in a sealed tube) 75 ºC (dec); ^{1}H NMR (C_6D_6, 500 MHz) δ 0.96 (t, J = 7 Hz, 6H), 2.59 (q, J = 7 Hz, 4H), 7.30 (m, 2H), 7.35 (m, 4H), 8.17 (dd, J = 8, 2 Hz, 4H); ^{11}B NMR (161 MHz) δ 50.8; ^{13}C NMR (C_6D_6, 126 MHz) δ 13.2 (CH_3), 48.6 (CH_2), 90.8 (4°, br), 127.8 (CH), 130.0 (CH), 134.2 (4°, br), 136.8 (CH), 143.3 (4°, br); solid state CP-MAS ^{11}B NMR (128 MHz) δ: −10.1; HRMS (APCI, positive) Calcd. For $C_{36}H_{40}{}^{11}B_2N_2$ [M^+]: 522.3384. Found: 522.3384; Anal. calcd. for $C_{36}H_{40}B_2N_2$: C, 82.78; H, 7.72; N, 5.36. Found: C, 82.88; H, 7.45; N, 5.40.

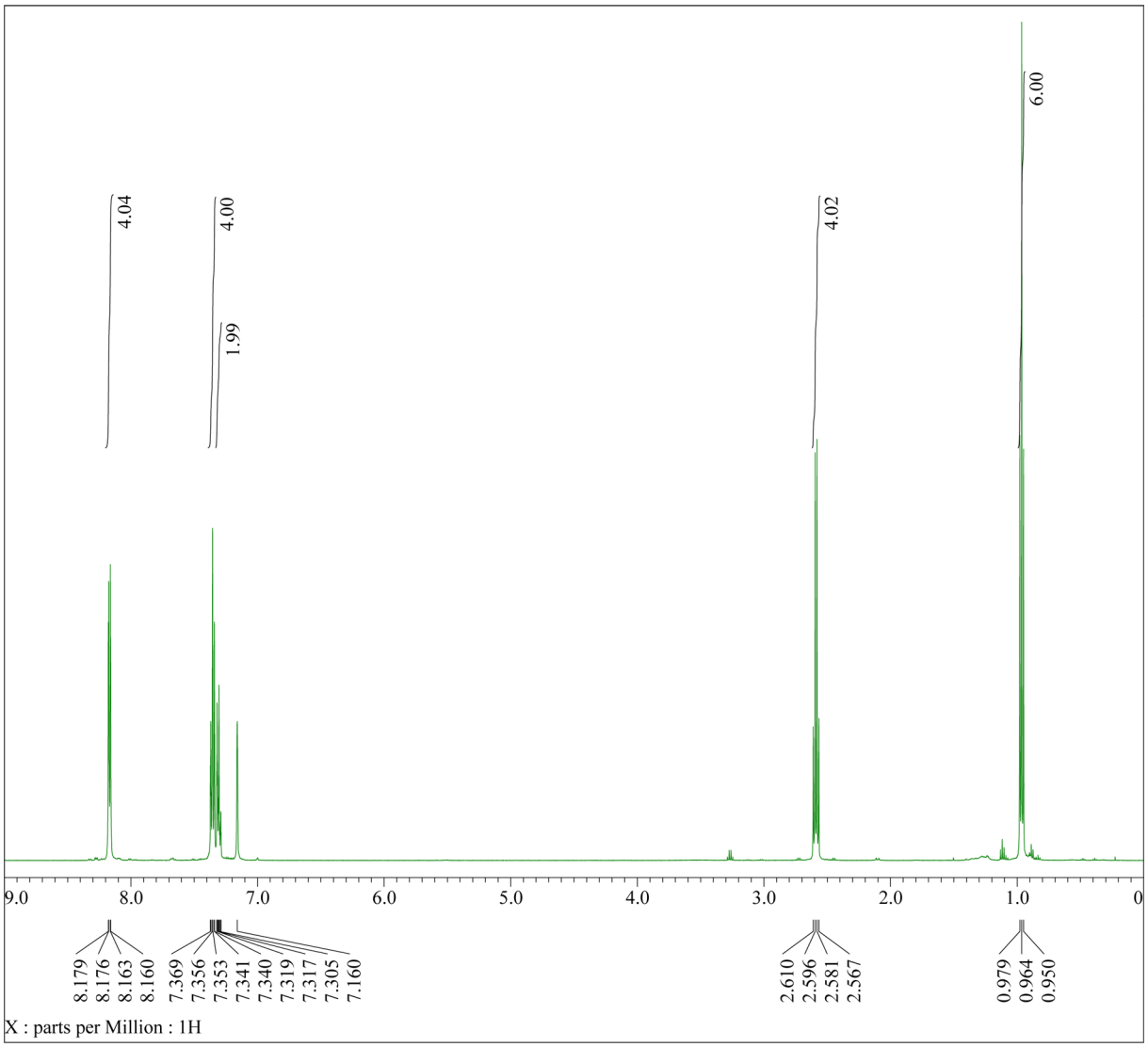

Fig. S1 ^{1}H NMR spectrum of $(\mathbf{1b})_2$ (500 MHz, C_6D_6).

Synthesis of 9-borabicyclononyl- and diethylamino-acetylene dimer $(\mathbf{1c})_2$

A toluene solution (3 mL) of *B*-chloroborabicyclo[3.3.1]nonane **3b** (238 mg, 1.52 mmol) was added to a solution of 1-trimethylstannyl-2-diethylaminoacetylene **2** (396 mg, 1.52 mmol) at –30 ºC. A reaction mixture was allowed to warm to room temperature and stirred for 12 h. After the removal of volatiles, the residue was recrystallized from toluene to give pure $(\mathbf{1c})_2$ as colorless crystals (258 mg, 0.594 mmol, 73%). In a solution state, the spectroscopic data indicated the dissociation of $(\mathbf{1c})_2$ to form a mixture between dimer $(\mathbf{1c})_2$ and monomer **1c** (Fig. S2): mp (in a sealed tube) 102 ºC (dec); ^{1}H NMR (C_6D_6, 500 MHz) δ 0.92 (t, J = 7 Hz, CH_3 ($\mathbf{1c}$)$_2$), 1.27 (br, CH_3 (**1c**)), 1.40-2.50 (m, BBN), 2.60 (br, CH_2(**1c**)), 2.66 (q, J = 7 Hz, CH_3 ($\mathbf{1c}$)$_2$); ^{11}B NMR (161 MHz) δ −2.9 for $(\mathbf{1c})_2$, 66.1 for **1c**; solid state CP-MAS ^{11}B NMR (128 MHz) δ −10.4; HRMS (APCI, positive) Calcd. For $C_{28}H_{48}{}^{10}B^{11}BN_2$ [M^+] (dimer): 433.4035. Found: 433.4058. Calcd. For $C_{14}H_{24}BN$ [M^+] (monomer): 217.1999. Found: 217.2020; Anal. calcd. for $C_{28}H_{48}B_2N_2$: C, 77.43; H, 11.14; N, 6.45. Found: C, 77.49; H, 11.31; N, 6.41.

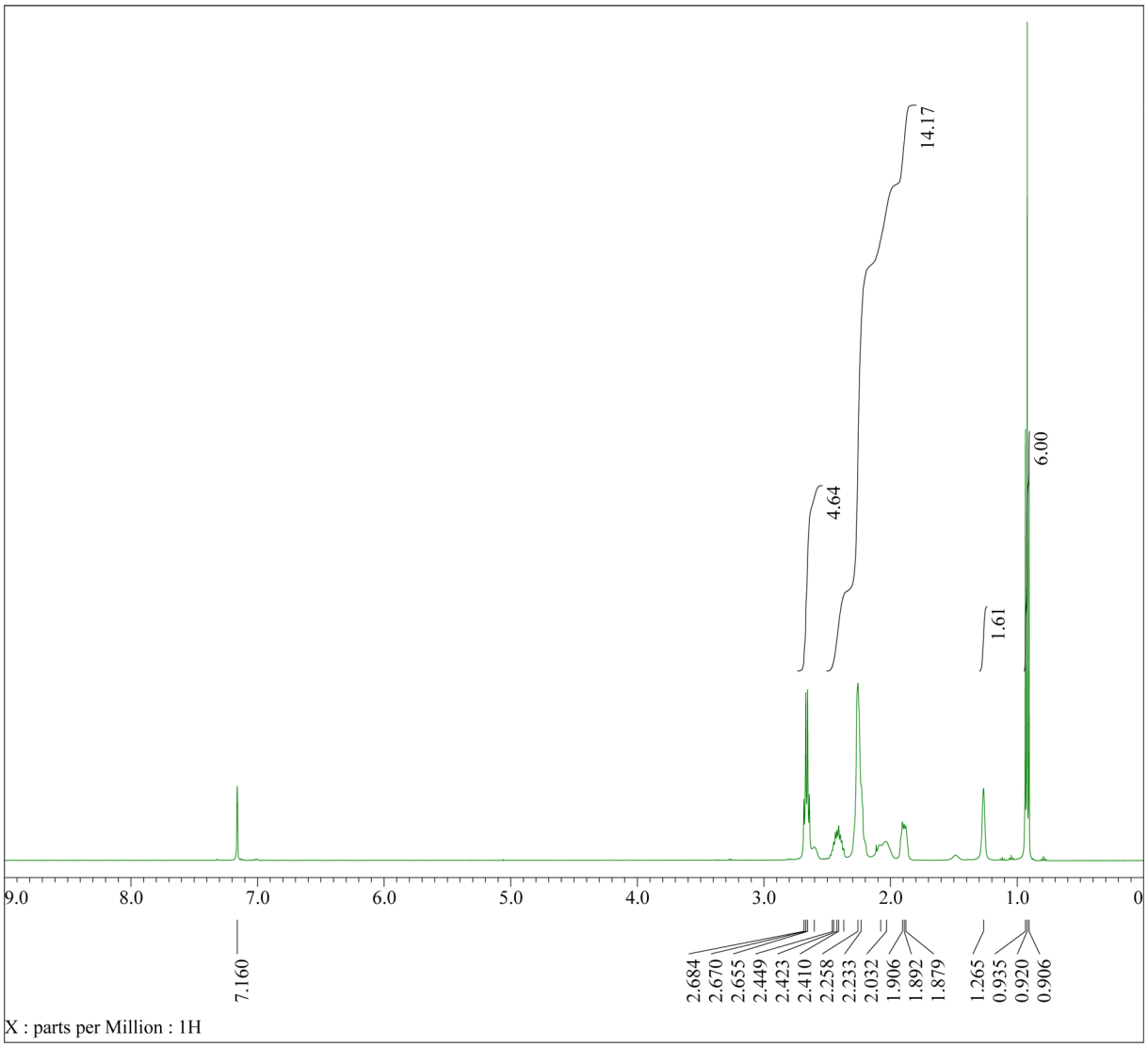

Fig. S2 ^{1}H NMR spectrum of $(\mathbf{1c})_2$ (500 MHz, C_6D_6).

2. X-ray Crystallographic Analysis

Crystallographic data for $(\mathbf{1b})_2$ and $(\mathbf{1c})_2$ are summarized in Table S1. The crystal was coated with oil (Immersion Oil, type B: Code 1248, Cargille Laboratories, Inc.) and put on a MicroMount™ (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Saturn CCD detectors using Mo$K\alpha$ radiation. The Bragg spots were integrated using the CrystalClear program package.[S4] Absorption corrections were applied. All the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface.[S5] The structures were solved by a direct method with programs of SIR-97 [S6] and refined by a full-matrix least squares method with the program of SHELXL-2014.[S7] Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1830300 for $(\mathbf{1b})_2$, CCDC 1830301 for $(\mathbf{1c})_2$. A copy of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk /products/csd/request.

Table S1: Crystallographic data for $(\mathbf{1b})_2$, and $(\mathbf{1c})_2$.

	$(\mathbf{1b})_2$	$(\mathbf{1c})_2$
Formula	$C_{36}H_{40}B_2N_2$	$C_{28}H_{48}B_2N_2$
M	522.32	434.30
T / K	93	93
Color	Colorless	colorless
size / mm	0.29 x 0.21 x 0.17	0.14 x 0.07 x 0.07
crystal system	Triclinic	Monoclinic
space group	P-1 (#2)	$P2_1/a$ (#14)
a / Å	9.3775(15)	13.356(3)
b / Å	9.7968(14)	10.8079(18)
c / Å	10.2151(19)	18.731(4)
α / °	62.343(8)	90
β / °	79.192(12)	102.739(3)
γ / °	65.439(10)	90
V / Å^3	756.0(2)	2637.2(8)
Z	1	4
D_x / g cm^{-3}	1.147	1.094
μ(Mo Kα) / mm^{-1}	0.065	0.061
F(000)	280	960
θ range / °	3.27 to 27.46	3.07 to 27.48
reflections collected	6209	21262
unique reflections	3336	6021
refined parameters	183	289
GOF on F^2	0.975	1.049
$R1$ [$I > 2\sigma(I)$][a]	0.0464	0.0681
w$R2$ (all data)[b]	0.1102	0.1754
$\Delta\rho_{min,\ max}$ / e Å^{-3}	+0.189, –0.338	+0.294, –0.344

[a] $R1 = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$, [b] $wR2 = [\Sigma\ \{w(Fo^2 - Fc^2)^2 / \Sigma\ w(Fo^2)^2\}]^{1/2}$

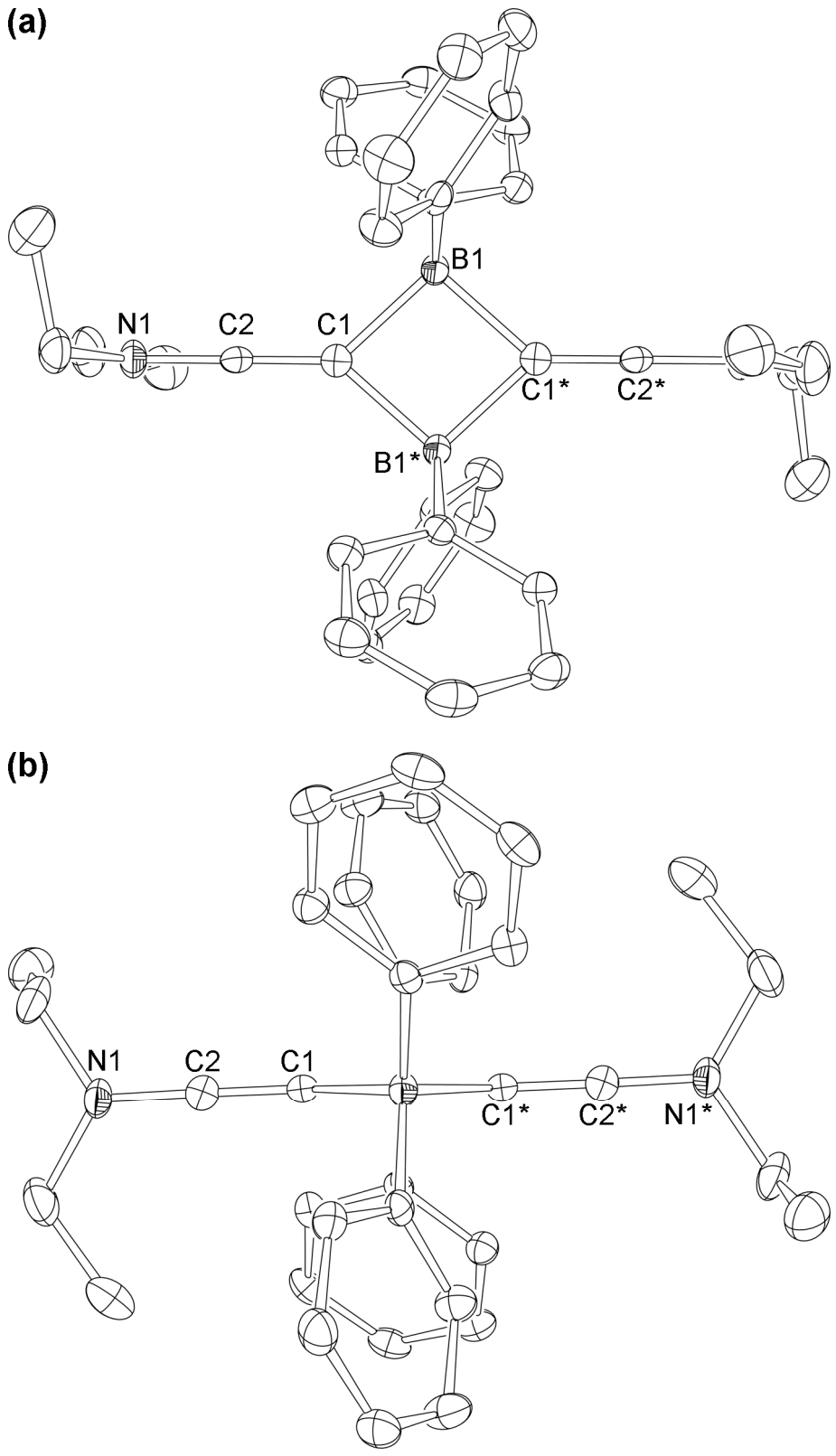

Fig. S3 Molecular structure of (**1b**)$_2$ (thermal ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°) for (**1b**)$_2$: B1–C1 = 1.6709(18), B1*–C1 = 1.6747(18), C1–C2 = 1.2430(16), C2–N1 = 1.2949(16), B1–C1–B1* = 84.69(9), C1–B1–C1* = 95.31(9), B1–C1–C2 = 136.58(12), B1*–C1–C2 = 138.65(12), C1–C2–N1 = 179.31(14).

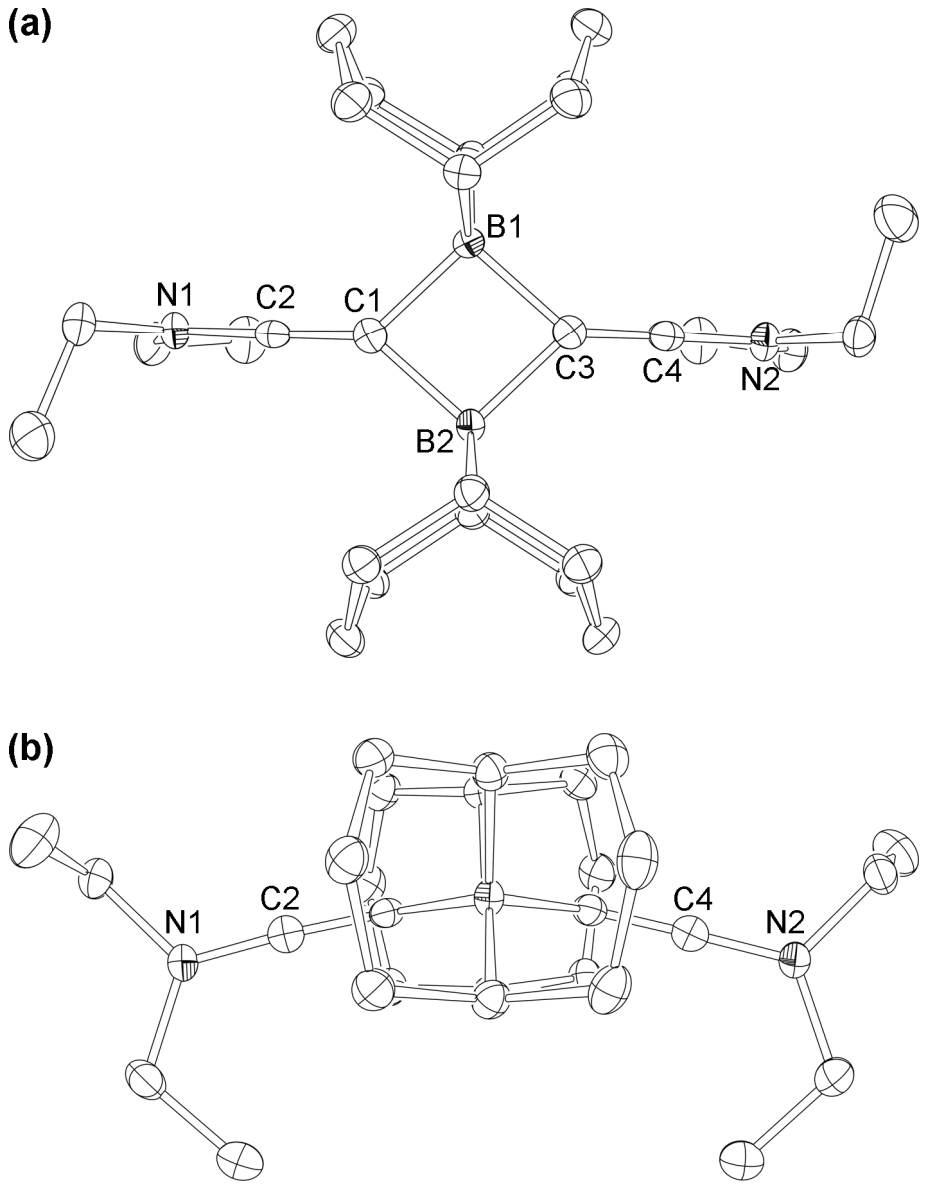

Fig. S4 Molecular structure of (**1c**)$_2$ (thermal ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°) for (**1c**)$_2$: B1–C1 = 1.677(3), B1–C3 =1.664(2), B2–C1 = 1.670(3), B2–C3 = 1.680(2), C1–C2 = 1.243(2), C3–C4 = 1.243(2), C2–N1 = 1.300(2), C4–N2 =1.298(2), B1–C1–B2 = 84.56(12), B1–C3–B2 = 84.65(12), C1–B1–C3 = 94.70(12), C1–B2–C3 = 94.37(12), B1–C1–C2 = 135.89(16), B2–C1–C2 = 139.19(16), B1–C3–C4 = 139.96(16), B2–C3–C4 = 134.37(16), C1–C2–N1 = 176.23(19), C3–C4–N2 = 178.5(2).

3. Theoretical Calculations

All calculations were curried out by using Gaussian09 program package.[S8] The geometry optimizations of **1b-1d**, $(\mathbf{1b})_2$, $(\mathbf{1c})_2$, and $(\mathbf{1d})_2$ were performed at the B3LYP/6-31G(d)[S9,10] level of theory. The optimized structures and selected structural parameters are shown in Fig. S5–8. The Wiberg bond index (WBI)[S11] and natural population analysis (NPA)[S12] charge distribution were calculated by natural bond orbital (NBO) method (Fig. S5–8).[S12]

Table S2: Calculated C-C triple bond vibrational frequencies of **1b**, **1c**, $(\mathbf{1b})_2$, and $(\mathbf{1c})_2$.

	calcd. frequency / cm^{-1}	corrected by scale factor[a] / cm^{-1}	experimentally obsd. / cm^{-1}
1b	2209.7378	2124.4419	2103 (heptane solution)
$(\mathbf{1b})_2$	2059.8647	1980.3539	1980 (solid)
1c	2201.6854	2116.7003	2101 (benzene soln.)
$(\mathbf{1c})_2$	2040.3359	1961.5789	1975 (solid), 1979 (benzene)

[a] scaling factor: 0.9614[S10]

Table S3: Calculated energies of **1b**, **1c**, **1d**, $(\mathbf{1b})_2$, $(\mathbf{1c})_2$, and $(\mathbf{1d})_2$.

	SCF / hartree	SCF + ZPE / hartree	Relative energy / hartree	Relative energy / kcal mol^{-1}
1b	-777.541701321	-777.204543	0.0	0.0
$(\mathbf{1b})_2$	-1555.07677070	-1554.401383	+0.007703	+4.83
1c	-627.514581021	-627.152111	0.0	0.0
$(\mathbf{1c})_2$	-1255.03242774	-1254.304946	-0.000724	-0.45

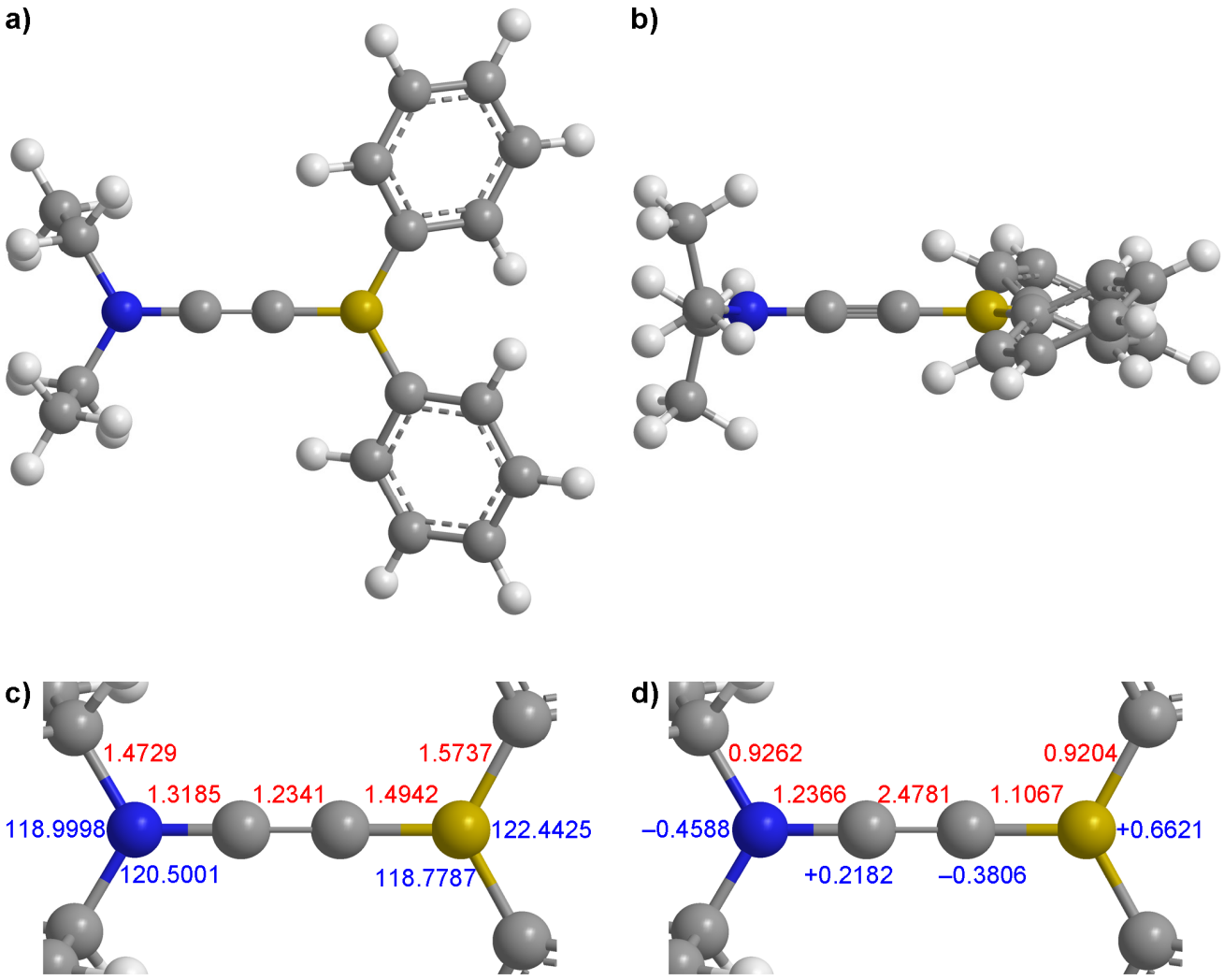

Fig. S5 (a) Top view and (b) side view of optimized structure of **1b** (C_2 symmetry) at the B3LYP/6-31G(d) level of theory (yellow: boron, gray: carbon, blue: nitrogen, and white: hydrogen). (c) Selected bond distances (Å, Red) and angles (°, Blue). (d) Bond orders based on Wiberg bond index (WBI, Red) and natural population analysis (NPA) charge (Blue) distributions calculated at the B3LYP/6-31G(d) level of theory.

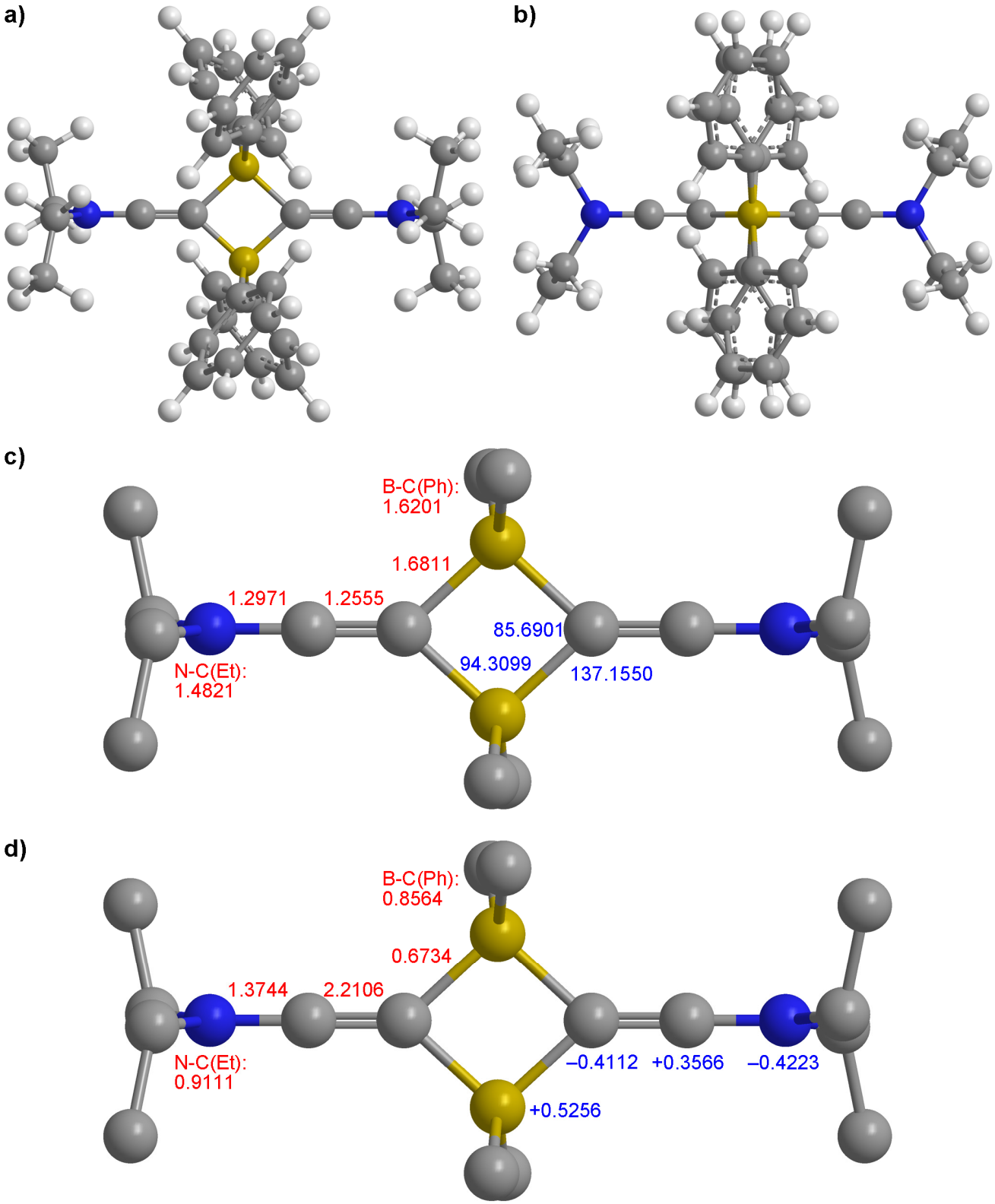

Fig. S6 (a) Top view and (b) side view of optimized structure of (**1b**)$_2$ (D_2 symmetry) at the B3LYP/6-31G(d) level of theory (yellow: boron, gray: carbon, blue: nitrogen, and white: hydrogen). (c) Selected bond distances (Å, Red) and angles (°, Blue). (d) Bond orders based on Wiberg bond index (WBI, Red) and natural population analysis (NPA) charge (Blue) distributions calculated at the B3LYP/6-31G(d) level of theory.

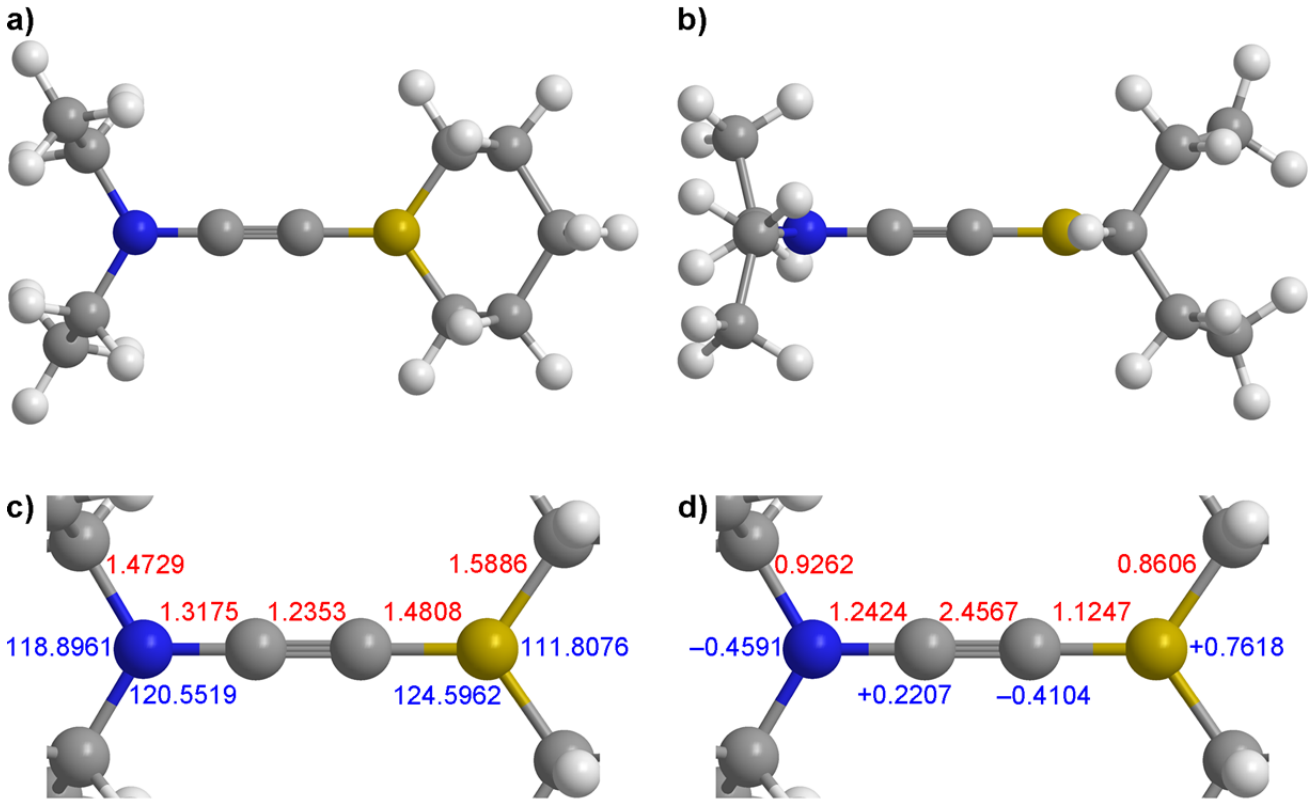

Fig S7. (a) Top view and (b) side view of optimized structure of **1c** (C_2 symmetry) at the B3LYP/6-31G(d) level of theory (yellow: boron, gray: carbon, blue: nitrogen, and white: hydrogen). (c) Selected bond distances (Å, Red) and angles (°, Blue). (d) Bond orders based on Wiberg bond index (WBI, Red) and natural population analysis (NPA) charge distributions (Blue) calculated at the B3LYP/6-31G(d) level of theory.

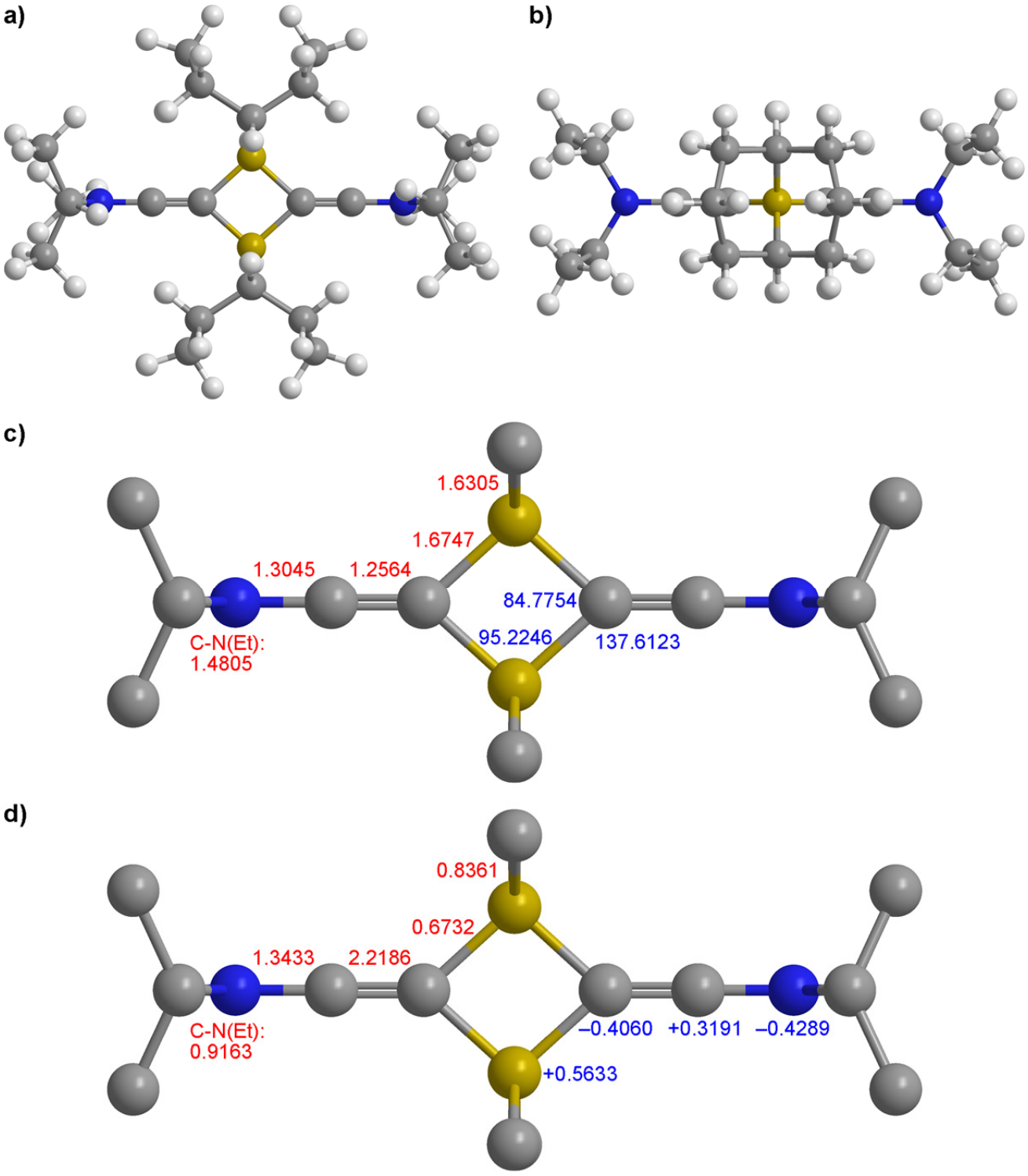

Fig. S8 (a) Top view and (b) side view of optimized structure of (**1c**)$_2$ (D_2 symmetry) at the B3LYP/6-31G(d) level of theory (yellow: boron, gray: carbon, blue: nitrogen, and white: hydrogen). (c) Selected bond distances (Å, Red) and angles (°, Blue). (d) Bond orders based on Wiberg bond index (WBI, Red) and natural population analysis (NPA) charge (Blue) distributions calculated at the B3LYP/6-31G(d) level of theory.

Table S4: Cartesian Coordinates for **1b**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	−2.022141	0.000000	0.000000
2	6	0	−0.527987	0.000000	0.000000
3	6	0	0.706162	0.000000	0.000000
4	7	0	2.024676	0.000000	0.000000
5	6	0	−2.779779	−1.377648	0.068480
6	6	0	−4.053617	−1.559998	−0.508203
7	6	0	−4.704067	−2.794130	−0.472190
8	6	0	−4.100771	−3.883089	0.159382
9	6	0	−2.838855	−3.732662	0.740716
10	6	0	−2.189127	−2.501370	0.683184
11	1	0	−4.535588	−0.723303	−1.006665
12	1	0	−5.681606	−2.906267	−0.935096
13	1	0	−4.608508	−4.843944	0.196034
14	1	0	−2.362726	−4.577380	1.233123
15	1	0	−1.202291	−2.395990	1.127367
16	6	0	2.772214	−1.267637	−0.060153
17	6	0	3.067851	−1.716346	−1.492657
18	1	0	3.703181	−1.132677	0.503304
19	1	0	2.184298	−2.026875	0.463820
20	1	0	3.622827	−2.661643	−1.489606
21	1	0	3.668527	−0.972415	−2.028060
22	1	0	2.134962	−1.865507	−2.045746
23	6	0	−2.779779	1.377648	−0.068480
24	6	0	−4.053617	1.559998	0.508203
25	6	0	−4.704067	2.794130	0.472190
26	6	0	−4.100771	3.883089	−0.159382
27	6	0	−2.838855	3.732662	−0.740716
28	6	0	−2.189127	2.501370	−0.683184
29	1	0	−4.535588	0.723303	1.006665
30	1	0	−5.681606	2.906267	0.935096
31	1	0	−4.608508	4.843944	−0.196034
32	1	0	−2.362726	4.577380	−1.233123
33	1	0	−1.202291	2.395990	−1.127367
34	6	0	2.772214	1.267637	0.060153
35	6	0	3.067851	1.716346	1.492657
36	1	0	3.703181	1.132677	−0.503304
37	1	0	2.184298	2.026875	−0.463820
38	1	0	3.622827	2.661643	1.489606
39	1	0	3.668527	0.972415	2.028060
40	1	0	2.134962	1.865507	2.045746

Table S5: Cartesian Coordinates for $(\mathbf{1b})_2$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	1.143184	0.000000
2	6	0	0.000000	0.000000	−1.232582
3	6	0	0.000000	0.000000	−2.488061
4	7	0	0.000000	0.000000	−3.785115
5	6	0	−1.366755	2.009553	0.078322
6	6	0	−2.529755	1.729126	−0.656761
7	6	0	−3.692182	2.495234	−0.522881
8	6	0	−3.723648	3.574700	0.358917
9	6	0	−2.580526	3.879292	1.103614
10	6	0	−1.427483	3.106558	0.961938
11	1	0	−2.533659	0.885481	−1.341989
12	1	0	−4.574249	2.245300	−1.108869
13	1	0	−4.624384	4.174913	0.463767
14	1	0	−2.585484	4.725899	1.787246
15	1	0	−0.542102	3.370014	1.537425
16	6	0	−1.271633	−0.082057	−4.541916
17	6	0	−1.689424	−1.523860	−4.827572
18	1	0	−2.035793	0.433453	−3.954765
19	1	0	−1.134389	0.481476	−5.471445
20	1	0	−1.853062	−2.067664	−3.891694
21	1	0	−2.622497	−1.536246	−5.402260
22	1	0	−0.926944	−2.054290	−5.409090
23	6	0	1.366755	2.009553	−0.078322
24	6	0	2.529755	1.729126	0.656761
25	6	0	3.692182	2.495234	0.522881
26	6	0	3.723648	3.574700	−0.358917
27	6	0	2.580526	3.879292	−1.103614
28	6	0	1.427483	3.106558	−0.961938
29	1	0	2.533659	0.885481	1.341989
30	1	0	4.574249	2.245300	1.108869
31	1	0	4.624384	4.174913	−0.463767
32	1	0	2.585484	4.725899	−1.787246
33	1	0	0.542102	3.370014	−1.537425
34	6	0	1.271633	0.082057	−4.541916
35	6	0	1.689424	1.523860	−4.827572
36	1	0	2.035793	−0.433453	−3.954765
37	1	0	1.134389	−0.481476	−5.471445
38	1	0	1.853062	2.067664	−3.891694
39	1	0	2.622497	1.536246	−5.402260
40	1	0	0.926944	2.054290	−5.409090

Table S5 (continued): Cartesian Coordinates for (**1b**)$_2$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
41	5	0	0.000000	−1.143184	0.000000
42	6	0	0.000000	0.000000	1.232582
43	6	0	0.000000	0.000000	2.488061
44	7	0	0.000000	0.000000	3.785115
45	6	0	−1.366755	−2.009553	−0.078322
46	6	0	−2.529755	−1.729126	0.656761
47	6	0	−3.692182	−2.495234	0.522881
48	6	0	−3.723648	−3.574700	−0.358917
49	6	0	−2.580526	−3.879292	−1.103614
50	6	0	−1.427483	−3.106558	−0.961938
51	1	0	−2.533659	−0.885481	1.341989
52	1	0	−4.574249	−2.245300	1.108869
53	1	0	−4.624384	−4.174913	−0.463767
54	1	0	−2.585484	−4.725899	−1.787246
55	1	0	−0.542102	−3.370014	−1.537425
56	6	0	−1.271633	0.082057	4.541916
57	6	0	−1.689424	1.523860	4.827572
58	1	0	−2.035793	−0.433453	3.954765
59	1	0	−1.134389	−0.481476	5.471445
60	1	0	−1.853062	2.067664	3.891694
61	1	0	−2.622497	1.536246	5.402260
62	1	0	−0.926944	2.054290	5.409090
63	6	0	1.366755	−2.009553	0.078322
64	6	0	2.529755	−1.729126	−0.656761
65	6	0	3.692182	−2.495234	−0.522881
66	6	0	3.723648	−3.574700	0.358917
67	6	0	2.580526	−3.879292	1.103614
68	6	0	1.427483	−3.106558	0.961938
69	1	0	2.533659	−0.885481	−1.341989
70	1	0	4.574249	−2.245300	−1.108869
71	1	0	4.624384	−4.174913	0.463767
72	1	0	2.585484	−4.725899	1.787246
73	1	0	0.542102	−3.370014	1.537425
74	6	0	1.271633	−0.082057	4.541916
75	6	0	1.689424	−1.523860	4.827572
76	1	0	2.035793	0.433453	3.954765
77	1	0	1.134389	0.481476	5.471445
78	1	0	1.853062	−2.067664	3.891694
79	1	0	2.622497	−1.536246	5.402260
80	1	0	0.926944	−2.054290	5.409090

Table S6: Cartesian Coordinates for **1c**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	−2.178859	0.000000	0.000000
2	6	0	−0.698025	0.000000	0.000000
3	6	0	0.537309	0.000000	0.000000
4	7	0	1.854829	0.000000	0.000000
5	6	0	−4.715291	−0.142564	1.569280
6	6	0	−3.920561	1.173039	1.421598
7	6	0	−3.080843	1.302324	0.118289
8	6	0	−3.921180	1.410298	−1.186460
9	1	0	−5.054342	−0.237233	2.610201
10	1	0	−5.630114	−0.087901	0.971431
11	1	0	−3.227887	1.260870	2.271769
12	1	0	−4.613040	2.024328	1.509631
13	1	0	−2.488774	2.223528	0.202049
14	1	0	−4.614132	2.263077	−1.118910
15	1	0	−3.229022	1.650765	−2.007083
16	6	0	2.603548	1.265617	0.084601
17	6	0	2.923901	1.861291	−1.287798
18	1	0	3.525624	1.073703	0.646500
19	1	0	2.005317	1.966045	0.674212
20	1	0	3.478522	2.800261	−1.176205
21	1	0	3.534330	1.177455	−1.888342
22	1	0	2.000932	2.069139	−1.838761
23	6	0	−4.715291	0.142564	−1.569280
24	6	0	−3.920561	−1.173039	−1.421598
25	6	0	−3.080843	−1.302324	−0.118289
26	6	0	−3.921180	−1.410298	1.186460
27	1	0	−5.054342	0.237233	−2.610201
28	1	0	−5.630114	0.087901	−0.971431
29	1	0	−3.227887	−1.260870	−2.271769
30	1	0	−4.613040	−2.024328	−1.509631
31	1	0	−2.488774	−2.223528	−0.202049
32	1	0	−4.614132	−2.263077	1.118910
33	1	0	−3.229022	−1.650765	2.007083
34	6	0	2.603548	−1.265617	−0.084601
35	6	0	2.923901	−1.861291	1.287798
36	1	0	3.525624	−1.073703	−0.646500
37	1	0	2.005317	−1.966045	−0.674212
38	1	0	3.478522	−2.800261	1.176205
39	1	0	3.534330	−1.177455	1.888342
40	1	0	2.000932	−2.069139	1.838761

Table S7: Cartesian Coordinates for $(\mathbf{1c})_2$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	1.129002	0.000000
2	6	0	0.000000	0.000000	−1.236949
3	6	0	0.000000	0.000000	−2.493348
4	7	0	0.000000	0.000000	−3.797869
5	6	0	−1.310126	2.099522	0.016905
6	1	0	−2.250320	1.527212	0.028420
7	6	0	−1.318487	2.948109	−1.277601
8	1	0	−1.510768	2.263690	−2.115441
9	1	0	−2.163371	3.655031	−1.268222
10	6	0	−0.019703	3.733721	−1.569048
11	1	0	−0.033385	4.071175	−2.615988
12	1	0	−0.011416	4.653095	−0.974977
13	6	0	1.310126	2.099522	−0.016905
14	1	0	2.250320	1.527212	−0.028420
15	6	0	1.285295	2.946006	−1.313316
16	1	0	1.454413	2.264350	−2.158870
17	1	0	2.130785	3.652023	−1.325779
18	6	0	−1.285295	2.946006	1.313316
19	1	0	−1.454413	2.264350	2.158870
20	1	0	−2.130785	3.652023	1.325779
21	6	0	0.019703	3.733721	1.569048
22	1	0	0.033385	4.071175	2.615988
23	1	0	0.011416	4.653095	0.974977
24	6	0	1.318487	2.948109	1.277601
25	1	0	1.510768	2.263690	2.115441
26	1	0	2.163371	3.655031	1.268222
27	6	0	−1.269728	−0.002519	−4.559310
28	6	0	−1.605382	1.352319	−5.185562
29	1	0	−2.053296	−0.306810	−3.862392
30	1	0	−1.202262	−0.775694	−5.333744
31	1	0	−2.558210	1.283200	−5.722513
32	1	0	−1.699198	2.124978	−4.416570
33	1	0	−0.843401	1.672057	−5.904459
34	6	0	1.269728	0.002519	−4.559310
35	6	0	1.605382	−1.352319	−5.185562
36	1	0	1.202262	0.775694	−5.333744
37	1	0	2.053296	0.306810	−3.862392
38	1	0	2.558210	−1.283200	−5.722513
39	1	0	0.843401	−1.672057	−5.904459
40	1	0	1.699198	−2.124978	−4.416570

Table S7 (continued): Cartesian Coordinates for (**1c**)$_2$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
41	5	0	0.000000	−1.129002	0.000000
42	6	0	0.000000	0.000000	1.236949
43	6	0	0.000000	0.000000	2.493348
44	7	0	0.000000	0.000000	3.797869
45	6	0	−1.310126	−2.099522	−0.016905
46	1	0	−2.250320	−1.527212	−0.028420
47	6	0	−1.318487	−2.948109	1.277601
48	1	0	−1.510768	−2.263690	2.115441
49	1	0	−2.163371	−3.655031	1.268222
50	6	0	−0.019703	−3.733721	1.569048
51	1	0	−0.033385	−4.071175	2.615988
52	1	0	−0.011416	−4.653095	0.974977
53	6	0	1.310126	−2.099522	0.016905
54	1	0	2.250320	−1.527212	0.028420
55	6	0	1.285295	−2.946006	1.313316
56	1	0	1.454413	−2.264350	2.158870
57	1	0	2.130785	−3.652023	1.325779
58	6	0	−1.285295	−2.946006	−1.313316
59	1	0	−1.454413	−2.264350	−2.158870
60	1	0	−2.130785	−3.652023	−1.325779
61	6	0	0.019703	−3.733721	−1.569048
62	1	0	0.033385	−4.071175	−2.615988
63	1	0	0.011416	−4.653095	−0.974977
64	6	0	1.318487	−2.948109	−1.277601
65	1	0	1.510768	−2.263690	−2.115441
66	1	0	2.163371	−3.655031	−1.268222
67	6	0	−1.269728	0.002519	4.559310
68	6	0	−1.605382	−1.352319	5.185562
69	1	0	−2.053296	0.306810	3.862392
70	1	0	−1.202262	0.775694	5.333744
71	1	0	−2.558210	−1.283200	5.722513
72	1	0	−1.699198	−2.124978	4.416570
73	1	0	−0.843401	−1.672057	5.904459
74	6	0	1.269728	−0.002519	4.559310
75	6	0	1.605382	1.352319	5.185562
76	1	0	1.202262	−0.775694	5.333744
77	1	0	2.053296	−0.306810	3.862392
78	1	0	2.558210	1.283200	5.722513
79	1	0	0.843401	1.672057	5.904459
80	1	0	1.699198	2.124978	4.416570

4. References

S1 (a) Himbert, G.; Regitz, M. *Chem. Ber.* 1972, **105,** 2963-2974; (b) Himbert, G. *Angew. Chem. Int. Ed. Engl.* 1979, **18,** 405-406.

S2 J. C. Thomas, J. C. Peters, *Inorg. Chem.* 2003, **42,** 5055-5073.

S3 H. C. Brown, S. U. Kulkarni, *J. Organomet. Chem.* 1979, **168,** 281-293.

S4 CrystalClear: Rigaku/MSC. Inc., 9009 New Trails Drive, The Woodlands TX 77381, USA (2005).

S5 C. Kabuto, S. Akine, E. Kwon, *J. Cryst. Soc. Jpn*. 2009, **51,** 218-224.

S6 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Molterni, G. Polidori, R. Spagna, *J. Appl. Cryst*. 1999, **32,** 115-119.

S7 (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64,** 112-122; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, **71,** 3-8.

S8 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S9 Becke, A. D. *J. Chem. Phys*. 1993, **98,** 5648-5652.

S10 (a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37,** 785-789; (b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett*. 1989, **157,** 200-206.

S11 O. V. Sizova, L. V. Skripnikov, A. Y. Sokolov, *THEOCHEM* 2008, **870,** 1-9.

S12 A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev*. 1988, **88,** 899-926.

S13 A. P. Scott, L. Radom, *J. Phys. Chem.* 1996, **100,** 16502-16513.