

Supporting Information

Synthesis and Structural Characterization of a C₄ Cumulene including 4-Pyridylidene Units, and Its Reactivity towards Ammonia-Borane

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1. Synthesis and spectroscopic data

General considerations: All reactions were performed under an atmosphere of argon or nitrogen by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were obtained with a Bruker AV 300, Bruker AVIII 400MHz BBFO1, Bruker AVIII 400MHz BBFO2, JEOL ECA400 SL spectrometers at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet doublet. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) and DART-TOF mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OpticMelt Stanford Research System.

Synthesis of Compound 2: A solution of 4-chloro-3-mesitylpyridine **1** (1.00 g, 4.32 mmol) in THF (10 mL) was added into 4 M HCl (2 mL) in 1,4-dioxane. After the mixture was stirred for 10 min, the solvent was removed under vacuum. NaI (4.00 g, 26.68 mmol) and MeCN (30 mL) were added to the residue, and then heated at 125 °C for 48 h. After cooling to r.t., an aq solution of 10% K₂CO₃ and 5% NaHSO₃ (10 mL) were added, and the mixture was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, and all volatiles were removed under vacuum. The crude product was purified by flash column chromatography with Hexane/CH₂Cl₂ (= 1/1), and **2** was obtained as a red solid (55%). ¹H NMR (300 MHz, CDCl₃) δ 1.93 (s, 6 H), 2.36 (s, 3 H), 6.97(s, 2 H), 7.91 (d, *J* = 5.4 Hz, 1 H), 8.17 (d, *J* = 5.4 Hz, 1 H), 8.28 (s, 1 H). ¹³C NMR (75 MHz, CDCl₃) δ 20.4, 21.3, 112.6, 128.5, 134.1, 136.0, 137.2, 138.4, 142.7, 148.3, 149.6; M.p.: 83 °C; HRMS (ESI): *m/z* calcd for C₁₄H₁₅NI: 324.0249 [(*M*+*H*)]⁺; found: 324.0240.

Synthesis of Compound 3: A THF (30 mL) solution of **2** (2.00 g, 6.19 mmol), trimethylsilyl acetylene (1.67 mL, 12.47 mmol), Pd(PPh₃)₄ (0.72 g, 0.62 mmol), and CuI (0.35 g, 1.86 mmol) in dry triethylamine (30 mL) was stirred at 90 °C overnight. The reaction mixture was cooled to room temperature, filtered through Celite and the solvents were evaporated under vacuum. The crude product was purified by flash column chromatography with Hexane/CH₂Cl₂ (= 3/1), and **3** was obtained as a yellow oil (53%). ¹H NMR (400 MHz, CDCl₃) δ -0.01 (s, 9 H), 1.97 (s, 6 H), 2.32 (s, 3 H), 6.93 (s, 2 H), 7.37 (d, *J* = 5.2 Hz, 1 H), 8.42 (s, 1 H), 8.54 (d, *J* = 5.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ -0.6, 20.4, 21.2, 101.2, 102.9, 125.2, 128.1, 131.4, 133.7, 136.4, 137.6, 139.3, 148.2, 150.5; HRMS (ESI): *m/z* calcd for C₁₉H₂₄NSi: 294.1678 [(*M*+*H*)]⁺; found: 294.1674.

Synthesis of Compound 5: A THF solution (4 mL) of **3** (0.78 g, 2.66 mmol), K₂CO₃ (0.92 g, 6.66 mmol), and methanol (8 mL) was stirred at room temperature for 8 h. The mixture was washed with water, and then extracted with dichloromethane. The combined organic layers were dried over MgSO₄, and evaporated under vacuum to afford a yellow oil of **4**, which was used for next step without further purification. A toluene (20 mL) solution of **4**, **2** (0.55 g, 1.70 mmol), Pd(PPh₃)₄ (0.20 g, 0.17 mmol), CuI (0.06 g, 0.30 mmol), and diisopropylamine (8 mL), was stirred at 150 °C overnight. The reaction mixture was cooled to room temperature, and filtered through Celite, and the solvent was evaporated in vacuo. The crude product was purified by flash column chromatography with Hexane/CH₂Cl₂ (= 1/2) followed by recrystallization from chloroform/hexanes solution, and **5** was obtained as a colorless crystal (42 %). ¹H NMR (400 MHz, CDCl₃) δ 1.78 (s, 12 H), 2.36 (s, 6 H), 6.88 (s, 4 H), 7.18 (d, *J* = 5.2 Hz, 2 H), 8.35 (s, 2 H), 8.51 (d, *J* = 5.2 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 20.3, 21.3, 91.6, 125.9, 128.3, 130.4, 133.3, 136.3, 137.6, 138.2, 148.1, 150.9; M.p.: 178 °C; HRMS (ESI): *m/z* calcd for C₃₀H₂₉N₂: 417.2331 [(*M*+*H*)]⁺; found: 417.2334.

Synthesis of Compound 6: Methyl trifluoromethanesulfonate (1.3 mL, 9.60 mmol) was added into a CH₂Cl₂ solution (50 mL) of **5** (2.00 g, 4.80 mmol), and the reaction mixture was stirred at room temperature for 12 h. All volatiles were removed under vacuum, and the resulting solid was washed with diethyl ether and dichloromethane to afford a yellow solid (80 %); ¹H NMR (300 MHz, CD₃CN) δ 1.73 (s, 12 H), 2.37 (s, 6 H), 4.27 (s, 6 H), 6.96 (s, 4 H), 8.03 (d, *J* = 6.3 Hz, 2 H), 8.45 (s, 2 H), 8.62 (d, *J* = 6.3 Hz, 2 H). ¹³C NMR (100 MHz, CD₃CN) δ 20.1, 21.3, 49.5, 96.1, 129.6, 129.7, 131.4, 136.9, 138.5, 140.7, 143.5, 145.2, 147.0, *Carbon for CF₃ could not be observed, presumably due to overlap with other peaks; ¹⁹F NMR (225.6 MHz, CD₃CN) δ -78.5; M.p.: 157 °C (Decomposed); HRMS (ESI): *m/z* calcd for C₁₆H₁₇N: 223.1361 [(*M*/2)]⁺; found: 223.1339.

Synthesis of Compound 7: THF (20 mL) was added at -78 °C to a mixture of **6** (0.30 g, 0.40 mmol) and KC₈ (0.12 g, 0.89 mmol). The reaction mixture was allowed to warm to room temperature, and stirred for 2 h. After the filtration, solvent was evaporated under vacuum. The residue was extracted with toluene (50 mL), and after evaporating the solvent under vacuum, **7** was obtained as a black solid (60 %); ¹H NMR (400 MHz, d₈-THF) δ 2.20 (s, 18 H), 2.81 (s, 6 H), 4.59 (d, *J* = 7.6 Hz, 2 H), 5.49 (d, *J* = 1.8 Hz, 2 H), 5.59 (dd, *J* = 1.8 Hz, *J* = 7.6 Hz, 2 H), 6.96 (s, 4 H). ¹³C NMR (100 MHz, d₈-THF) δ 20.1, 21.0, 40.5, 104.6, 113.2, 123.9, 128.0, 128.1, 129.7, 130.0, 135.7, 136.1, 137.5; M.p.: 155 °C; HRMS (ESI): *m/z* calcd for C₃₂H₃₅N₂:

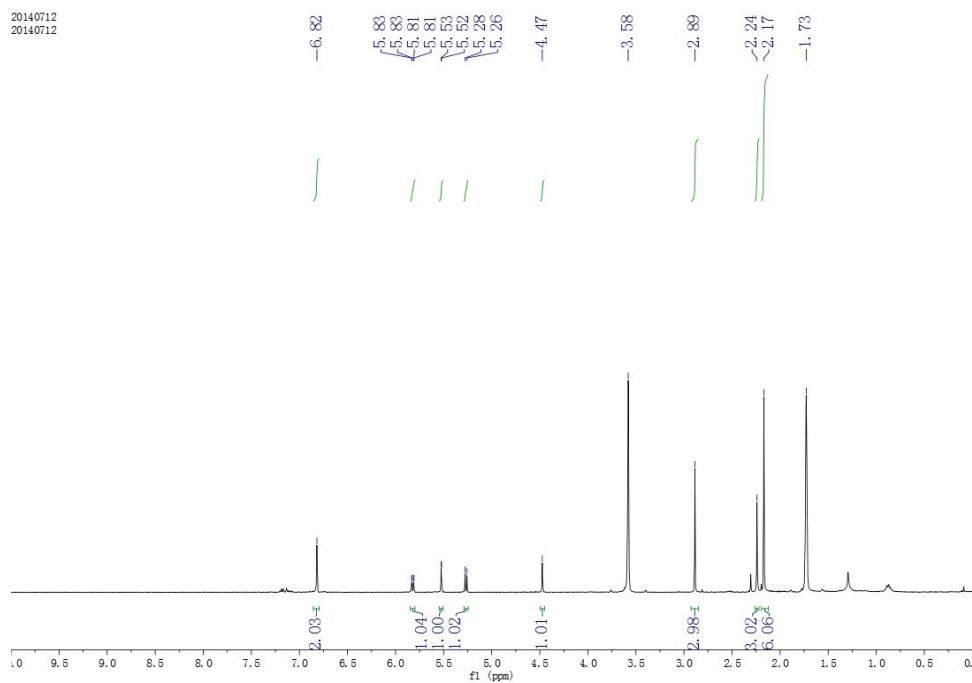
447.2800 [(M+H)]⁺; found: 447.2823.

Synthesis of Compound 8(H): THF (3 mL) was added to a mixture of **7** (28 mg, 0.062 mmol) and ammonia borane (4.0 mg, 0.13 mmol). The solution was then stirred at 60 °C for 6 h. After the solvent was removed under vacuum, the residue was recrystallized from THF, and **8(H)** was obtained as a black solid (50%); ¹H NMR (400 MHz, d₈-THF) δ 2.17 (s, 12 H) 2.24 (s, 6 H), 2.89 (s, 6 H), 4.47 (s, 2 H), 5.27 (d, *J* = 7.7 Hz, 2 H), 5.52 (d, *J* = 1.6 Hz, 2 H), 5.82 (dd, *J* = 1.6 Hz, *J* = 7.7 Hz, 2 H), 6.82 (s, 4 H); ¹³C NMR (100 MHz, d₈-THF) δ 19.6, 20.9, 40.2, 101.9, 107.7, 124.4, 126.1, 127.9, 129.7, 131.2, 135.5, 135.8, 137.6; M.p.: 182 °C; HRMS (ESI): *m/z* calcd for C₃₂H₃₆N₂Na: 471.2776 [(M+Na)]⁺; found: 471.2799.

Synthesis of Compound 8(D): Reaction was performed with same condition for the synthesis of **8(H)** using D₃NBD₃ instead of H₃NBH₃. A pure **8(D)** was obtained by recrystallization from THF in 47% yield; HRMS (ESI): *m/z* calcd for C₃₂H₃₅D₂N₂: 451.3082 [(M+H)]⁺; found: 451.3062.

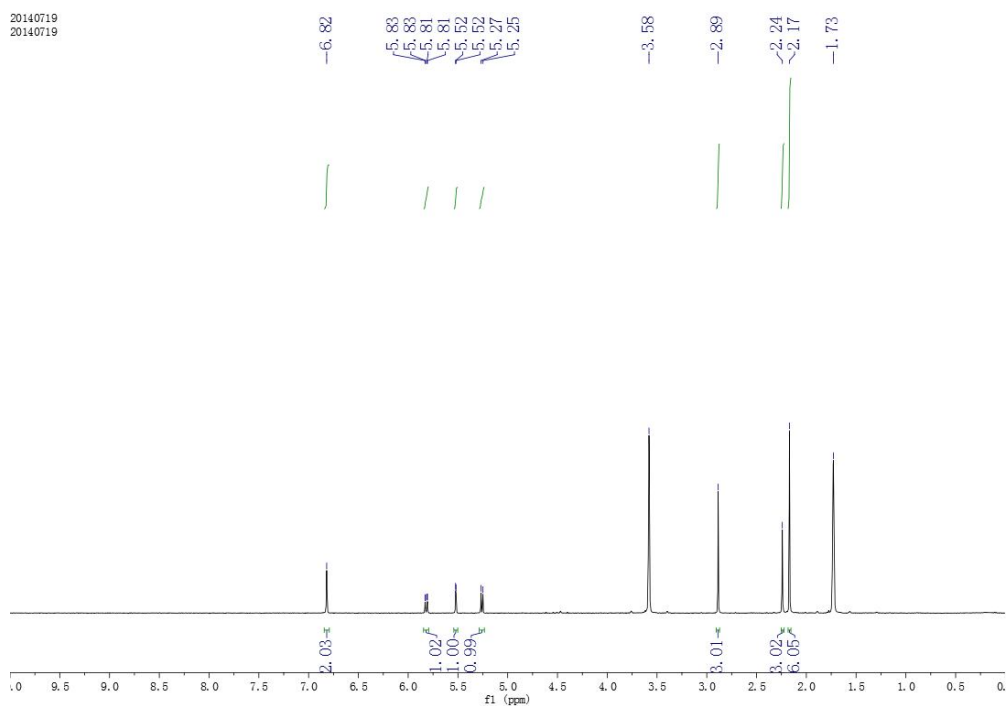
¹H NMR (d₈-THF) spectrum of compounds 8(H)*:

* a peak at 4.47ppm corresponds to the protons at the central *sp*²-carbons of 8(H).



¹H NMR (d₈-THF) spectrum of compounds 8(D)*:

* No peak was observed at 4.47ppm.



2. Crystal structural parameters of Compounds 5, 7 and 8

X-ray data collection and structural refinement. Intensity data for compounds **5**, **7** and **8** were collected using a Bruker APEX II diffractometer. The crystals of **5**, **7** and **8** were measured at 103(2) K. The structure was solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on F^2 .^[S1] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1016579-1016581 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Summary of Data Collection and Structure Refinement.

	5	7	8
Formula	C ₃₀ H ₂₈ N ₂	C ₃₂ H ₃₄ N ₂	C ₃₂ H ₃₆ N ₂
Fw	416.54	446.61	448.63
cryst syst	monoclinic	trigonal	trigonal
space group	<i>P</i> 1 21/ <i>n</i> 1	<i>R</i> -3	<i>R</i> -3
Size (mm ³)	0.280 x 0.340 x 0.400	0.190 x 0.200 x 0.220	0.400 x 0.410 x 0.420
T, K	103(2)	103(2)	103(2)
<i>a</i> , Å	10.9355(13)	23.567(3)	23.7045(15)
<i>b</i> , Å	18.231(2)	23.567(3)	23.7045(15)
<i>c</i> , Å	12.2805(15)	12.0950(14)	11.9100(8)
α , deg	90	90	90
β , deg	109.896(4) ^o	90	90
γ , deg	90	120	120
V, Å ³	2302.2(5)	5817.6(17)	5795.7(8)
Z	4	9	9
d_{calcd} g·cm ⁻³	1.202	1.147	1.157
μ , mm ⁻¹	0.070	0.066	0.067
Refl collected	28904	9257	24989
$T_{\text{min}}/T_{\text{max}}$	0.867	0.789	0.926
N _{measd}	5735	3114	3935
[R _{int}]	0.0450	0.0641	0.0808
<i>R</i> [I>2sigma(I)]	0.0457	0.0875	0.0635
<i>R</i> _w [I>2sigma(I)]	0.1322	0.3040	0.1720
GOF	1.035	1.074	1.022
Largest diff peak/hole[e·Å ⁻³]	0.306/-0.223	0.371/-0.398	0.379 /-0.355

3. DFT calculation results

Gaussian 09 was used for all density functional theory (DFT) calculations.^[S2] Geometry optimization, frequency calculations, and Natural bond order (NBO) analysis on compound **7** were performed at the M05-2X/6-311G(d,p) level of theory.

Table S2 Optimized structure of **7** (atom, x-, y-, z- positions in Å)

C	4.165933	4.636439	-0.13996	H	4.335309	4.817418	-1.20523
N	3.204047	3.576983	0.085042	H	1.587111	4.895007	0.049783
C	1.849751	3.846793	0.04542	H	4.675285	2.092288	0.037485
C	3.606279	2.256391	0.038332	H	-0.12842	3.134426	0.016871
C	0.920359	2.875832	0.022358	H	2.219367	0.296349	2.535876
C	2.742536	1.222635	0.015002	H	3.935865	0.649546	2.682091
C	1.301696	1.473564	0.014353	H	3.291395	-0.85487	3.351603
C	3.233178	-0.18246	0.003094	H	4.053423	-2.69341	2.120283
C	0.41071	0.471535	0.005576	H	3.954529	-2.69388	-2.14901
C	3.455273	-0.85094	1.211521	H	3.792497	0.67164	-2.68511
C	3.398887	-0.85149	-1.21416	H	2.091579	0.265822	-2.49354
C	-0.41083	-0.47192	-0.00421	H	3.173232	-0.84666	-3.34879
C	3.213368	-0.15229	2.523743	H	0.127939	-3.13493	-0.01623
C	3.88179	-2.17527	1.183839	H	4.218369	-4.80532	-0.90707
C	3.826034	-2.17569	-1.20572	H	4.246342	-4.81	0.860488
C	3.098711	-0.15239	-2.5137	H	5.668716	-4.298	-0.04458
C	-1.30192	-1.47385	-0.01371	H	-1.58784	-4.89523	-0.05044
C	4.080043	-2.85049	-0.01597	H	-4.6756	-2.09205	-0.03871
C	-0.92079	-2.87617	-0.02205	H	-5.1122	-4.36912	-0.32975
C	-2.74273	-1.22271	-0.015	H	-3.80522	-5.55347	-0.3228
C	4.577353	-4.27261	-0.02737	H	-4.33663	-4.81761	1.203432
C	-1.85032	-3.84698	-0.04583	H	-2.21495	-0.29432	-2.53466
C	-3.60662	-2.25632	-0.03904	H	-3.93108	-0.64837	-2.68319
C	-3.23313	0.182478	-0.00301	H	-3.28654	0.856673	-3.35128
N	-3.20456	-3.57696	-0.08591	H	-4.04936	2.694868	-2.12003
C	-3.4531	0.851731	-1.2114	H	-3.95739	2.692772	2.149418
C	-3.40066	0.850815	1.214374	H	-3.79737	-0.67272	2.684096
C	-4.16671	-4.63634	0.138302	H	-2.0959	-0.26811	2.494969
C	-3.2092	0.153782	-2.52362	H	-3.17784	0.844807	3.349293
C	-3.87936	2.176137	-1.18361	H	-4.21782	4.805329	0.907806
C	-3.82749	2.17511	1.206028	H	-4.24474	4.810456	-0.85977
C	-3.10273	0.150867	2.513977	H	-5.66777	4.298537	0.044331
C	-4.0794	2.850685	0.016275				
C	-4.5764	4.272916	0.027755				
H	5.111694	4.369492	0.327707				
H	3.80453	5.553654	0.321052				

Table S3. The NPA charges of **7** calculated at M05-2X/6-311G(d,p) level of theory.

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	-0.35001	1.99931	4.33685	0.01385	6.35001
N	2	-0.43585	1.99925	5.42417	0.01243	7.43585
C	3	0.01339	1.99910	3.96505	0.02245	5.98661
C	4	0.02750	1.99893	3.95101	0.02256	5.97250
C	5	-0.23794	1.99908	4.22175	0.01711	6.23794
C	6	-0.07948	1.99896	4.06043	0.02008	6.07948
C	7	-0.14466	1.99884	4.12990	0.01592	6.14466
C	8	-0.06878	1.99882	4.05301	0.01696	6.06878
C	9	-0.04206	1.99862	4.02872	0.01472	6.04206
C	10	0.02111	1.99893	3.96617	0.01378	5.97889
C	11	0.02248	1.99893	3.96479	0.01379	5.97752
C	12	-0.04206	1.99862	4.02872	0.01472	6.04206
C	13	-0.60882	1.99928	4.60010	0.00945	6.60882
C	14	-0.23687	1.99895	4.22196	0.01596	6.23687
C	15	-0.23695	1.99895	4.22204	0.01596	6.23695
C	16	-0.60947	1.99928	4.60077	0.00942	6.60947
C	17	-0.14467	1.99884	4.12990	0.01592	6.14467
C	18	-0.00636	1.99902	3.99359	0.01376	6.00636
C	19	-0.23795	1.99908	4.22176	0.01711	6.23795
C	20	-0.07947	1.99896	4.06042	0.02008	6.07947
C	21	-0.60127	1.99928	4.59220	0.00980	6.60127
C	22	0.01340	1.99910	3.96505	0.02245	5.98660
C	23	0.02749	1.99893	3.95102	0.02256	5.97251
C	24	-0.06878	1.99882	4.05300	0.01696	6.06878
N	25	-0.43584	1.99925	5.42417	0.01243	7.43584
C	26	0.02114	1.99893	3.96614	0.01379	5.97886
C	27	0.02246	1.99893	3.96482	0.01379	5.97754
C	28	-0.35001	1.99931	4.33685	0.01385	6.35001
C	29	-0.60884	1.99928	4.60012	0.00945	6.60884
C	30	-0.23688	1.99895	4.22197	0.01596	6.23688
C	31	-0.23695	1.99895	4.22204	0.01596	6.23695
C	32	-0.60945	1.99928	4.60075	0.00942	6.60945
C	33	-0.00636	1.99902	3.99359	0.01376	6.00636
C	34	-0.60127	1.99928	4.59220	0.00980	6.60127
H	35	0.20007	0.00000	0.79842	0.00151	0.79993
H	36	0.19940	0.00000	0.79896	0.00164	0.80060
H	37	0.18591	0.00000	0.81104	0.00306	0.81409
H	38	0.20436	0.00000	0.79367	0.00197	0.79564

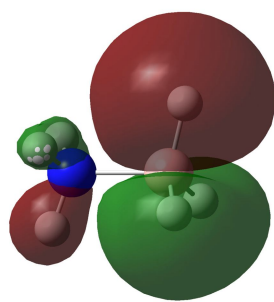
H	39	0.21138	0.00000	0.78596	0.00266	0.78862
H	40	0.23289	0.00000	0.76447	0.00263	0.76711
H	41	0.22961	0.00000	0.76836	0.00203	0.77039
H	42	0.21381	0.00000	0.78433	0.00186	0.78619
H	43	0.20515	0.00000	0.79320	0.00165	0.79485
H	44	0.20578	0.00000	0.79070	0.00352	0.79422
H	45	0.20588	0.00000	0.79059	0.00353	0.79412
H	46	0.21373	0.00000	0.78429	0.00198	0.78627
H	47	0.23075	0.00000	0.76724	0.00201	0.76925
H	48	0.20503	0.00000	0.79333	0.00164	0.79497
H	49	0.23289	0.00000	0.76448	0.00263	0.76711
H	50	0.20816	0.00000	0.79008	0.00176	0.79184
H	51	0.20828	0.00000	0.78995	0.00177	0.79172
H	52	0.21386	0.00000	0.78418	0.00196	0.78614
H	53	0.20436	0.00000	0.79367	0.00197	0.79564
H	54	0.21138	0.00000	0.78596	0.00266	0.78862
H	55	0.20007	0.00000	0.79842	0.00151	0.79993
H	56	0.19940	0.00000	0.79896	0.00164	0.80060
H	57	0.18591	0.00000	0.81104	0.00306	0.81409
H	58	0.22963	0.00000	0.76834	0.00203	0.77037
H	59	0.21383	0.00000	0.78431	0.00186	0.78617
H	60	0.20515	0.00000	0.79320	0.00165	0.79485
H	61	0.20578	0.00000	0.79070	0.00352	0.79422
H	62	0.20588	0.00000	0.79059	0.00353	0.79412
H	63	0.21372	0.00000	0.78431	0.00198	0.78628
H	64	0.23073	0.00000	0.76727	0.00200	0.76927
H	65	0.20504	0.00000	0.79332	0.00164	0.79496
H	66	0.20817	0.00000	0.79007	0.00176	0.79183
H	67	0.20827	0.00000	0.78996	0.00177	0.79173
H	68	0.21386	0.00000	0.78418	0.00196	0.78614

* Total * 0.00000 67.96707 171.44256 0.59037 240.00000

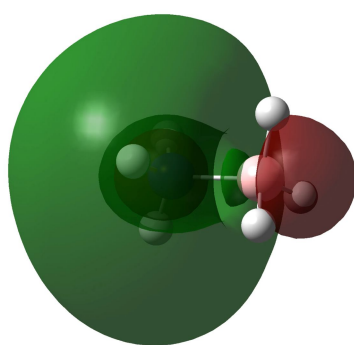
Geometry optimization and frequency calculations on **AB** performed at the M05-2X/6-311G(d,p) level of theory.

Table S4 Optimized structure of **AB** (atom, x-, y-, z- positions in Å)

N	-0.0001	-0.73233	0
H	-0.94775	-1.09018	0
H	0.474155	-1.08877	0.820998
H	0.474155	-1.08877	-0.821
B	-0.0001	0.933961	0
H	1.167626	1.240517	0
H	-0.5835	1.241863	1.011082
H	-0.5835	1.241863	-1.01108



HOMO (-9.2318 eV)



LUMO (1.2974 eV)

Figure Frontier orbitals of **AB**.

4. References

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