Supporting Information

Sandwiched Sodium and Half-sandwiched Copper Carbonyl Complexes Featuring Polyfluorinated Tris(triazolyl)borate $[HB(3,5\text{-}(CF_3)_2Tz)_3]^-$

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Experimental:

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere single-station dry-box equipped with a -25 °C refrigerator. Solvents were purchased from commercial sources, purified prior to use. NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 and JEOL Eclipse 300 spectrometer (^{1}H, 500.16 MHz and 300.53 MHz; ^{13}C, 125.78 MHz, and 75.59 MHz; ^{19}F, 470.62 MHz, and 282.78 MHz). Proton and carbon chemical shifts are reported in ppm versus Me_4Si. ^{19}F NMR values were referenced to external $CFCl_3$. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. 3,5-Bis(trifluoromethyl)-1*H*-1,2,4-triazole (^{19}F NMR ($CDCl_3$): δ *(ppm)* -64.8 (s); ^{13}C NMR ($CDCl_3$): δ *(ppm)* 118.7 (q,^1J(C,F) = 270.9 Hz, *C*F_3), 150.9 (q, ^2J(C,F) = 41.4 Hz, *C*=N)) was prepared as reported previously (Abdul-Ghani, M. M; Tipping, A. E. *Journal of Fluorine Chemistry* **1995,** *72***,** 95-106).

$[HB(3,5\text{-}(CF_3)_2Tz)_3]Na$: $NaBH_4$ (0.092 g, 2.4 mmol) and 3,5-bis(trifluoromethyl)triazole, 3,5-$(CF_3)_2TzH$ (2.0 g, 9.8 mmol) were mixed in a Schlenk tube fitted with a condenser cooled with air. The mixture was heated at 205-210 °C for 6 h under N_2. During this period, heat gun was

used to transfer the triazole condensed on the wall of flask back to the reaction mixture from time to time. The mixture was allowed to cool to room temperature, and the resulting solid was transferred to a sublimation apparatus and sublimed at 140 °C under vacuum to remove the unreacted 3,5-$(CF_3)_2$TzH. [HB(3,5-$(CF_3)_2Tz)_3$]Na was obtained as a white powder (1.5 g, yield 94% based on $NaBH_4$). Mp: 303-305 °C (changed to black solid at 300 °C and melt as black liquid). ^{19}F NMR (Acetone-d^6): δ *(ppm)* -64.5 (s), -62.3 (d, ^5J(H,F) = 3.4 Hz). ^{13}C NMR (DMSO-d^6): δ *(ppm)* 117.8 (q, ^1J(C,F) = 269.7 Hz, CF_3), 118.9 (q, ^1J(C,F) = 269.3 Hz, CF_3), 149.2 (q, ^2J(C,F) = 39.3 Hz, CCF_3), 152.7 (q, ^2J(C,F) = 39.1 Hz, CCF_3). The solid is hydroscopic. Samples used for CHN analysis agrees with the [HB(3,5-$(CF_3)_2Tz)_3$]Na(H_2O): Anal. Calcd for $C_{12}H_3BF_{18}N_9NaO$: C, 21.65; H, 0.45; N, 18.95. Found: C, 21.65; H, 0.63; N, 18.87. The solid [HB(3,5-$(CF_3)_2Tz)_3$]Na(H_2O) is stable in air and has good solubility in DMSO, acetone and THF; limited solubility in CH_2Cl_2, toluene and hexane. Crystals suitable for X-ray diffraction were obtained from toluene/THF (3:1) at -33°C after 2 days. It crystallizes as **[Na(THF)$_6$]{[HB(3,5-$(CF_3)_2Tz)_3$]$_2$Na}**: ^{1}H NMR (Acetone-d^6): δ *(ppm)* 1.77 (m, THF), 3.68 (m, THF). ^{19}F NMR (Acetone-d^6): δ *(ppm)* -64.5 (s), -62.3 (d, ^5J(H,F) = 3.4 Hz). Mp: 320-325 °C.

[HB(3,5-$(CF_3)_2Tz)_3$]CuCO: Solid [HB(3,5-$(CF_3)_2Tz)_3$]Na(H_2O) (0.13 g, 0.20 mmol) and copper(I) chloride (0.04 g, 0.40 mmol) were placed in a Schlenk flask with THF (20 mL) and the resulting solution was stirred for 5 hrs. The CO gas was gently bubbled through the solution at the beginning and later about 2-3 times (30s each time) during this period. The mixture was filtered under N_2 through a bed of Celite, the filtrate was collected, and the solvent was removed under reduced pressure to obtain [HB(3,5-$(CF_3)_2Tz)_3$]CuCO as a gray solid (0.13 g, 90%). This was extracted into ether (saturated with CO), filtered, and the solvent was removed under vacuum to obtain a colorless solid. Anal. Calc. for $(C_{13}HBCuF_{18}N_9O)(C_4H_{10}O)_{0.2}$: C, 22.67; H, 0.41; N, 17.26; Found: C, 22.47; H, 1.01; N, 16.85 (presence of some diethyl ether was confirmed by

NMR). X-ray quality crystals of $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$ were grown from toluene/THF (4:1) under CO atmosphere at -33°C. M.p. 245 °C with decomposition. ^{19}F NMR (C_6D_6): δ *(ppm)* -61.7 (d, $^5J(H,F)$ = 3.3 Hz), -64.3 (s); ^{19}F NMR (DMSO-d^6): δ *(ppm)* -64.2 (s), -61.6 (d, $^5J(H,F)$ = 3.1 Hz). IR (only selected peaks are given), cm^{-1}, in KBr, 2648 (BH, w), 2138 (CO, vs), 2084 (^{13}CO isotopomer); in Nujol, cm^{-1}: 2138 (CO), 2084 (^{13}CO isotopomer). Raman (only selected peaks are given), cm^{-1}: 2137 (CO). It appears that this adduct lose CO slowly in solution as evident from the formation of poorly soluble solids in C_6H_6 or CH_2Cl_2. These solids dissolve when CO is bubbled through the solution. Addition of excess CO to a C_6D_6 solution of $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$ leads to the broadening of the doublet in the ^{19}F NMR spectrum.

It is also possible to obtain $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$ using $[Cu(OTf)]_2 \bullet C_6H_6$ (0.12 g, 0.23 mmol) and $[HB(3,5\text{-}(CF_3)_2Tz)_3]Na(H_2O)$ (0.30 g, 0.46 mmol) in CO saturated THF (15 mL) after about 4 h of stirring. Attempts to crystallize the product directly from this mixture led to a mixture of crystals containing $(NaOTf)_4(THF)_3$ and $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$.

X-ray crystallographic data:

A suitable crystal covered with a layer of hydrocarbon oil was selected and mounted with paratone-N oil in a cryo-loop and immediately placed in the low-temperature nitrogen stream for the low temperature work. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package. Additional details are in the cif files.

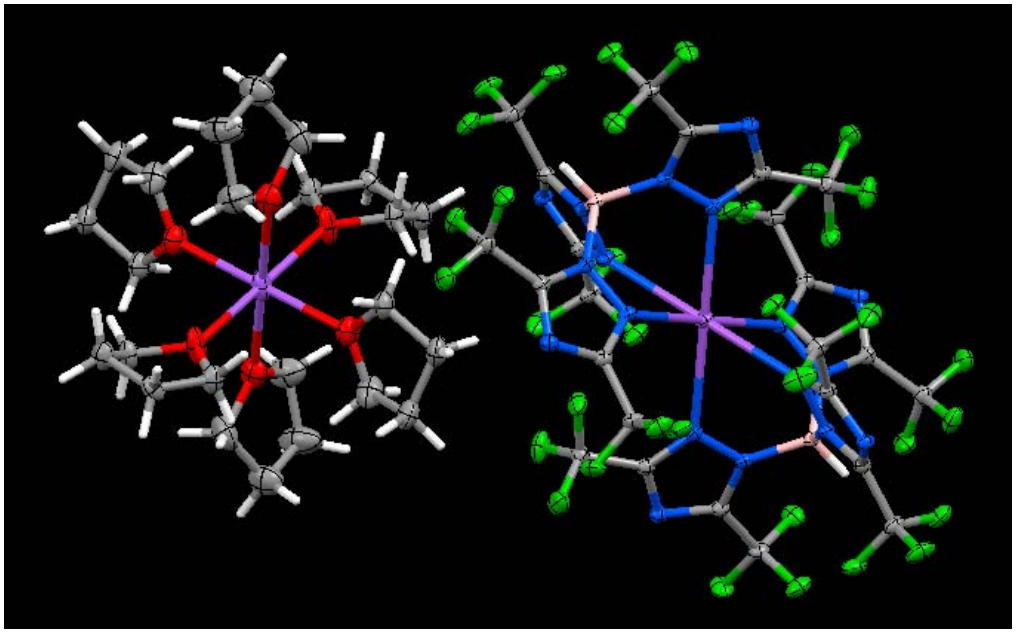


Figure S1. Crystal structure of $[Na(THF)_6]\{[HB(3,5\text{-}(CF_3)_2Tz)_3]_2Na\}$

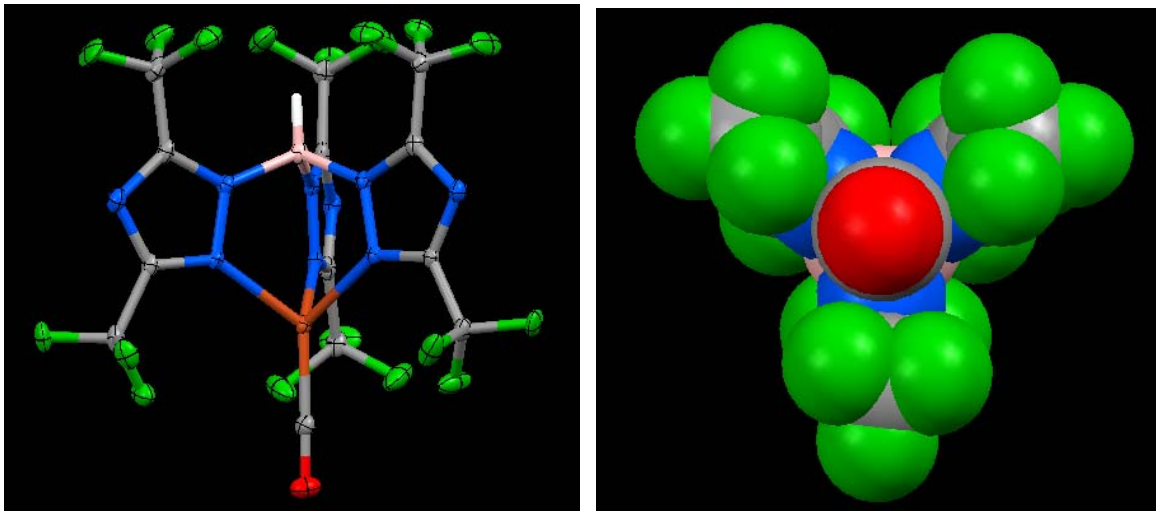


Figure S2. ORTEP diagram and space-filling diagram (a view down the O-C bond) of $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$

Computational Methods

B3LYP[i,ii] geometry optimization utilized the Gaussian03[iii] suite of programs; the 6-311+G(d) basis set was employed.

No symmetry constraints were employed in geometry optimization. Calculation of the energy Hessian was performed to confirm species as minima on their respective potential energy surfaces at this level of theory.

Modeling of open-shell species with density functional theory employed restricted Kohn-Sham methods. Enthalpic and free energy corrections use unscaled vibrational frequencies and assume a temperature of 298.15 K and 1 atm.

Gas Phase Acidity is defined as the negative of the free energy of the following reaction:

$$L_x + H^+ \rightarrow L_xH^+$$

Note that the negative of the enthalpy of this same reaction is defined as the proton affinity.

Table S-1. B3LYP/6-311++G(d,p) Calculated Enthalpies (a.u.) and Free Energies (a.u.) and Relative Energetics (Δ, kcal/mol) for Substituted Pyrazole, Triazole Ligands and their Conjugate Acids.

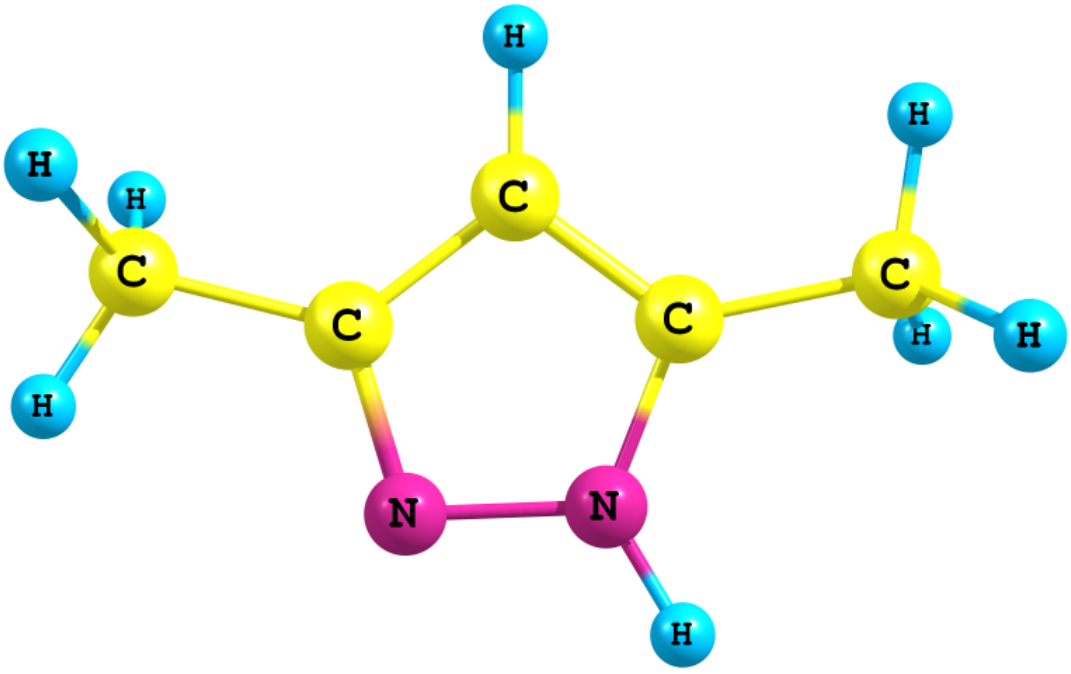
	H	G
L_1H^+	-305.1492	-305.1913
L_1	-304.7932	-304.8333
H^+	0.0024	-0.0107
Δ	224.9	217.9
L_2H^+	-321.2060	-321.2462
L_2	-320.8655	-320.9063
H^+	0.0024	-0.0107
ΔE	215.2	206.6
L_3H^+	-900.7689	-900.8212
L_3	-900.4648	-900.5168
H^+	0.0024	-0.0107
ΔE	192.3	184.3
L_4H^+	-916.8112	-916.8629
L_4	-916.5235	-916.5753
H^+	0.0024	-0.0107
ΔE	182.0	173.8

- Optimized Cartesian coordinates for these species are given in Table S-2. Note that L_XH is the protonated form of L_X. L_1 = 3,5-$(Me)_2$PzH, L_1H^+ = [3,5-$(Me)_2PzH_2]^+$, L_2 = 3,5-$(Me)_2$TzH, L_2H^+ = [3,5-$(Me)_2TzH_2]^+$, L_3 = 3,5-$(CF_3)_2$PzH, L_3H^+ = [3,5-$(CF_3)_2PzH_2]^+$, L_4 = 3,5-$(CF_3)_2$TzH, L_4H^+ = [3,5-$(CF_3)_2TzH_2]^+$ (structural details are given below; Pz = pyrazolate; Tz = triazolate).

Table S-2. B3LYP/6-311++G(d,p) Calculated Geometries for Substituted Pyrazole and Triazole Ligands and their Conjugate Acids. First Column is Atom Label, Second Column is Atomic Number, Third, Fourth and Fifth Columns are x, y, and z Coordinates in Å.

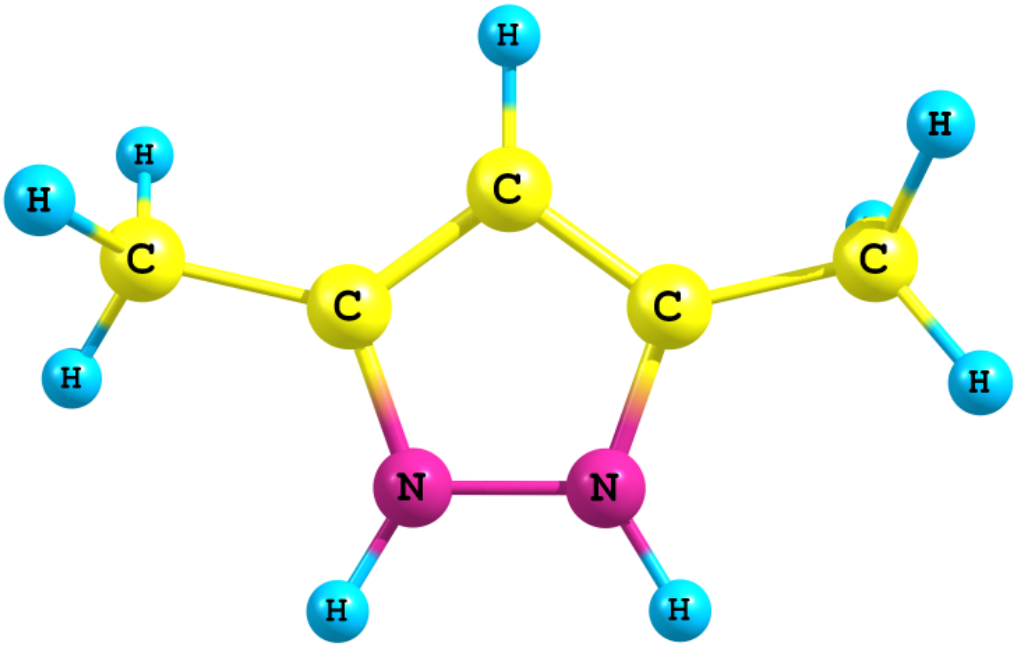
L_1

1	7	-0.730932	1.163919	0.196058
2	7	0.622574	1.101885	0.180092
3	6	-1.128734	-0.092682	0.022365
4	6	-0.013451	-0.962575	-0.105382
5	6	1.103970	-0.157833	0.001220
6	1	1.149229	1.952374	0.296208
7	1	-0.023326	-2.030907	-0.254905
8	6	2.565143	-0.468444	-0.050102
9	1	3.071361	-0.189086	0.879482
10	1	3.062044	0.056657	-0.872158
11	1	2.713233	-1.538190	-0.200964
12	6	-2.585581	-0.435266	-0.017730
13	1	-3.182223	0.468495	0.112340
14	1	-2.849871	-1.140895	0.775679
15	1	-2.859461	-0.895729	-0.971787



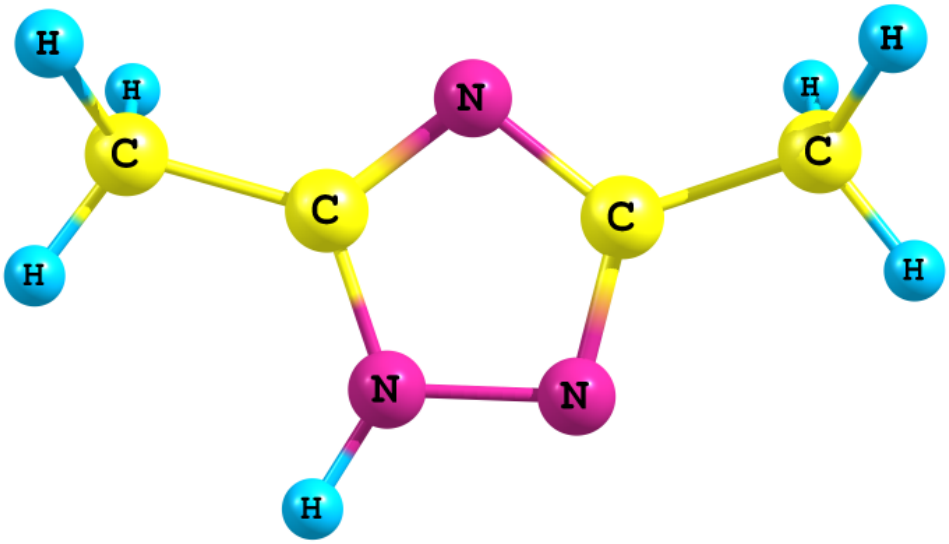
L_1H^+

1	7	-0.681801	1.074019	0.017142
2	7	0.674611	1.079241	-0.016833
3	6	-1.125200	-0.199748	0.019125
4	6	0.004475	-1.018207	-0.000167
5	6	1.127797	-0.191104	-0.019169
6	1	1.198028	1.944610	0.001131
7	1	0.008610	-2.095737	-0.000332
8	6	2.581111	-0.516963	-0.016143
9	1	2.896187	-0.821525	0.985860
10	1	3.189192	0.335096	-0.323555
11	1	2.780364	-1.347020	-0.695257
12	6	-2.575919	-0.536960	0.016060
13	1	-3.190760	0.310603	0.322448
14	1	-2.768814	-1.367875	0.695968
15	1	-2.888307	-0.844986	-0.985719
16	1	-1.211850	1.935347	-0.000586



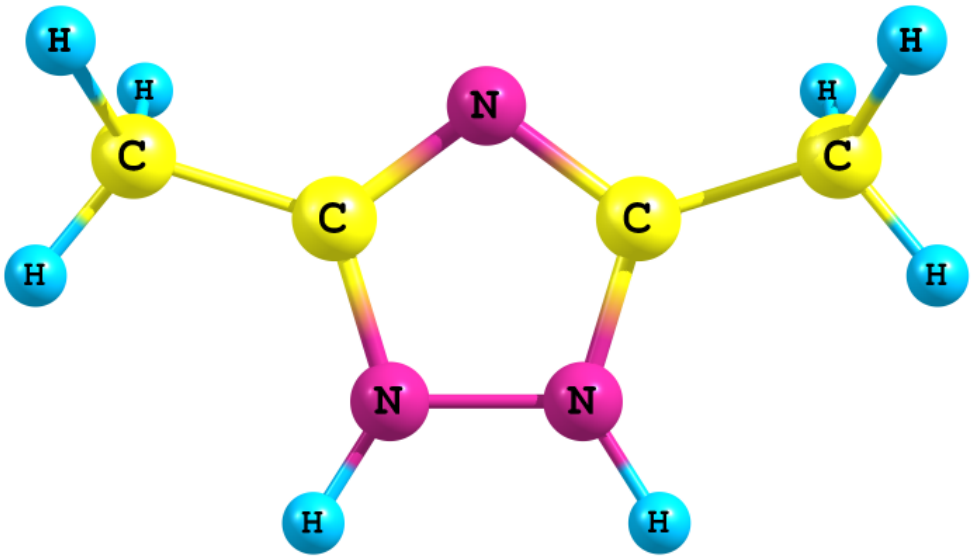
L_2

1	7	0.746338	-1.163851	-0.300154
2	7	-0.612812	-1.118727	-0.275261
3	6	1.074736	0.088539	-0.023914
4	7	0.003264	0.918257	0.173134
5	6	-1.044952	0.130872	0.008642
6	1	-1.147402	-1.953949	-0.456073
7	6	-2.480640	0.521522	0.111796
8	1	-2.694525	0.916859	1.107303
9	1	-3.141024	-0.328284	-0.073198
10	1	-2.712328	1.305240	-0.612859
11	6	2.490054	0.550733	0.063888
12	1	2.698623	0.959681	1.055889
13	1	2.679907	1.343724	-0.664074
14	1	3.169414	-0.279480	-0.128884



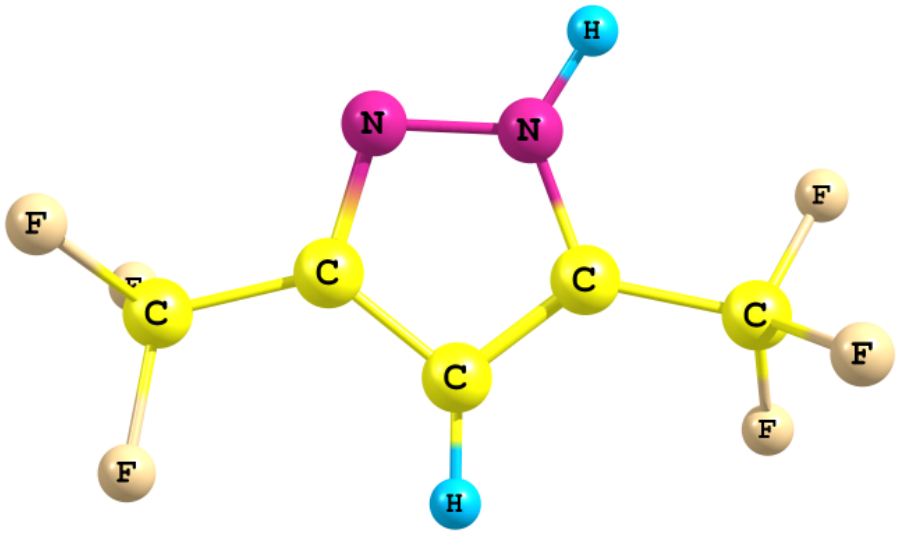
L_2H^+

1	7	0.680772	-1.124283	0.200922
2	7	-0.680418	-1.125246	0.196524
3	6	1.071884	0.145757	-0.016317
4	7	-0.000197	0.929371	-0.153360
5	6	-1.072069	0.144364	-0.021515
6	1	-1.219977	-1.970160	0.343487
7	6	-2.487392	0.577585	-0.098851
8	1	-3.179942	-0.252457	0.040547
9	1	-2.669769	1.040304	-1.071587
10	1	-2.674218	1.335742	0.665298
11	6	2.487157	0.580255	-0.087502
12	1	3.179766	-0.248570	0.058684
13	1	2.668950	1.341230	0.675042
14	1	2.674504	1.039794	-1.060809
15	1	1.220579	-1.969724	0.343856



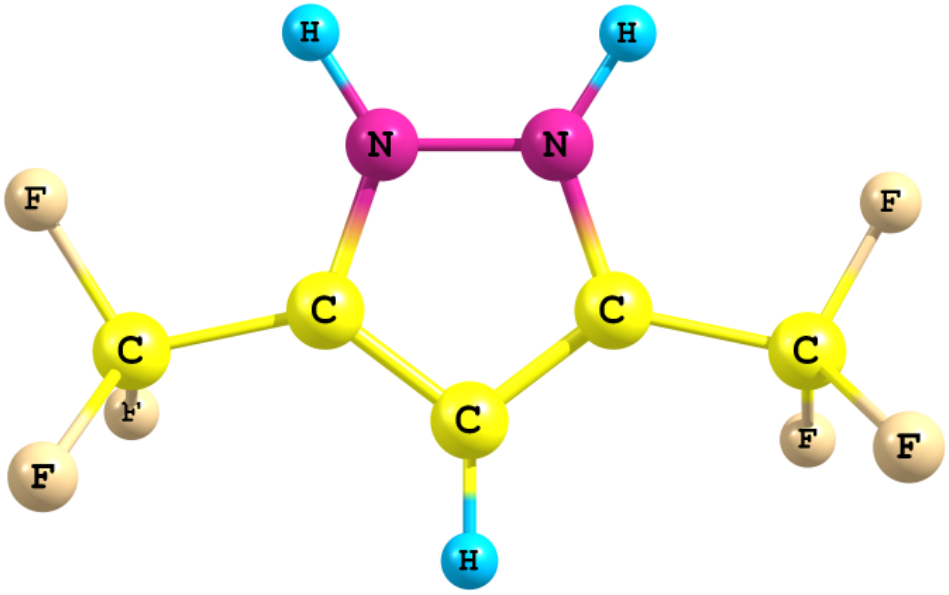
L_3

1	7	0.691851	1.419031	0.101715
2	7	-0.639156	1.355182	0.104840
3	6	1.085053	0.152493	0.000258
4	6	-1.106188	0.080646	0.017266
5	1	-1.179916	2.203551	0.192485
6	6	-2.565696	-0.222443	-0.048896
7	6	2.545943	-0.185141	0.005723
8	9	-3.003516	-0.361633	-1.319575
9	9	-3.284902	0.783942	0.505361
10	9	2.732122	-1.463210	-0.395625
11	9	3.084486	-0.074928	1.240343
12	9	3.258121	0.609547	-0.811140
13	9	-2.865515	-1.359137	0.601134
14	6	-0.002862	-0.742368	-0.056059
15	1	0.016483	-1.815515	-0.138695



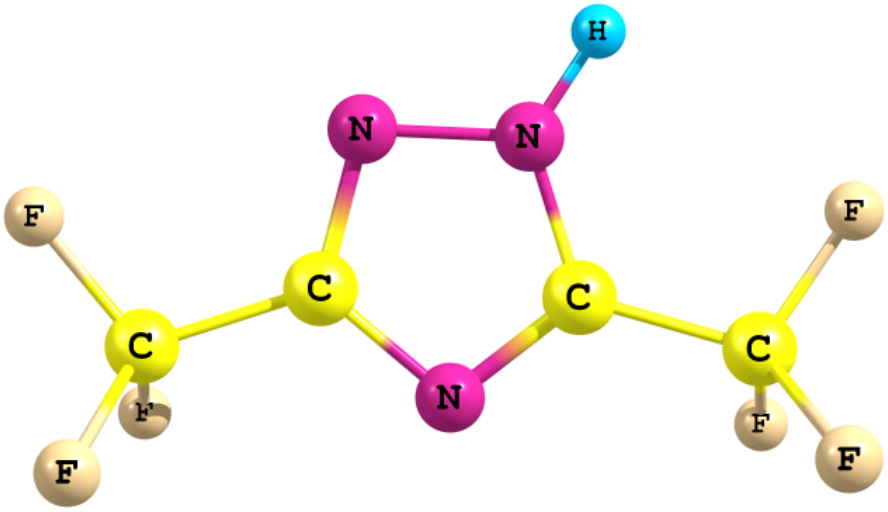
L_3H^+

1	7	0.671195	1.380735	-0.001792
2	7	-0.671182	1.380743	0.001331
3	6	1.105559	0.109433	-0.004500
4	6	-1.105559	0.109447	0.004477
5	1	-1.216698	2.238547	0.011125
6	6	-2.592742	-0.202358	-0.005649
7	6	2.592738	-0.202384	0.005734
8	1	1.216720	2.238530	-0.011881
9	9	-3.279382	0.948392	0.116658
10	9	-2.898767	-1.007164	1.007486
11	9	2.929290	-0.788491	1.152713
12	9	3.279391	0.948316	-0.116966
13	9	2.898755	-1.007540	-1.007126
14	9	-2.929302	-0.788853	-1.152427
15	6	-0.000005	-0.733612	0.000132
16	1	-0.000011	-1.812070	0.000317



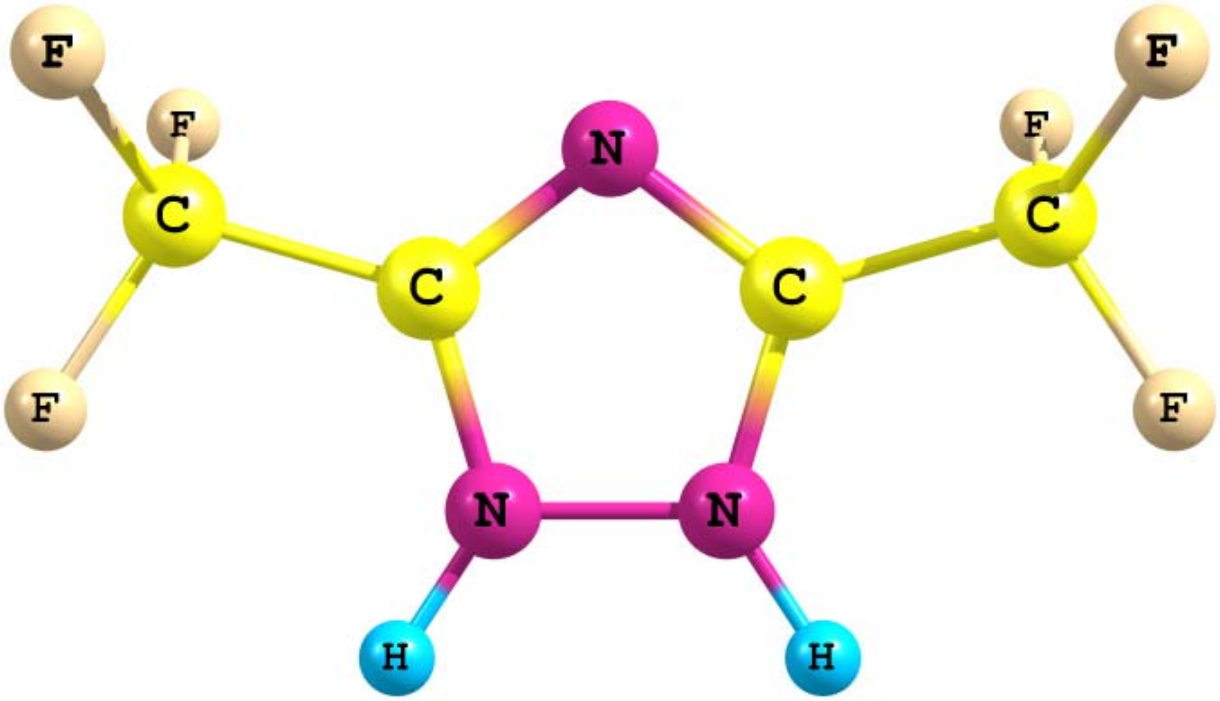
L_4

1	7	0.713494	1.522735	0.140772
2	7	-0.627052	1.450392	0.168356
3	6	1.055392	0.256009	-0.024065
4	7	0.021439	-0.620218	-0.102336
5	6	-1.022786	0.165551	0.022868
6	1	-1.186456	2.283672	0.287918
7	6	-2.466552	-0.255668	0.001958
8	6	2.491847	-0.189923	-0.108247
9	9	-2.736951	-1.152504	0.957285
10	9	-2.812226	-0.785914	-1.178645
11	9	2.722093	-0.855919	-1.255713
12	9	2.797244	-1.020115	0.908415
13	9	3.330418	0.854033	-0.056972
14	9	-3.250593	0.831213	0.213832



L_4H^+

1	7	0.674762	1.100858	-0.000325
2	7	-0.674760	1.100847	0.000069
3	6	1.051254	-0.186214	-0.000118
4	7	0.000019	-0.994456	-0.000034
5	6	-1.051230	-0.186232	-0.000023
6	1	-1.233669	1.952430	-0.000858
7	6	-2.521412	-0.606456	-0.000093
8	6	2.521442	-0.606415	0.000085
9	1	1.233658	1.952450	0.000438
10	9	-3.266873	0.515128	0.000305
11	9	-2.787104	-1.314846	1.086118
12	9	2.787352	-1.313184	1.087347
13	9	3.266886	0.515179	-0.001244
14	9	2.787023	-1.315650	-1.085586
15	9	-2.787189	-1.314079	-1.086816



([i]) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
([ii]) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
([iii]) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.