Nitron: a stable N-heterocyclic carbene that has been commercially available for more than a century

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Supplementary Information

Chemical Syntheses and Compound Characterisation

General

All reactions were carried out under N_2 in oven-dried glassware by applying standard Schlenk techniques. Solvents were dried and freshly distilled from the drying agent indicated prior to use (THF and hexanes: potassium, toluene: sodium). Nitron was purchased from Acros Organics (95% purity) and used as received. NMR: Varian MR 400 spectrometer operating at 399.87 MHz for ^{1}H. IR: Bruker Alpha FT-IR spectrometer. Electrospray ionisation (ESI) mass spectra: Finnigan LCQ Deca. High-resolution mass spectra (HRMS): Bruker Daltonics micrOTOF. Melting points: Stuart Scientific smp 3 melting point apparatus. Elemental analyses were performed by the microanalytical laboratory of the University of Kassel.

NMR spectroscopic investigation of Nitron in solution

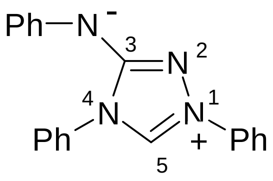


Fig. S1 Conventional Lewis structure of Nitron (**2**) with numbering scheme for the heterocyclic ring.

^{1}H and ^{13}C NMR spectroscopic data are available for Nitron in DMSO-d_6 solution,[S1] which are in accord with the conventional Lewis structure **2** (Figure S1). We can confirm the published data and have found no indication for the presence of any other species than **2**. In addition, we have carefully inspected the spectra obtained with other solvents ($CDCl_3$, CD_2Cl_2) and come to the same conclusion.

^{1}H NMR (DMSO-d_6): δ = 10.25 (s, 1H, C-5–*H*); 8.00–7.97 (m, 4H); 7.66–7.58 (m, 4H); 7.51–7.48 (m, 2H); 7.39–7.37 (m, 2H); 7.13–7.09 (m, 2H); 6.64–6.61 (m, 1H). **^{13}C NMR (DMSO-d_6):** δ = 153.9 (*C*-3); 150.4 (phenyl-C_{ipso}); 136.1 (phenyl-C_{ipso}); 134.1 (phenyl-C_{ipso}); 133.5 (*C*-5); 129.6; 128.8; 128.4; 128.0; 127.9; 125.0; 122.0; 119.1; 117.1.

^{1}H NMR (CDCl$_3$): δ = 8.74 (s, 1H); 7.74–7.64 (m, 4H); 7.54–7.46 (m, 4H); 7.44–7.36 (m, 3H); 7.34–7.28 (m, 1H); 7.24–7.20 (m, 2H); 6.82–6.76 (m, 1H). **^{13}C NMR (CDCl$_3$):** δ = 154.8 (*C*-3); 149.9 (phenyl-C_{ipso}); 136.1 (phenyl-C_{ipso}); 133.6 (phenyl-C_{ipso}); 129.6; 129.2; 129.0; 128,5; 128.4; 124.6; 122.5; 119.5; 118.8.

^{1}H NMR (CD$_2$Cl$_2$): δ = 8.80 (s, 1H); 7.78–7.76 (m, 2H); 7.70–7.66 (m, 2H); 7.58–7.53 (m, 2H); 7.51–7.46 (m, 3H); 7.44–7.40 (m, 3H); 7.21–7.16 (m, 2H); 6.77–6.73 (m, 1H). **^{13}C NMR (CD$_2$Cl$_2$):** δ = 155.4 (*C*-3); 150.8 (phenyl-C_{ipso}); 136.5 (phenyl-C_{ipso}); 134.1 (phenyl-C_{ipso}); 130.2 (*C*-5); 130.1; 129.6; 129.5; 129.0; 128.7; 125.4; 122.7; 120.0; 118.8.

Synthesis of the triazolinethione 2'=S

Sulfur (11.6 mg, 0.045 mmol S$_8$) was added to a solution of Nitron (113 mg, 0.36 mmol) in THF (3 mL) and the mixture stirred for 30 min, giving a pale pink solution. Volatile components were removed *in vacuo* to afford the product as an off-white, microcrystalline solid in essentially quantitative yield. **M.p.** 179.5–180.5 °C (dec.). **^{1}H NMR (CDCl$_3$):** δ = 8.23–8.19 (m, 2H); 7.71–7.61 (m, 3H); 7.54–7.48 (m, 4H); 7.44–7.30 (m, 5H); 7.09–7.04 (m, 1H); 5.80 (s, 1H, N*H*). **^{13}C NMR (CDCl$_3$):** δ = 164.5; 146.6; 138.4; 137.6; 132.0; 130.8; 130.6; 129.2; 128.8; 128.6; 127.4; 123.8; 123.1; 117.7. **IR (CH$_2$Cl$_2$):** ν = 3685 (w); 3412 (m); 1624 (s); 1603 (s); 1549 (s); 1498 (s); 1387 (s); 1337 (m); 1303 (m); 1023 (w). **HRMS/ESI(+):** *m*/*z* = 367.098347 [M + Na]$^+$; 367.098788 calcd. for [C$_{20}$H$_{16}$N$_4$NaS]$^+$. Anal. calcd. for C$_{20}$H$_{16}$N$_4$S (%): C, 69.74; H, 4.68; N, 16.27. Found: C, 68.89; H, 4.68; N, 15.87.

Synthesis of the dithiocarboxylate 2$'^{+}$–CS$_2^{-}$

CS$_2$ (50 µL, 0.40 mmol) was added to a solution of Nitron (73 mg, 0.24 mmol) in THF (4 mL). The stirred mixture was heated to gentle reflux for 6 h and was subsequently allowed to cool to room temperature. Volatile components were removed *in vacuo* and the residue subjected to column chromatography (silica gel, CH$_2$Cl$_2$), affording the product as a red, microcrystalline solid. Yield: 60 mg (64%). **M.p.** 175.5–176.5 °C. Single-crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution. **^{1}H NMR (CDCl$_3$):** δ = 8.04–8.01 (m, 2H); 7.73–7.70 (m, 2H); 7.67–7.63 (m, 3H); 7.53–7.47 (m, 3H); 7.46–7.42 (m, 2H); 7.40–7.35 (m, 2H); 7.17–7.12 (m, 1H); 6.01 (s, 1H, N*H*). **^{13}C NMR (CDCl$_3$):** δ = 219.9; 149.0; 147.3; 136.4; 135.6; 132.1; 130.8; 130.0; 129.5; 129.4; 129.0;

128.0; 124.4; 123.5; 118.5. **IR (CH_2Cl_2):** ν = 1065 (s). **HRMS/ESI(+):** *m*/*z* = 411.069709 [M + Na]$^+$; 411.070859 calcd. for $[C_{21}H_{16}N_4NaS_2]^+$.

Synthesis of [RhCl(2’)(CO)$_2$]

[{Rh(μ-Cl)(CO)$_2$}$_2$] (62.3 mg, 0.16 mmol) was added to a solution of Nitron (100 mg, 0.32 mmol) in CH_2Cl_2 (5 mL) and the mixture stirred for 3 h. Volatile components were removed *in vacuo* to afford the product as a beige, microcrystalline solid in essentially quantitative yield. Single-crystals suitable for an X-ray diffraction study were obtained by recrystallisation from CH_2Cl_2–Et_2O (1:10). **M.p.** 106.5–107.5 ºC (dec.) **^{1}H NMR ($CDCl_3$):** δ = 8.35–8.32 (m, 2H); 7.75–7.67 (m, 5H); 7.57–7.52 (m, 2H); 7.49–7.42 (m, 3H); 7.37–7.33 (m, 2H); 7.11–7.07 (m, 1H); 6.04 (s, 1H, N*H*). **^{13}C NMR ($CDCl_3$):** δ = 184.9 (d, $^1J_{CRh}$ = 55.8 Hz, *C*O); 181.7 (d, $^1J_{CRh}$ = 73.8 Hz, *C*O); 175.9 (d, $^1J_{CRh}$ = 43.8 Hz, *C*-5); 150.3 (d, $^3J_{CRh}$ = 1.5 Hz, *C*-3); 139.3; 137.5; 133.3; 131.1; 130.5; 129.4; 129.0; 128.8; 128.4 (br.); 123.7; 123.5; 117.8. **IR (CH_2Cl_2):** ν = 2086 (s), 2007 (s). **ESI(+):** *m*/*z* (%) = 460 (60) [M – Cl – CO]$^+$;. Anal. calcd. for $C_{22}H_{16}N_4ClO_2Rh$ (%): C, 52.14; H, 3.18; N, 11.06. Found: C, 51.80; H, 3.13; N, 11.07.

Synthesis of [RhCl(2’)(COD)]

[{Rh(μ-Cl)(COD)}$_2$] (36.8 mg, 0.075 mmol) was added to a solution of Nitron (46.6 mg, 0.15 mmol) in THF (3 mL) and the mixture stirred for 10 min. Volatile components were removed *in vacuo* to afford the product as a yellow, microcrystalline solid in essentially quantitative yield. Single-crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution. **M.p.** 143.5–144.0 ºC. **^{1}H NMR ($CDCl_3$):** δ = 8.86–8.83 (m, 2H); 8.07–8.03 (m, 2H); 7.72–7.64 (m, 3H); 7.59–7.54 (m, 2H); 7.45–7.40 (m, 3H); 7.34–7.29 (m, 2H); 7.06–7.01 (m, 1H); 6.15 (s, 1H, N*H*); 5.03–4.97 (m, 1H); 4.93–4.87 (m, 1H); 2.99–2.94 (m, 1H); 2.83–2.78 (m, 1H); 2.22–2.12 (m, 1H); 2.02–1.93 (m, 1H); 1.83–1.62 (m, 4H); 1.57-–1.43 (m, 2H). **^{13}C NMR ($CDCl_3$):** δ = 184.9 (d, $^1J_{CRh}$ = 50.8 Hz, *C*-5); 149.5 (d, $^3J_{CRh}$ = 1.3 Hz, *C*-3); 139.7; 137.9; 134.5; 130.1; 129.8; 129.2; 128.5; 127.6; 122.9; 122.6; 117.5; 98.9 (d, $^1J_{CRh}$ = 7.3 Hz, *C*H); 97.5 (d, $^1J_{CRh}$ = 7.2 Hz, *C*H); 69.4 (d, $^1J_{CRh}$ = 14.4 Hz, *C*H); 68.6 (d, $^1J_{CRh}$ = 14.4 Hz, *C*H); 32.8 (d, $^2J_{CRh}$ = 0.6 Hz, *C*H$_2$); 31.4 (d, $^2J_{CRh}$ = 0.6 Hz, *C*H$_2$); 28.9; 28.2. **IR (KBr):** ν = 3244 (w), 2933 (w), 2874 (m), 2829 (w), 1621 (s), 1603 (s), 1585 (s), 1551 (m), 1495 (s), 755 (m), 690 (m). **HRMS/ESI(+):** *m*/*z* = 523.136041 [M – Cl]$^+$ calcd. for $C_{28}H_{28}N_4Rh$ = 523.136352.

X-ray Structure Analyses

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo-K_{α} radiation (λ = 0.71073 Å) was made on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector. Absorption correction was done by integration using X-red.[S2] The data sets were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97).[S3] All non-hydrogen atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2 fold isotropic displacement parameters, except for H4 in $\mathbf{2'}^{+}$–CS_2·$CHCl_3$ and H33 in [RhCl(**2'**)(COD)]·$CHCl_3$, which were found in the difference Fourier maps, and H4 in [RhCl(**2'**)$(CO)_2$]·OEt_2 which was also found in the difference Fourier maps and has been included to the model with freely refined isotropic displacement parameters and without position constraints. Graphical representations were made using ORTEP-3 win.[S4]

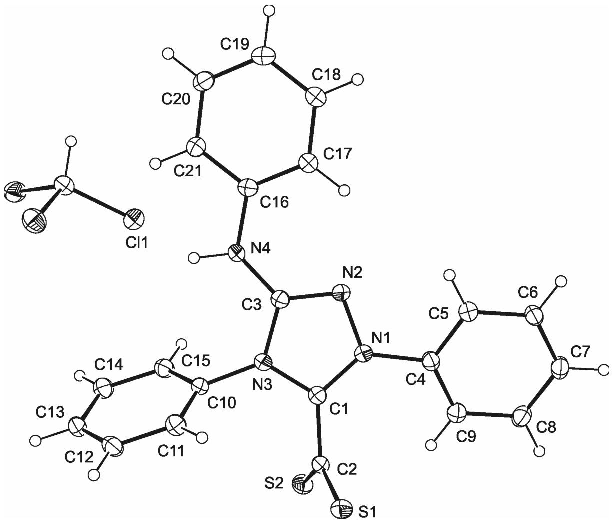


Fig. S2 Molecular structure of $\mathbf{2'}^{+}$–CS_2^{-}·$CHCl_3$ in the crystal (ellipsoids drawn at the 30% probability level).

Crystallographic data for $\mathbf{2'}^{+}$–CS_2^{-}·$CHCl_3$:

$C_{22}H_{17}Cl_3N_4S_2$, M_r = 507.87, triclinic, P -1, red block, a = 10.1388(11), b = 10.3661(10), c = 12.2102(12) Å, α = 85.985(8), β = 73.991(8), γ = 64.991(8)°, T = 100(2) K, Z = 2, R1 (I > 2σ(I)) = 0.0555, S (all data)= 1.090

Crystallographic data for [RhCl(**2'**)(CO)$_2$]·OEt$_2$:

$C_{26}H_{26}ClN_4O_3Rh$, M_r = 580.87, orthorhombic, $P\,n\,a\,2_1$, colorless plate, a = 16.4133(9), b = 24.4635(16), c = 6.4734(4) Å, T = 123(2) K, Z = 4, $R1$ ($I > 2\sigma(I)$) = 0.0366, S (all data)= 0.979

Crystallographic data for [RhCl(**2'**)(COD)]·CHCl$_3$:

$C_{29}H_{29}Cl_4N_4Rh$, M_r = 678.27, monoclinic, $P\,2_1/n$, yellow plate, a = 11.2724(9), b = 16.7158(10), c = 15.8324(12) Å, β = 101.116(6)°, T = 100(2) K, Z = 4, $R1$ ($I > 2\sigma(I)$) = 0.0465, S (all data) = 0.945

Computational Details

The geometry optimisations were performed at the BP86 level of theory, using Becke´s exchange functional[S5] and Perdew´s correlation functional.[S6] Ahlrich´s def2-SVP was chosen as basis set.[S7] The Gaussian03 program package was used for all calculations.[S8] Stationary points were characterised with frequency calculations at BP86/def2-SVP. The absolute energies and the Cartesian coordinates of the minimum structures of **2', 2** and **1** are respectively given in Tables S1, S2 and S3. The geometries are shown in Figs. S3, S4 and S5. The frontier orbitals of **2'** and **1** are respectively shown in Figs. 6 and 7. Molekel[S9] was used for the visualisation of the structures and orbitals. The charges were determined by Natural Population Analysis. Note that the atom numbering schemes are not identical with the ones used by the crystallographer and do not conform to IUPAC rules.

Table S1 Cartesian Coordinates of **2’** in Å. E(BP86/def2-SVP) = –990.019683 a.u.

N	-3.595388	0.465005	9.004936
C	-3.453268	1.702220	9.609040
N	-4.397342	2.419489	8.947966
N	-5.111994	1.733750	7.958336
C	-4.592134	0.526051	8.006838
N	-4.890736	-0.553083	7.214733
C	-5.840686	-0.670268	6.182685
C	-6.721906	0.375713	5.823326
C	-7.648054	0.173416	4.786793
C	-7.716519	-1.049186	4.097406
C	-6.837005	-2.087005	4.456974
C	-5.907048	-1.903860	5.488704
C	-4.708896	3.793317	9.186254
C	-5.700606	4.437953	8.421483
C	-5.994413	5.789555	8.668682
C	-5.309261	6.500526	9.668140
C	-4.319776	5.845694	10.425786
C	-4.014735	4.497195	10.192883
C	-2.802698	-0.677566	9.341748
C	-3.415207	-1.919757	9.613115
C	-2.618606	-3.033309	9.934353
C	-1.221045	-2.907863	10.006036
C	-0.618454	-1.660402	9.758018
C	-1.401807	-0.546339	9.420588
H	-6.228783	3.873498	7.641927
H	-6.770931	6.289620	8.068054
H	-5.544119	7.559665	9.857628
H	-3.775888	6.391890	11.213037
H	-3.247539	3.965507	10.773770
H	-4.513170	-2.004872	9.608752
H	-3.100142	-3.999998	10.150539
H	-0.600693	-3.780087	10.264770
H	0.475814	-1.553605	9.823319
H	-0.951818	0.438611	9.228417
H	-6.665764	1.331671	6.359909
H	-8.329119	0.996058	4.515638
H	-8.446792	-1.193745	3.286386
H	-6.872618	-3.053062	3.928637
H	-5.221017	-2.722792	5.764137
H	-4.296043	-1.371211	7.368457

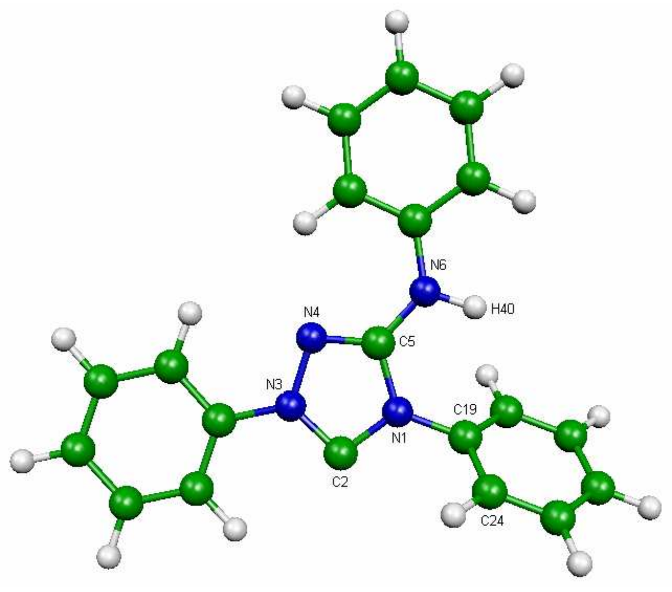


Fig. S3 Minimum structure of **2’**.

C2-N3 = 1.357 Ǻ
N3-N4 = 1.400 Ǻ
N4-C5 = 1.316 Ǻ
C5-N1 = 1.412 Ǻ
N1-C2 = 1.384 Ǻ
N6-H40 = 1.023 Ǻ

C2-N3-N4 = 116.1°
N3-N4-C5 = 102.8°
N4-C5-N1 = 110.2°
C5-N1-C2 = 110.0°
N1-C2-N3 = 100.9°
H40-N6-C5 = 114.6°

C2-N1-C19-C24 = -48.5°

Table S2 Cartesian Coordinates of **2** in Å. E(BP86/def2-SVP) = –990.028424 a.u.

C	-1.486334	-0.482040	9.786052
C	-2.810804	-0.706814	9.346243
C	-3.323544	-2.020714	9.281804
C	-2.509348	-3.093738	9.676395
C	-1.197869	-2.875786	10.134531
C	-0.690261	-1.565336	10.187179
N	-3.625286	0.401085	8.980282
C	-3.538653	1.638722	9.522881
N	-4.414668	2.424915	8.880850
N	-5.111141	1.763501	7.913318
C	-4.660469	0.465659	7.937394
C	-4.694705	3.796368	9.163937
C	-5.953611	4.316161	8.805372
C	-6.244340	5.658955	9.090318
C	-5.294543	6.477921	9.726785
C	-4.036750	5.949469	10.070368
C	-3.725671	4.611794	9.782698
N	-4.965336	-0.594035	7.257957
C	-5.872295	-0.652734	6.203220
C	-6.596387	0.447503	5.658571
C	-7.484339	0.257864	4.587112
C	-7.685188	-1.015580	4.025351
C	-6.973760	-2.111621	4.551170
C	-6.083265	-1.933343	5.616937
H	-6.677618	3.653170	8.311962
H	-7.228532	6.067664	8.812707
H	-5.529279	7.530880	9.946615
H	-3.280041	6.588522	10.551591
H	-2.724450	4.217819	10.014357
H	-4.341311	-2.173326	8.900972
H	-2.911906	-4.117777	9.625719
H	-0.568170	-3.725568	10.440951
H	0.341509	-1.382638	10.526536
H	-1.067400	0.536344	9.787355
H	-6.448398	1.448993	6.084541
H	-8.031295	1.126628	4.183558
H	-8.385631	-1.153268	3.186292
H	-7.113757	-3.117686	4.122178
H	-5.516595	-2.783730	6.027890
H	-2.946719	1.918577	10.398441

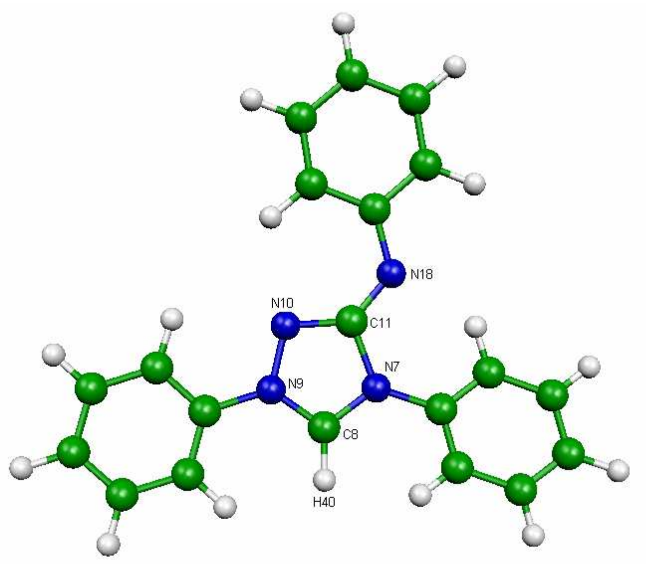


Fig. S4 Minimum structure of **2**.

C8-N9 = 1.340 Å
N9-N10 = 1.363 Å
N10-C11 = 1.373 Å
C11-N7 = 1.470 Å
N7-C8 = 1.354 Å
C8-H40 = 1.085 Å

C8-N9-N10 = 112.9°
N9-N10-C11 = 106.2°
N10-C11-N7 = 106.5°
C11-N7-C8 = 106.8°
N7-C8-N9 = 107.6°
H40-C8-N7 = 126.5°

Table S3 Cartesian Coordinates of **1** in Å. E(BP86/def2-SVP) = –934.700071 a.u.

C	-1.352470	-0.581621	9.645834
C	-2.743673	-0.712874	9.474888
C	-3.390435	-1.922491	9.793769
C	-2.633974	-3.008856	10.263630
C	-1.242845	-2.888317	10.428166
C	-0.606961	-1.671154	10.123716
N	-3.498073	0.418357	9.013536
C	-3.377494	1.660121	9.605553
N	-4.327973	2.359385	8.918932
N	-5.014718	1.649212	7.952993
C	-4.489584	0.442109	8.011717
C	-4.644890	3.740692	9.122222
C	-5.627137	4.362443	8.327187
C	-5.926574	5.718393	8.538643
C	-5.256088	6.453514	9.531419
C	-4.276366	5.820129	10.318595
C	-3.965517	4.466697	10.121471
C	-4.890965	-0.650382	7.105202
H	-6.139840	3.774627	7.553754
H	-6.694662	6.203702	7.915550
H	-5.495415	7.516436	9.692088
H	-3.745048	6.386278	11.100206
H	-3.205696	3.949122	10.724443
H	-4.481611	-2.006678	9.682715
H	-3.141257	-3.953951	10.513584
H	-0.654940	-3.741581	10.801232
H	0.481067	-1.566475	10.259238
H	-0.877077	0.382732	9.414318
C	-6.242422	-0.730265	6.689611
C	-6.651402	-1.726571	5.791328
C	-5.720176	-2.655003	5.291243
C	-4.374158	-2.575341	5.689966
C	-3.957801	-1.581435	6.589603
H	-6.962798	0.002570	7.082980
H	-7.706626	-1.779583	5.479680
H	-6.042851	-3.438173	4.587033
H	-3.636661	-3.289851	5.291474
H	-2.898444	-1.518280	6.879100

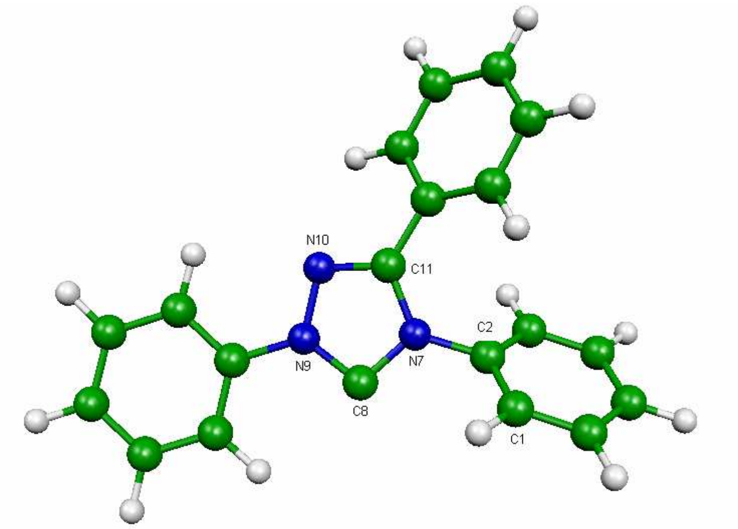


Fig. S5 Minimum structure of **1**.

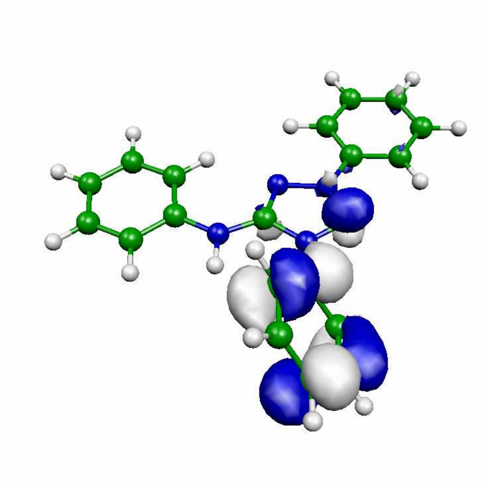
C8-N9 = 1.365 Ǻ
N9-N10 = 1.382 Ǻ
N10-C11 = 1.318 Ǻ
C11-N7 = 1.410 Ǻ
N7-C8 = 1.381 Ǻ

C8-N9-N10 = 115.7°
N9-N10-C11 = 104.0°
N10-C11-N7 = 109.1°
C11-N7-C8 = 110.5°
N7-C8-N9 = 100.6°

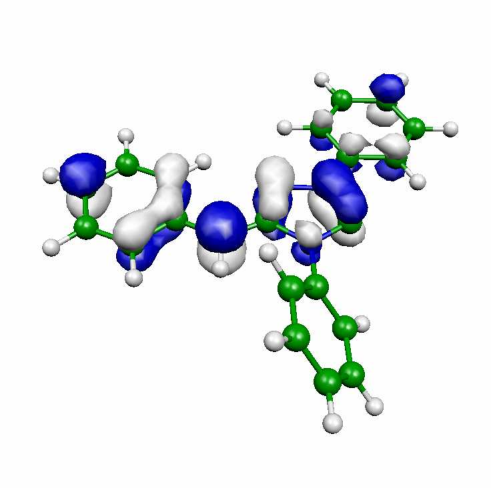
C8-N7-C2-C1 = -50.2°

Figure S6. Frontier orbitals of **2'**.

LUMO (–1.93 eV)



HOMO (–5.04 eV)



HOMO – 1 (–5.18 eV)

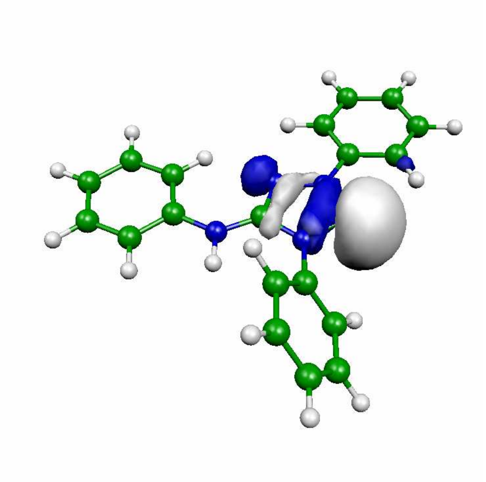
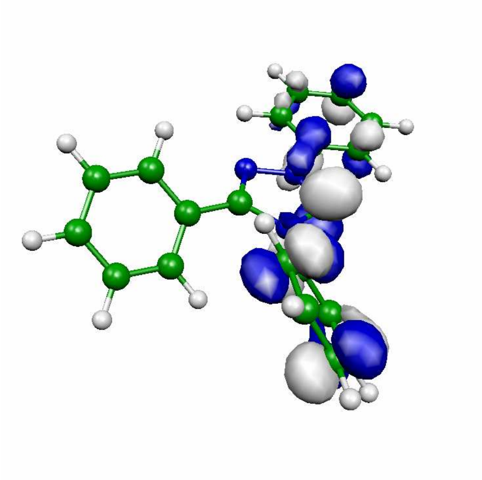
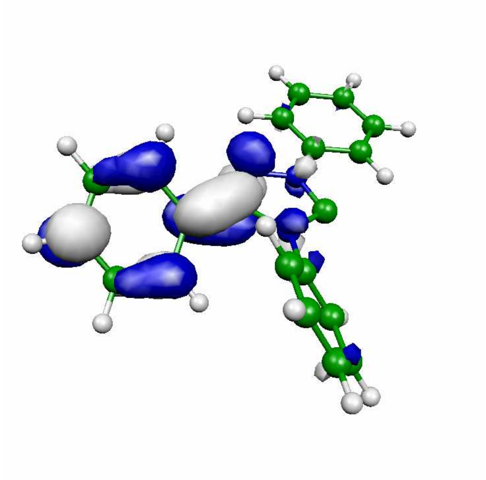


Figure S7. Frontier orbitals of **1**.

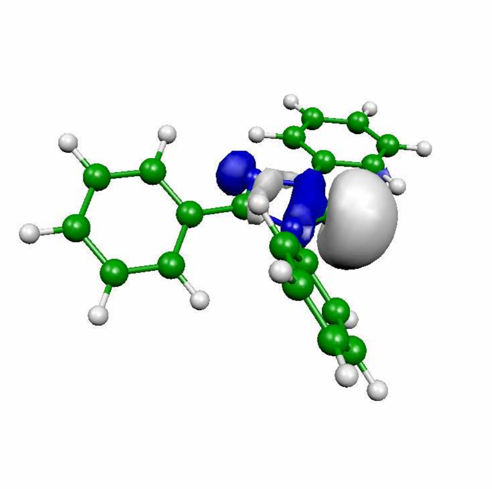
LUMO + 1 (–1.73 eV)



LUMO (–2.18 eV)



HOMO (–5.15 eV)



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