Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Bent and twisted: the electronic structure of 2-azapropenylium ions obtained by guanidine oxidation

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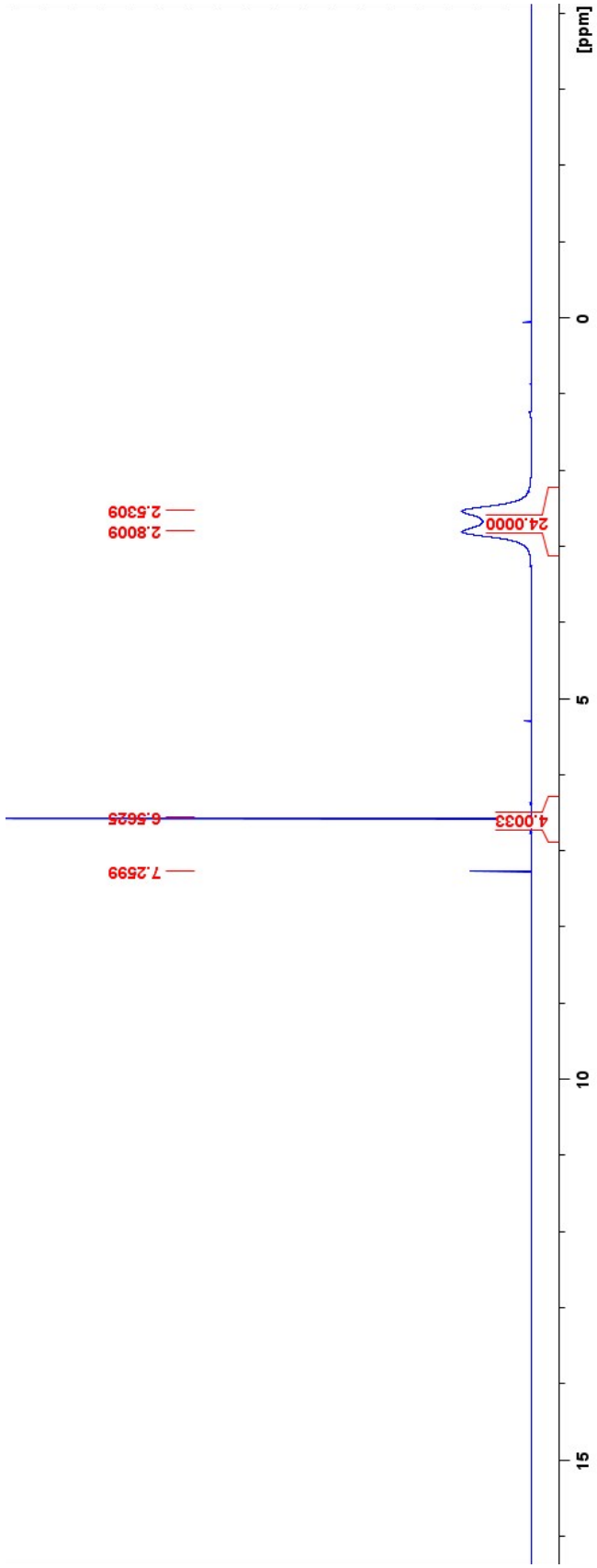
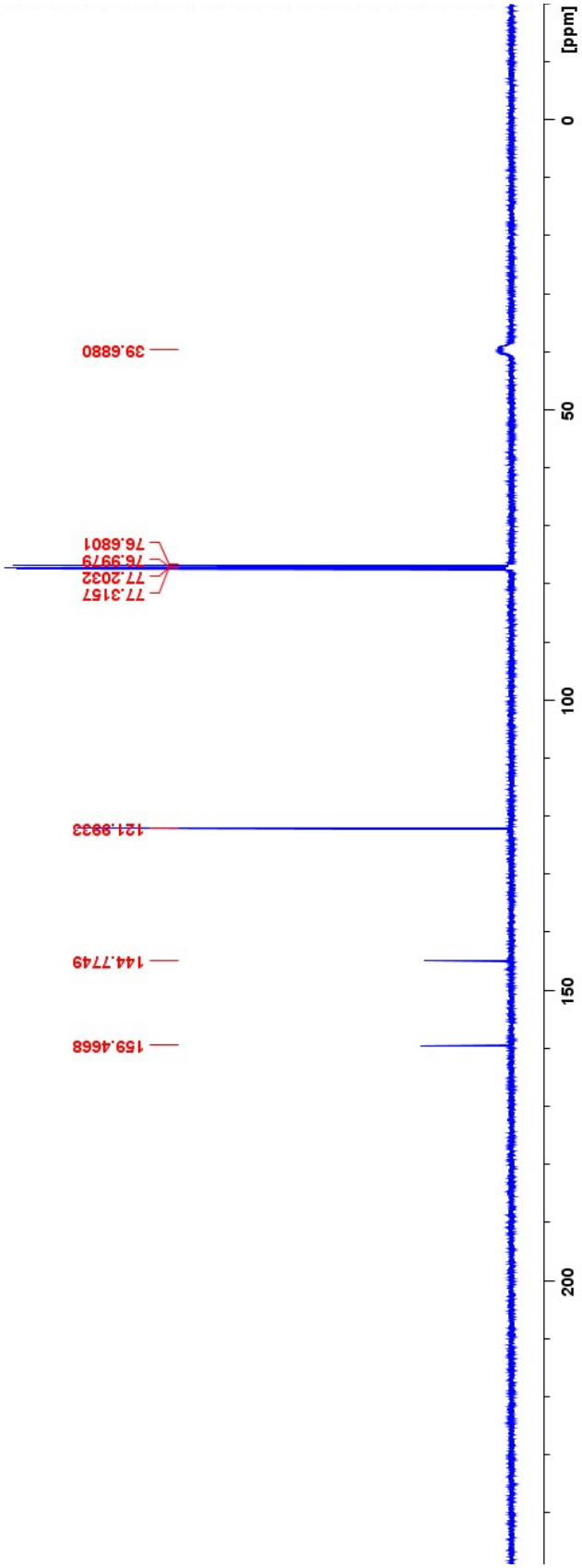
Content

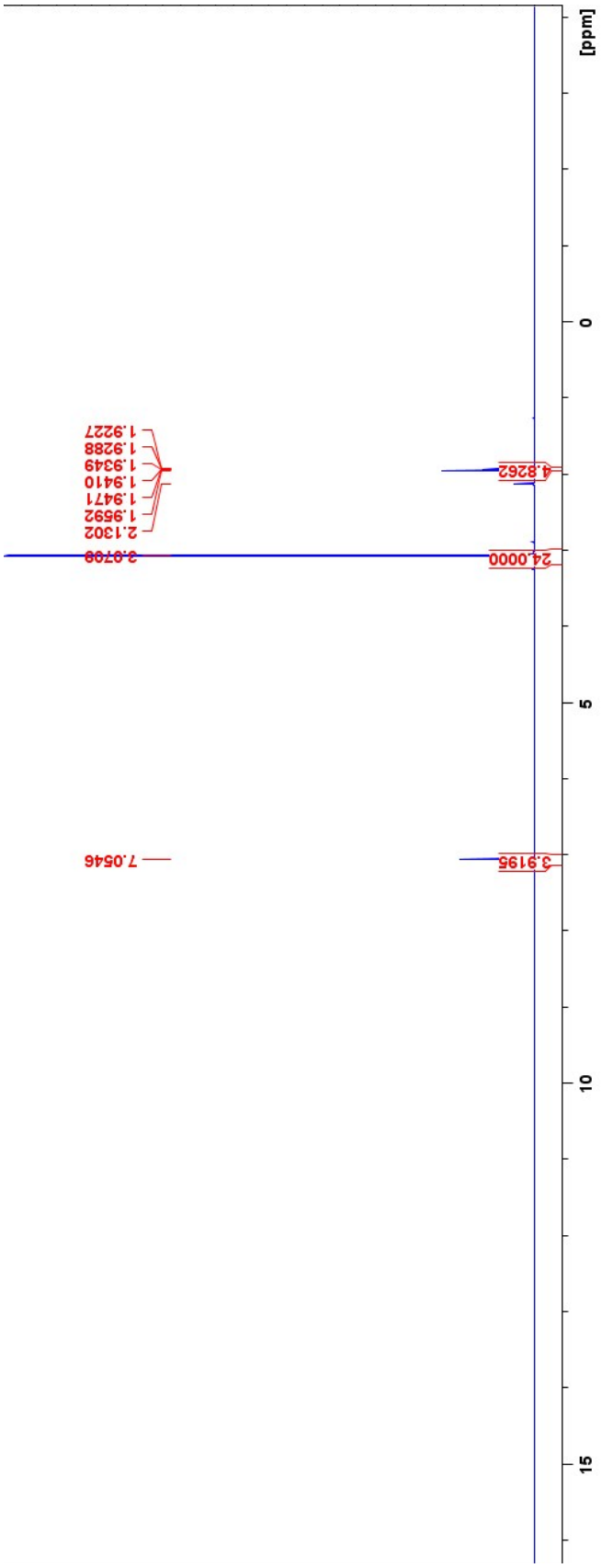
^{1}H NMR of **1** (399.89 MHz, $CDCl_3$, 295.8 K)



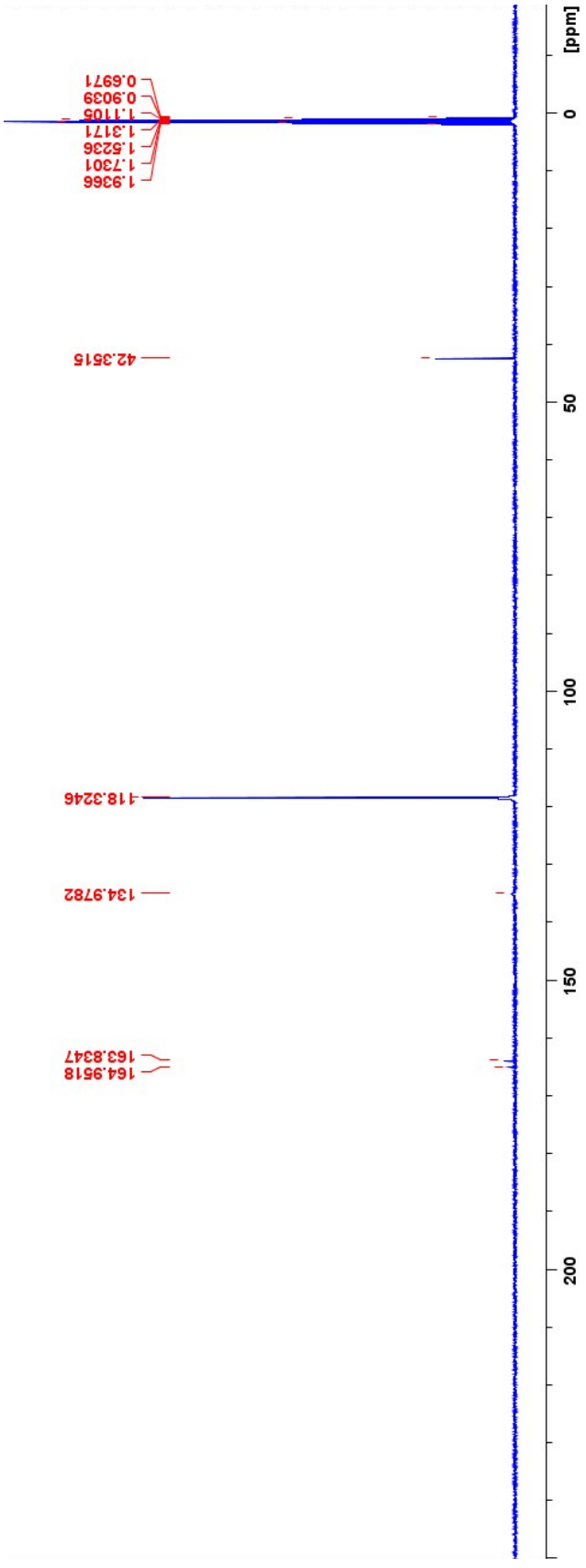
^{13}C NMR of **1** (100.55 MHz, $CDCl_3$, 297.5 K)



^{1}H NMR of **1**$(PF_6)_2$ (399.89 MHz, CD_3CN, 296.5 K)



^{13}C NMR of **1**$(PF_6)_2$ (100.55 MHz, CD_3CN, 298.0 K)



Comparison of 1 with GFA compounds and bisguanidines

Table S1 compares the redox potential of **1** with GFA compounds. The redox potential of **1** is significantly higher than that of **3** ($E_{1/2}$ = -0.73 V vs. Fc/Fc^+ in CH_3CN). As expected, the electron donor capacity increases with the number of guanidino groups attached to the aromatic system.

Table S1. Redox potentials obtained from CV measurements ($^nBu_4NPF_6$ as supporting electrolyte, scan speed 100 $mV \cdot s^{-1}$, CH_3CN solution for **1**, **3** and **4**, CH_2Cl_2 solution for **5**.

	$E_{1/2}$ / V vs. Fc/Fc^+	
Compound	1st redox step	2nd redox step
1	-0.22	-0.22
3	-0.73	-0.73
4	-0.65	-0.65
5	-0.76	-0.76

In Table S2, the calculated (B3LYP/def2-TZVP) adiabatic first and second ionization energies for several compounds are compared. Solvation effects, which were shown to be very substantial,[16] were considered with COSMO (COnductor-like Screening MOdel). According to these calculations, the I_1 value for **1** is smaller than that of 1,4-bis(dimethylamino)benzene in the gas-phase (5.36 vs. 5.80 eV), but quite similar in polar solvents such as CH_3CN (4.21 vs. 4.16 eV), in line with the experimentally determined $E_{1/2}$ values. Compound **1**, on the other hand, is a much better two-electron donor. Its I_2 value in the gas-phase is 1.80 eV lower than that of 1,4-bis(dimethylamino)benzene. In polar solvents, the I_2 value of **1** is predicted to be only 0.54 eV higher than the I_1 value. By contrast, for 1,4-bis(dimethylamino)benzene the I_2 value is still 1.19 eV higher than the I_1 value. Therefore it is not surprising that the CV measurements show clearly separated one-electron redox events in the case of 1,4-bis(dimethylamino)benzene, but not for **1**.

Table S2. Comparison between the first (I_1) and second (I_2) ionization energy calculated on the B3LYP/def2-TZVP level. The solvent effects were studied with the COSMO module (ε(THF) = 7.6, ε(CH_3CN) = 37.5). ε = 1 if not stated otherwise.

compound	I_1 / eV	I_2 / eV
1	5.36	8.73
1 (ε = 37.5)	4.21	4.75
1 (ε = 7.6)	4.38	5.35
2	5.96	9.42
3	4.66	7.31
4 (ε = 37.5)	3.68	4.00

Table S2 also includes the ionization energies for *p*-bisguanidino-benzene [**2**, $(C_6H_4)(NC(NH_2)_2)_2$]. In the absence of the methyl groups, the ionization energies increase considerably. Hence the I_1 and I_2 values of **2** are by 0.60 respectively 0.69 eV higher than for **1**. The methyl groups also have a significant influence on the redox potentials of diamino-benzene. For *p*-diamino-benzene ($C_6H_4(NH_2)_2$), a redox potential for the first redox process of $E_{1/2}$ = -0.12 V vs. Fc/Fc^+ was measured in CH_3CN solution.[1]

[1] J. R. Quinn, F. W. Foss Jr., L. Venkataraman, R. Breslow, *J. Am. Chem. Soc.,* 2007, **129**, 12376 – 12377.

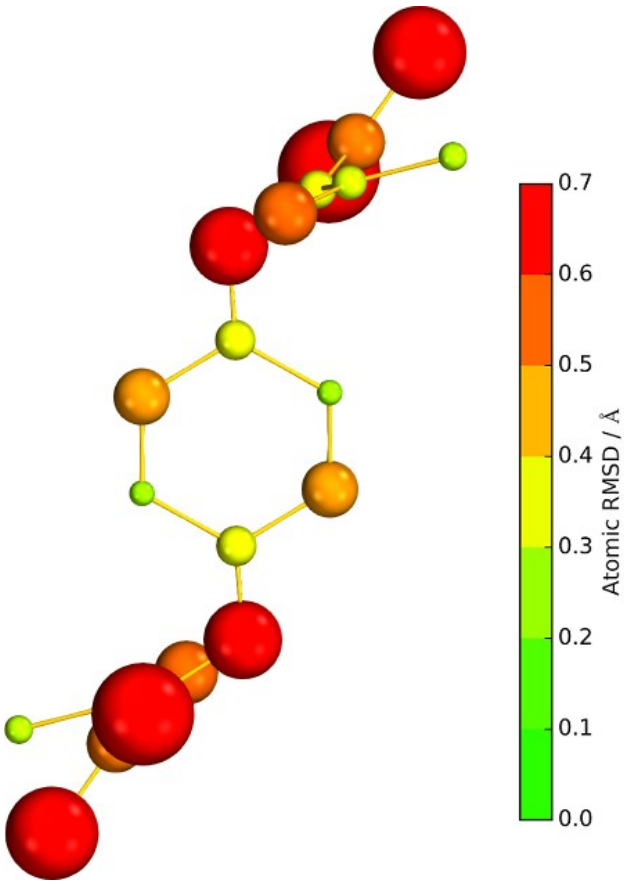


Figure S1. aRMSD plot comparing the calculated structure of $\mathbf{1}^{2+}$ with the experimental determined solid state structure. The size of the respective atom and color represents the deviation (in Å) between the two structures.

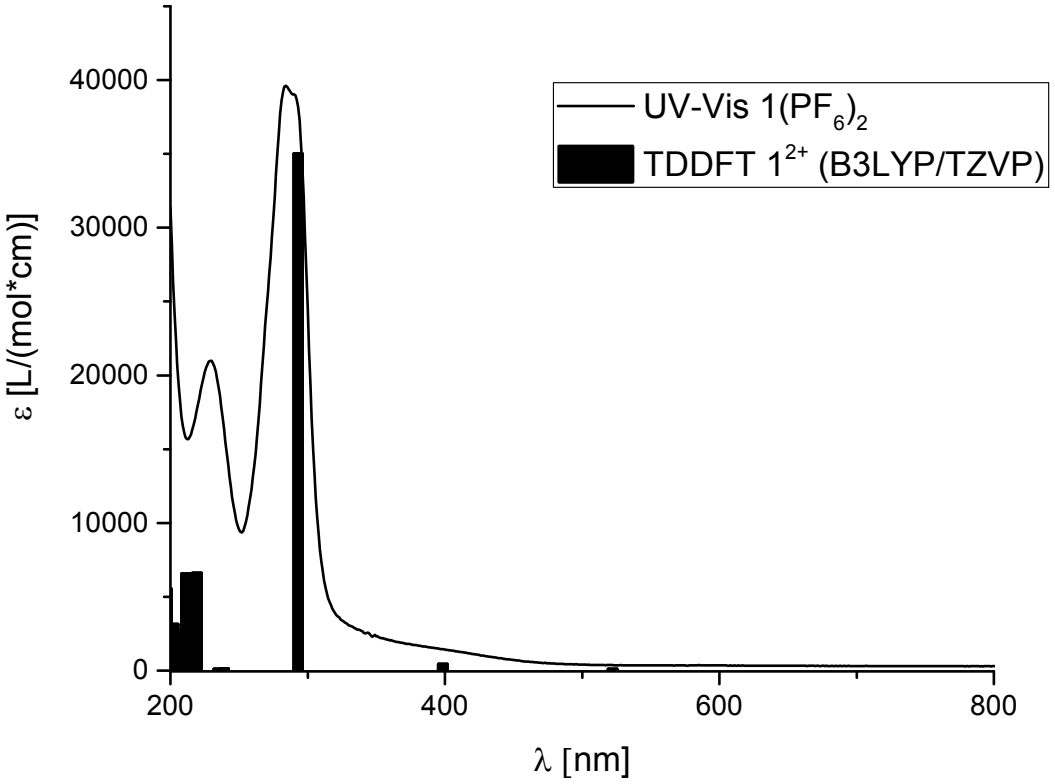


Figure S2: UV/Vis spectrum for **1**$(PF_6)_2$ in CH_3CN and TD-DFT electronic transitions as calculated with B3LYP/def2-TZVP.

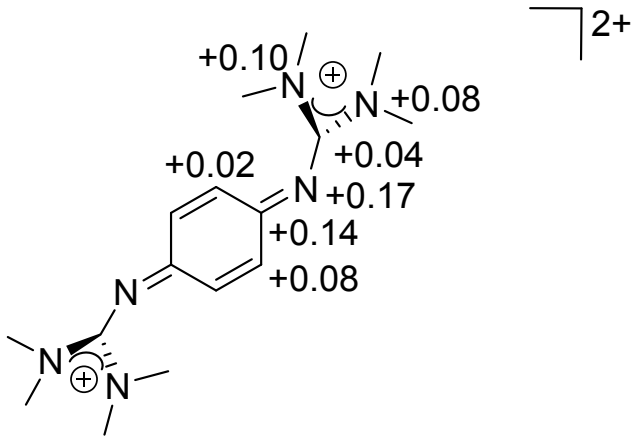


Figure S3. Results of a natural population analysis (NPA) for $\mathbf{1}^{2+}$. The numbers indicate changes of elementary charges (in e) upon oxidation of neutral **1**.

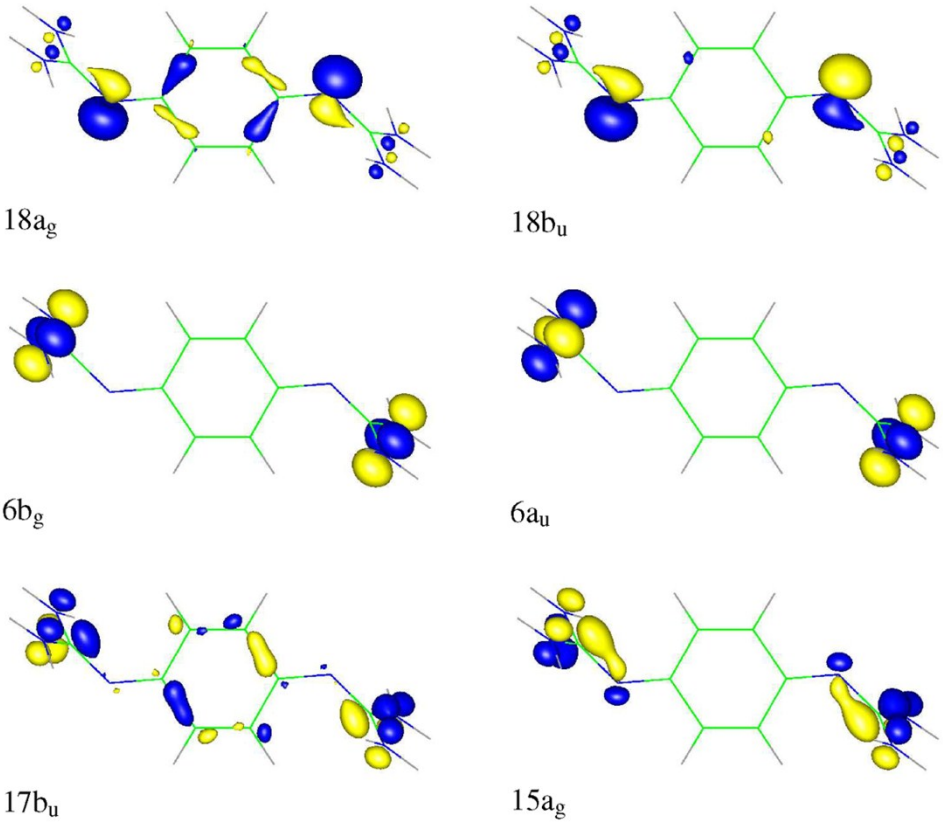


Figure S4. Isosurfaces (±0.09) of selected orbitals of $\mathbf{2}^{2+}$ by density functional calculations with the B3LYP functional and the def2-TZVP basis set. The orbitals 18 a_g and 18 b_u (HOMO-2 and HOMO-3) are essentially the nitrogen lone pairs. They show a polarisation towards the C(NR2) groups. The 15 a_g orbital (HOMO-11) clearly shows an interaction between the π sytem of the C(NR2) group and the nitrogen lone pair.

Results of the calculations (B3LYP/def2-TZVP) with restrictions imposed by symmetry

2^{2+}-C_{2h}-orthogonal (Energy = -639.9164010109) minimum

C	-0.9615312	1.0582683	0.0000000
C	0.3395946	1.3787039	0.0000000
C	1.3819270	0.3446193	0.0000000
C	0.9615312	-1.0582683	0.0000000
C	-0.3395946	-1.3787039	0.0000000
C	-1.3819270	-0.3446193	0.0000000
H	-1.7188784	1.8323860	0.0000000
H	0.6742621	2.4082734	0.0000000
H	1.7188784	-1.8323860	0.0000000
H	-0.6742621	-2.4082734	0.0000000
N	2.6028463	0.7521343	0.0000000
N	-2.6028463	-0.7521343	0.0000000
C	3.7424903	0.0058553	0.0000000
C	-3.7424903	-0.0058553	0.0000000
N	4.3077394	-0.3042249	1.1575206
N	4.3077394	-0.3042249	-1.1575206
N	-4.3077394	0.3042249	-1.1575206
N	-4.3077394	0.3042249	1.1575206
H	-3.8975072	-0.0207607	-2.0198317
H	-5.2348437	0.7022957	-1.2116410
H	-5.2348437	0.7022957	1.2116410
H	-3.8975072	-0.0207607	2.0198317
H	3.8975072	0.0207607	2.0198317
H	5.2348437	-0.7022957	1.2116410
H	5.2348437	-0.7022957	-1.2116410
H	3.8975072	0.0207607	-2.0198317

2^{2+}-C_{2h}-planar

Energy = -639.8890254148

C	-0.8502043	1.1491403	0.0000000
C	0.4832401	1.3096192	0.0000000
C	1.4351197	0.1874348	0.0000000
C	0.8502043	-1.1491403	0.0000000
C	-0.4832401	-1.3096192	0.0000000
C	-1.4351197	-0.1874348	0.0000000
H	-1.4573564	2.0403232	0.0000000
H	0.9260833	2.2968893	0.0000000
H	1.4573564	-2.0403232	0.0000000
H	-0.9260833	-2.2968893	0.0000000
N	2.6742808	0.5718640	0.0000000
N	-2.6742808	-0.5718640	0.0000000
C	3.8586380	-0.1285749	0.0000000
C	-3.8586380	0.1285749	0.0000000
N	4.0272772	-1.4451107	0.0000000
N	4.9129909	0.6699972	0.0000000
N	-4.9129909	-0.6699972	0.0000000
N	-4.0272772	1.4451107	0.0000000
H	-4.7545766	-1.6674565	0.0000000
H	-5.8660840	-0.3349459	0.0000000
H	-4.9503753	1.8574237	0.0000000
H	-3.2582152	2.0872324	0.0000000
H	3.2582152	-2.0872324	0.0000000
H	4.9503753	-1.8574237	0.0000000
H	5.8660840	0.3349459	0.0000000
H	4.7545766	1.6674565	0.0000000

2^{2+}-D_{2h}-orthogonal (Energy = -639.8883960647)

C	0.0000000	-1.2624065	-0.6695320
C	0.0000000	-1.2624065	0.6695320
C	0.0000000	0.0000000	1.4272772
C	0.0000000	1.2624065	0.6695320
C	0.0000000	1.2624065	-0.6695320
C	0.0000000	0.0000000	-1.4272772
H	0.0000000	-2.1854568	-1.2352805
H	0.0000000	-2.1854568	1.2352805
H	0.0000000	2.1854568	1.2352805
H	0.0000000	2.1854568	-1.2352805
N	0.0000000	0.0000000	2.6924266
N	0.0000000	0.0000000	-2.6924266
C	0.0000000	0.0000000	3.9969994
C	0.0000000	0.0000000	-3.9969994
N	1.1579428	0.0000000	4.6665370
N	-1.1579428	0.0000000	4.6665370
N	-1.1579428	0.0000000	-4.6665370
N	1.1579428	0.0000000	-4.6665370
H	-2.0388792	0.0000000	-4.1805436
H	-1.1797556	0.0000000	-5.6739921
H	1.1797556	0.0000000	-5.6739921
H	2.0388792	0.0000000	-4.1805436
H	2.0388792	0.0000000	4.1805436
H	1.1797556	0.0000000	5.6739921
H	-1.1797556	0.0000000	5.6739921
H	-2.0388792	0.0000000	4.1805436

2^{2+}-D_{2h}-planar (Energy = -639.8436142373)

C	0.0000000	-1.2523319	-0.6712978
C	0.0000000	-1.2523319	0.6712978
C	0.0000000	0.0000000	1.4414999
C	0.0000000	1.2523319	0.6712978
C	0.0000000	1.2523319	-0.6712978
C	0.0000000	0.0000000	-1.4414999
H	0.0000000	-2.1805211	-1.2279719
H	0.0000000	-2.1805211	1.2279719
H	0.0000000	2.1805211	1.2279719
H	0.0000000	2.1805211	-1.2279719
N	0.0000000	0.0000000	2.7166651
N	0.0000000	0.0000000	-2.7166651
C	0.0000000	0.0000000	4.0423802
C	0.0000000	0.0000000	-4.0423802
N	0.0000000	1.1510650	4.7132991
N	0.0000000	-1.1510650	4.7132991
N	0.0000000	-1.1510650	-4.7132991
N	0.0000000	1.1510650	-4.7132991
H	0.0000000	-2.0191807	-4.2030907
H	0.0000000	-1.2023183	-5.7229846
H	0.0000000	1.2023183	-5.7229846
H	0.0000000	2.0191807	-4.2030907
H	0.0000000	2.0191807	4.2030907
H	0.0000000	1.2023183	5.7229846
H	0.0000000	-1.2023183	5.7229846
H	0.0000000	-2.0191807	4.2030907

1^{2+}-C_i (Energy = -954.2569962402) Minimum

C	-0.9923342	-0.4237885	-0.9331438
C	0.2804334	-0.3433970	-1.3460816
C	1.3567553	0.0851491	-0.4443468
C	0.9923342	0.4237885	0.9331438
C	-0.2804334	0.3433970	1.3460816
C	-1.3567553	-0.0851491	0.4443468
H	-1.7716532	-0.7482269	-1.6117760
H	0.5684530	-0.5974628	-2.3582213
H	1.7716532	0.7482269	1.6117760
H	-0.5684530	0.5974628	2.3582213
N	2.5449802	0.1247772	-0.9314576
N	-2.5449802	-0.1247772	0.9314576
C	3.7101139	0.5136196	-0.3029765
C	-3.7101139	-0.5136196	0.3029765
N	4.0736893	1.7930413	-0.4209201
N	4.4776936	-0.4223628	0.2608365
N	-4.0736893	-1.7930413	0.4209201
N	-4.4776936	0.4223628	-0.2608365
C	3.4197139	2.6901169	-1.3855954
H	2.6466061	3.2895629	-0.9003835
H	4.1763327	3.3611964	-1.7900241
H	2.9864749	2.1193959	-2.2015509
C	5.0471357	2.4484844	0.4642095
H	5.9871477	2.6491050	-0.0507616
H	4.6174532	3.3997410	0.7791406
H	5.2321789	1.8458894	1.3474979
C	3.9347396	-1.7416950	0.6138988
H	3.9804712	-2.4219513	-0.2394622
H	4.5401131	-2.1480518	1.4219782
H	2.9114359	-1.6680080	0.9676025
C	5.9522843	-0.3792719	0.2187762
H	6.3748666	-0.2352465	1.2130022
H	6.2992229	-1.3355013	-0.1731861
H	6.2962064	0.4034970	-0.4483728
C	-5.0471357	-2.4484844	-0.4642095
H	-4.6174532	-3.3997410	-0.7791406
H	-5.9871477	-2.6491050	0.0507616
H	-5.2321789	-1.8458894	-1.3474979
C	-3.4197139	-2.6901169	1.3855954
H	-4.1763327	-3.3611964	1.7900241
H	-2.6466061	-3.2895629	0.9003835
H	-2.9864749	-2.1193959	2.2015509
C	-3.9347396	1.7416950	-0.6138988
H	-4.5401131	2.1480518	-1.4219782
H	-3.9804712	2.4219513	0.2394622
H	-2.9114359	1.6680080	-0.9676025
C	-5.9522843	0.3792719	-0.2187762
H	-6.2992229	1.3355013	0.1731861
H	-6.3748666	0.2352465	-1.2130022
H	-6.2962064	-0.4034970	0.4483728

1^{2+}-C_{2h}-orthogonal (Energy = -954.2430524483)

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C	-0.8243719	-1.1636111	0.0000000
C	0.5069879	-1.3220218	0.0000000
C	1.4202037	-0.1735851	0.0000000
C	-0.5069879	1.3220218	0.0000000
C	0.8243719	1.1636111	0.0000000
H	-1.4792250	-2.0259471	0.0000000
H	0.9631668	-2.3039031	0.0000000
H	-0.9631668	2.3039031	0.0000000
H	1.4792250	2.0259471	0.0000000
N	-2.6805308	0.4328737	0.0000000
N	2.6805308	-0.4328737	0.0000000
C	-3.6952217	-0.5181081	0.0000000
C	3.6952217	0.5181081	0.0000000
N	-4.1626331	-0.8769939	-1.2003114
N	-4.1626331	-0.8769939	1.2003114
N	4.1626331	0.8769939	-1.2003114
N	4.1626331	0.8769939	1.2003114
C	-3.6341454	-0.2302609	-2.4199206
H	-4.4676383	-0.0585221	-3.0975178
H	-2.9045960	-0.8737649	-2.9154116
H	-3.1839848	0.7282697	-2.1865603
C	-5.2546622	-1.8375189	-1.4706743
H	-5.2853662	-1.9909901	-2.5448401
H	-5.0661170	-2.8024011	-1.0134141
H	-6.2204088	-1.4469328	-1.1561514
C	-3.6341454	-0.2302609	2.4199206
H	-4.4676383	-0.0585221	3.0975178
H	-2.9045960	-0.8737649	2.9154116
H	-3.1839848	0.7282697	2.1865603
C	-5.2546622	-1.8375189	1.4706743
H	-5.2853662	-1.9909901	2.5448401
H	-5.0661170	-2.8024011	1.0134141
H	-6.2204088	-1.4469328	1.1561514
C	3.6341454	0.2302609	-2.4199206
H	4.4676383	0.0585221	-3.0975178
H	3.1839848	-0.7282697	-2.1865603
H	2.9045960	0.8737649	-2.9154116
C	3.6341454	0.2302609	2.4199206
H	4.4676383	0.0585221	3.0975178
H	3.1839848	-0.7282697	2.1865603
H	2.9045960	0.8737649	2.9154116
C	5.2546622	1.8375189	-1.4706743
H	5.2853662	1.9909901	-2.5448401
H	6.2204088	1.4469328	-1.1561514
H	5.0661170	2.8024011	-1.0134141
C	5.2546622	1.8375189	1.4706743
H	5.2853662	1.9909901	2.5448401
H	6.2204088	1.4469328	1.1561514
H	5.0661170	2.8024011	1.0134141

1^{2+}-C_{2h}-planar (Energy = -954.1659639182)

C	-1.4616568	-0.1847375	0.0000000
C	-0.5367038	-1.3205201	0.0000000
C	0.7939111	-1.1310281	0.0000000
C	1.4616568	0.1847375	0.0000000
C	-0.7939111	1.1310281	0.0000000
C	0.5367038	1.3205201	0.0000000
H	-0.9007094	-2.3302325	0.0000000
H	1.4548919	-1.9864839	0.0000000
H	-1.4548919	1.9864839	0.0000000
H	0.9007094	2.3302325	0.0000000
N	-2.7502687	-0.1150663	0.0000000
N	2.7502687	0.1150663	0.0000000
C	-4.0129895	-0.6221838	0.0000000
C	4.0129895	0.6221838	0.0000000
N	-4.3099502	-1.9394006	0.0000000
N	-4.9339455	0.3729011	0.0000000
N	4.3099502	1.9394006	0.0000000
N	4.9339455	-0.3729011	0.0000000
C	-3.2200720	-2.9203452	0.0000000
H	-3.6481536	-3.9156315	0.0000000
H	-2.6116647	-2.8230626	0.8976052
H	-2.6116647	-2.8230626	-0.8976052
C	-5.6668056	-2.5405815	0.0000000
H	-5.5488726	-3.6175133	0.0000000
H	-6.2231354	-2.2744088	0.8929723
H	-6.2231354	-2.2744088	-0.8929723
C	-4.4615081	1.7784293	0.0000000
H	-5.3335932	2.4221861	0.0000000
H	-3.8725654	1.9924808	0.8889111
H	-3.8725654	1.9924808	-0.8889111
C	-6.4067086	0.2291988	0.0000000
H	-6.8358291	1.2235445	0.0000000
H	-6.7620363	-0.2764904	0.8927006
H	-6.7620363	-0.2764904	-0.8927006
C	3.2200720	2.9203452	0.0000000
H	3.6481536	3.9156315	0.0000000
H	2.6116647	2.8230626	-0.8976052
H	2.6116647	2.8230626	0.8976052
C	4.4615081	-1.7784293	0.0000000
H	5.3335932	-2.4221861	0.0000000
H	3.8725654	-1.9924808	-0.8889111
H	3.8725654	-1.9924808	0.8889111
C	5.6668056	2.5405815	0.0000000
H	5.5488726	3.6175133	0.0000000
H	6.2231354	2.2744088	-0.8929723
H	6.2231354	2.2744088	0.8929723
C	6.4067086	-0.2291988	0.0000000
H	6.8358291	-1.2235445	0.0000000
H	6.7620363	0.2764904	-0.8927006
H	6.7620363	0.2764904	0.8927006

1^{2+}-D_{2h}-orthogonal (Energy = -954.2062494846)

C	-1.4359054	0.0000000	0.0000000
C	-0.6697166	-1.2582239	0.0000000
C	0.6697166	-1.2582239	0.0000000
C	1.4359054	0.0000000	0.0000000
C	-0.6697166	1.2582239	0.0000000
C	0.6697166	1.2582239	0.0000000
H	-1.2335940	-2.1825066	0.0000000
H	1.2335940	-2.1825066	0.0000000
H	-1.2335940	2.1825066	0.0000000
H	1.2335940	2.1825066	0.0000000
N	-2.6981582	0.0000000	0.0000000
N	2.6981582	0.0000000	0.0000000
C	-4.0247456	0.0000000	0.0000000
C	4.0247456	0.0000000	0.0000000
N	-4.6219317	0.0000000	-1.2108609
N	-4.6219317	0.0000000	1.2108609
N	4.6219317	0.0000000	-1.2108609
N	4.6219317	0.0000000	1.2108609
C	-3.7458474	0.0000000	-2.3937704
H	-4.3654087	0.0000000	-3.2834276
H	-3.1167639	-0.8912884	-2.4198699
H	-3.1167639	0.8912884	-2.4198699
C	-6.0778699	0.0000000	-1.4621722
H	-6.2177320	0.0000000	-2.5376587
H	-6.5576497	-0.8926105	-1.0702004
H	-6.5576497	0.8926105	-1.0702004
C	-3.7458474	0.0000000	2.3937704
H	-4.3654087	0.0000000	3.2834276
H	-3.1167639	-0.8912884	2.4198699
H	-3.1167639	0.8912884	2.4198699
C	-6.0778699	0.0000000	1.4621722
H	-6.2177320	0.0000000	2.5376587
H	-6.5576497	-0.8926105	1.0702004
H	-6.5576497	0.8926105	1.0702004
C	3.7458474	0.0000000	-2.3937704
H	4.3654087	0.0000000	-3.2834276
H	3.1167639	-0.8912884	-2.4198699
H	3.1167639	0.8912884	-2.4198699
C	3.7458474	0.0000000	2.3937704
H	4.3654087	0.0000000	3.2834276
H	3.1167639	-0.8912884	2.4198699
H	3.1167639	0.8912884	2.4198699
C	6.0778699	0.0000000	-1.4621722
H	6.2177320	0.0000000	-2.5376587
H	6.5576497	-0.8926105	-1.0702004
H	6.5576497	0.8926105	-1.0702004
C	6.0778699	0.0000000	1.4621722
H	6.2177320	0.0000000	2.5376587
H	6.5576497	-0.8926105	1.0702004
H	6.5576497	0.8926105	1.0702004

1^{2+}-D_{2h}-planar (Energy = -954.1617510825)

C	-1.4620895	0.0000000	0.0000000
C	-0.6717745	-1.2403640	0.0000000
C	0.6717745	-1.2403640	0.0000000
C	1.4620895	0.0000000	0.0000000
C	-0.6717745	1.2403640	0.0000000
C	0.6717745	1.2403640	0.0000000
H	-1.2059547	-2.1779666	0.0000000
H	1.2059547	-2.1779666	0.0000000
H	-1.2059547	2.1779666	0.0000000
H	1.2059547	2.1779666	0.0000000
N	-2.7405989	0.0000000	0.0000000
N	2.7405989	0.0000000	0.0000000
C	-4.0774008	0.0000000	0.0000000
C	4.0774008	0.0000000	0.0000000
N	-4.7024667	-1.2012667	0.0000000
N	-4.7024667	1.2012667	0.0000000
N	4.7024667	1.2012667	0.0000000
N	4.7024667	-1.2012667	0.0000000
C	-3.8652542	-2.4139317	0.0000000
H	-4.5171310	-3.2799913	0.0000000
H	-3.2433729	-2.4567629	0.8928809
H	-3.2433729	-2.4567629	-0.8928809
C	-6.1613629	-1.4484339	0.0000000
H	-6.3160932	-2.5208531	0.0000000
H	-6.6352805	-1.0505162	0.8924845
H	-6.6352805	-1.0505162	-0.8924845
C	-3.8652542	2.4139317	0.0000000
H	-4.5171310	3.2799913	0.0000000
H	-3.2433729	2.4567629	0.8928809
H	-3.2433729	2.4567629	-0.8928809
C	-6.1613629	1.4484339	0.0000000
H	-6.3160932	2.5208531	0.0000000
H	-6.6352805	1.0505162	0.8924845
H	-6.6352805	1.0505162	-0.8924845
C	3.8652542	2.4139317	0.0000000
H	4.5171310	3.2799913	0.0000000
H	3.2433729	2.4567629	-0.8928809
H	3.2433729	2.4567629	0.8928809
C	3.8652542	-2.4139317	0.0000000
H	4.5171310	-3.2799913	0.0000000
H	3.2433729	-2.4567629	-0.8928809
H	3.2433729	-2.4567629	0.8928809
C	6.1613629	1.4484339	0.0000000
H	6.3160932	2.5208531	0.0000000
H	6.6352805	1.0505162	-0.8924845
H	6.6352805	1.0505162	0.8924845
C	6.1613629	-1.4484339	0.0000000
H	6.3160932	-2.5208531	0.0000000
H	6.6352805	-1.0505162	-0.8924845
H	6.6352805	-1.0505162	0.8924845