

Electronic Supplementary Information

N-Confused Porphyrin Tautomers: Lessons from Density Functional Theory

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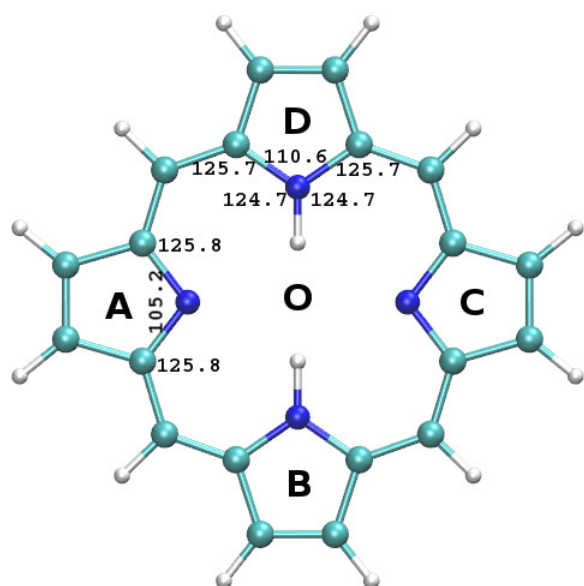
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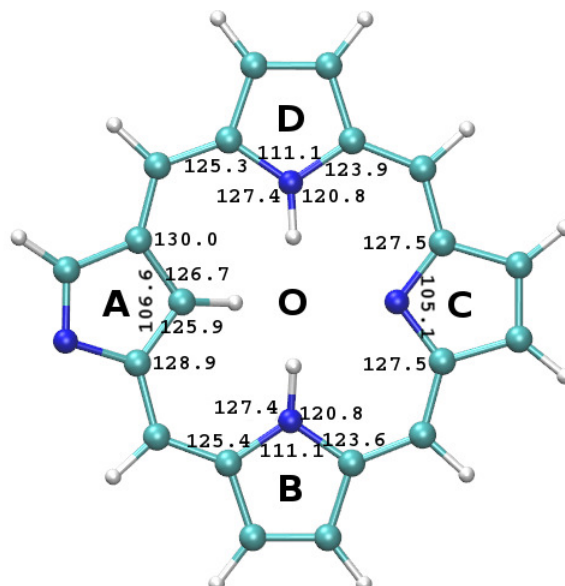
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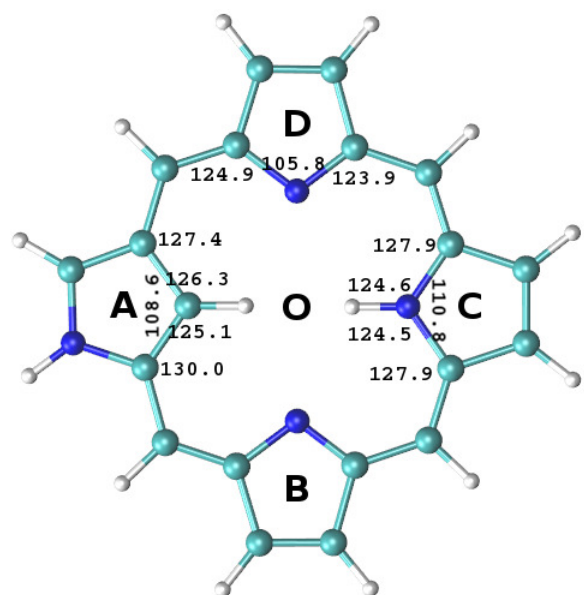
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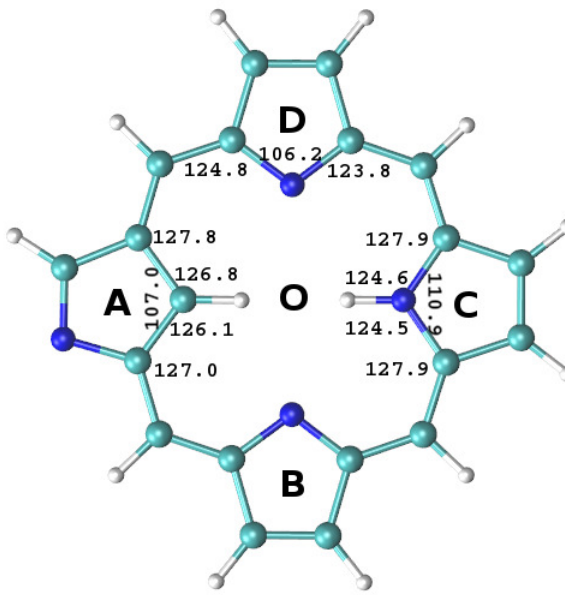
Porphyrin



NCP-3H



NCP-2H



NCP-2H-dep

Fig. S 1 Angle values (°) in porphyrin and selected N-confused analogues in their optimized singlet electronic ground states. O, A, B, C, and D: naming convention for the cycles.

Table S 1 NICS (ppm) for all the rings of the optimized structure of NCP-2H in DMF, DCM, and gas phase (see the labels of the rings in Fig. 2 in the main text).

	O	A	B	C	D
DMF	-7.45	-4.77	-1.78	-7.43	-1.73
DCM	-7.36	-4.94	-1.74	-7.40	-1.69
Gas	-6.83	-5.90	-1.51	-7.23	-1.49

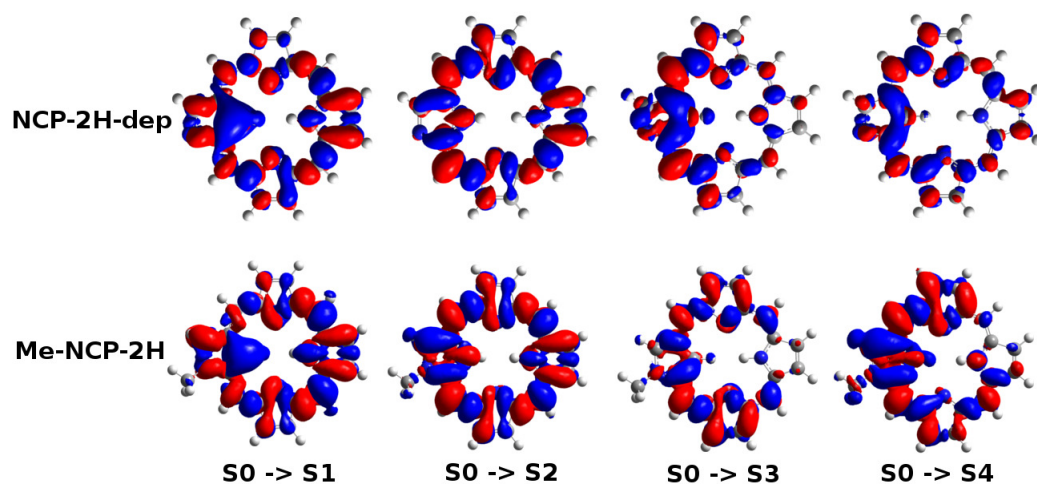


Fig. S 2 Electronic density difference between the first four excited-states and the ground-state in NCP-2H-dep and Me-NCP-2H. Blue (red) regions indicate zones of decrease (increase) of electron density upon photon absorption.

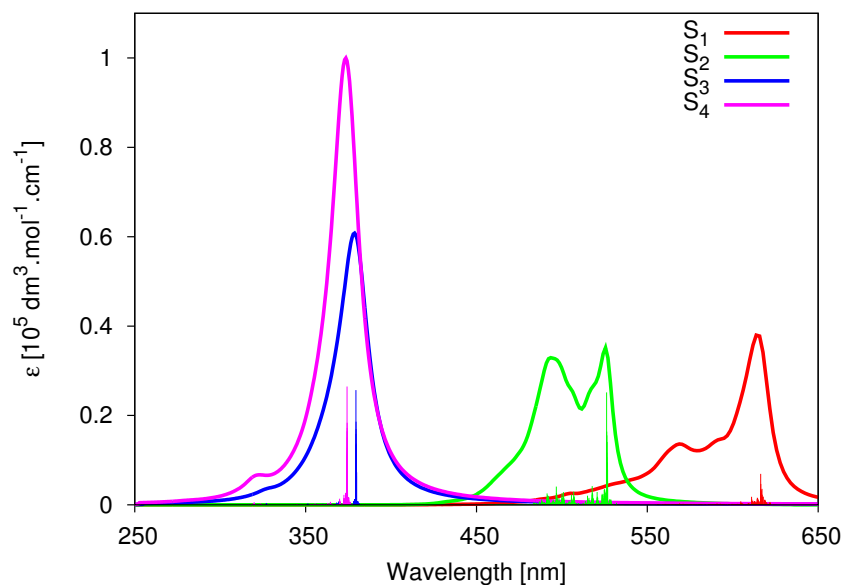


Fig. S 3 Decomposed vibronic spectrum of NCP-3H in DCM.

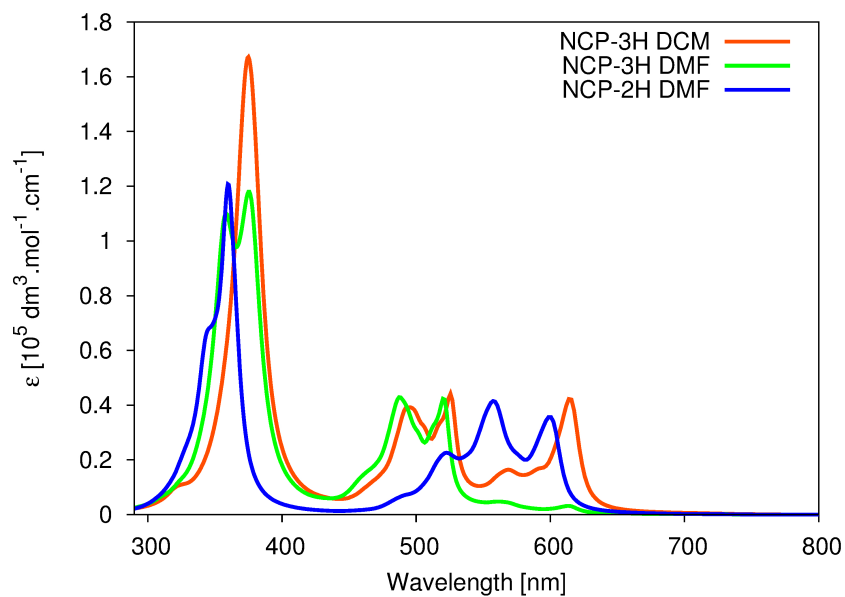


Fig. S 4 Vibronic spectra of NCP-3H in DCM and DMF and NCP-2H in DMF. The obtained theoretical curve is the sum of the contributions of the first four excited states.

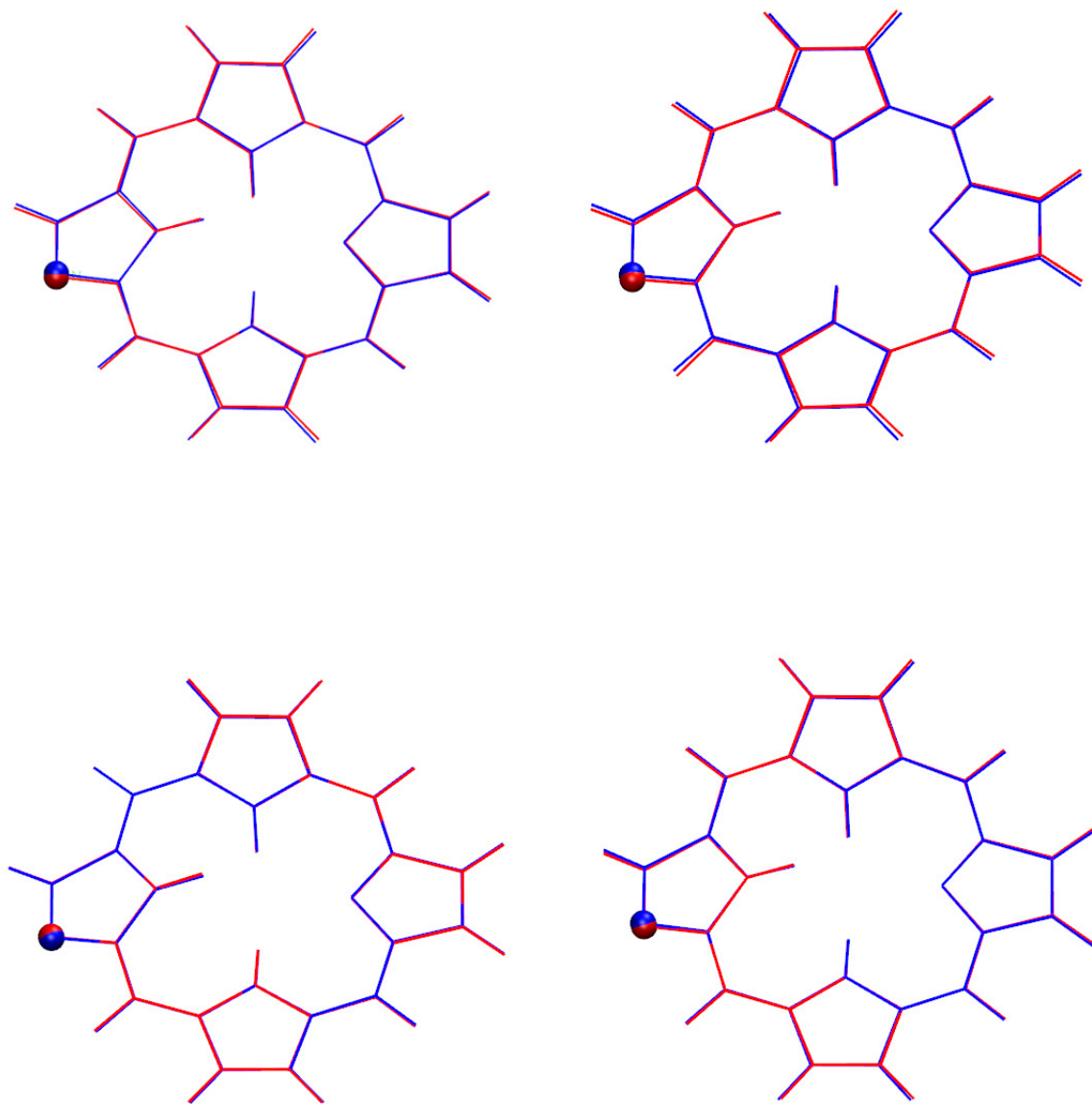


Fig. S 5 Superimposed equilibrium structures of S_0 (blue) and the first four excited states (red) of NCP-3H. Top left: S_1 ; top right: S_2 ; bottom left: S_3 ; bottom right: S_4 .

Optimized Cartesian coordinates (in Å) of NCP-3H and NCP-2H in their (singlet) electronic ground states and first four excited states.

NCP-3H (S_0)

C	-2.413557	-2.428281	0.028104
C	-2.417734	2.437141	0.040139
C	2.432677	2.493432	-0.124571
C	2.446344	-2.463540	-0.081108
N	-1.946594	0.005013	0.043685
C	-2.775478	-1.083096	0.077695
C	-4.175518	-0.674200	0.151296
C	-4.176266	0.674647	0.156455
C	-2.776221	1.085422	0.084046
N	-0.002682	2.185877	-0.076483
C	-1.128379	2.953398	-0.049323
C	-0.698200	4.320575	-0.122322
C	0.668639	4.327204	-0.168069
C	1.128925	2.968088	-0.135658
C	2.779422	1.135261	-0.132808
C	4.091894	0.586386	0.219088
C	2.798348	-1.115069	-0.106257
N	0.003491	-2.170638	-0.045516
C	1.137841	-2.944976	-0.105439
C	0.688978	-4.301625	-0.165257
C	-0.682675	-4.303388	-0.139894
C	-1.118112	-2.944372	-0.050954
H	-3.219719	-3.154815	0.043402
H	-3.225834	3.160757	0.069253
H	3.221196	3.237249	-0.051166
H	3.242174	-3.195515	0.017764
H	-5.016571	-1.354728	0.188002
H	-5.018099	1.353925	0.198027
H	-1.366435	5.170513	-0.133621
H	1.324006	5.185288	-0.231474
H	4.965798	1.179232	0.475923
H	1.349738	-5.154934	-0.235321
H	-1.344949	-5.157194	-0.176093
H	-0.054073	-1.175528	0.135694
H	-0.052500	1.187590	0.087730
N	4.113276	-0.712161	0.235246
C	1.986697	0.005083	-0.366931
H	1.016981	-0.013274	-0.841748

NCP-3H (S_1)

C	-2.412445	-2.435426	0.039812
C	-2.425712	2.441746	0.053008
C	2.441493	2.501893	-0.117919
C	2.456094	-2.476897	-0.089287
N	-1.981265	0.004077	0.087759
C	-2.809146	-1.078128	0.111484
C	-4.197767	-0.678509	0.176422
C	-4.201855	0.681768	0.181967
C	-2.816468	1.089791	0.119340
N	-0.000045	2.174210	-0.027559
C	-1.134683	2.945313	-0.044379
C	-0.704476	4.306051	-0.179356
C	0.663693	4.313954	-0.225005
C	1.128059	2.958425	-0.126589
C	2.825012	1.147098	-0.093213
C	4.109728	0.596457	0.261960
C	2.841868	-1.125372	-0.075678
N	0.010177	-2.154938	-0.030426
C	1.139532	-2.934366	-0.116224
C	0.681728	-4.293016	-0.219042
C	-0.685445	-4.291878	-0.183951
C	-1.125761	-2.931481	-0.052043
H	-3.210645	-3.171909	0.039221
H	-3.224724	3.177240	0.057711
H	3.215409	3.263499	-0.074794
H	3.237705	-3.226676	-0.014015
H	-5.040042	-1.357680	0.204740
H	-5.048083	1.355814	0.214776
H	-1.373292	5.153695	-0.239107
H	1.316526	5.169194	-0.334223
H	4.988092	1.175522	0.529506
H	1.340013	-5.144530	-0.323422
H	-1.349640	-5.142745	-0.250523
H	-0.041672	-1.172894	0.206844
H	-0.047518	1.186896	0.188225
N	4.122356	-0.723305	0.274769
C	2.026854	0.006929	-0.354168
H	1.073174	-0.005077	-0.865085

NCP-3H (S₂)

C	-2.413945	-2.436007	0.027965
C	-2.428820	2.433677	0.071666
C	2.441338	2.496215	-0.139096
C	2.462886	-2.464179	-0.036042
N	-1.950853	-0.001279	0.078975
C	-2.779346	-1.074334	0.092794
C	-4.181755	-0.669363	0.157494
C	-4.185995	0.680730	0.176053
C	-2.790085	1.098361	0.117854
N	0.002077	2.200846	-0.045187
C	-1.125067	2.969235	-0.031571
C	-0.710519	4.322156	-0.145025
C	0.669799	4.334529	-0.211168
C	1.128851	2.986293	-0.145228
C	2.774520	1.132229	-0.132238
C	4.088861	0.577786	0.234698
C	2.811990	-1.133350	-0.093610
N	0.010211	-2.179215	-0.011344
C	1.132577	-2.954431	-0.094267
C	0.691735	-4.303558	-0.206029
C	-0.687219	-4.307612	-0.184633
C	-1.123630	-2.955249	-0.052128
H	-3.223904	-3.158536	0.022559
H	-3.234922	3.160582	0.097421
H	3.236889	3.232864	-0.077210
H	3.251134	-3.194886	0.114411
H	-5.022125	-1.351270	0.178540
H	-5.031210	1.356133	0.214190
H	-1.381892	5.168913	-0.176595
H	1.319304	5.193221	-0.308826
H	4.959032	1.175025	0.494712
H	1.354509	-5.151885	-0.305276
H	-1.348417	-5.159062	-0.264575
H	-0.041034	-1.188255	0.198656
H	-0.039135	1.202626	0.126632
N	4.119283	-0.718722	0.251153
C	1.992572	0.005220	-0.387388
H	1.039134	-0.020702	-0.896800

NCP-3H (S₃)

C	-2.424795	-2.434867	0.046481
C	-2.422730	2.437125	0.041812
C	2.450114	2.501609	-0.092000
C	2.452830	-2.472007	-0.095562
N	-1.949782	0.000901	0.064632
C	-2.784312	-1.089755	0.094858
C	-4.189445	-0.673963	0.159819
C	-4.186771	0.671988	0.157810
C	-2.779978	1.083112	0.092358
N	0.006006	2.193547	-0.042460
C	-1.132525	2.960357	-0.043932
C	-0.707800	4.321627	-0.149139
C	0.666891	4.332639	-0.192909
C	1.127137	2.978921	-0.120220
C	2.788605	1.149643	-0.108361
C	4.099654	0.584041	0.231229
C	2.807346	-1.120339	-0.106851
N	0.001822	-2.171119	-0.046206
C	1.138451	-2.947132	-0.119655
C	0.688160	-4.305737	-0.184665
C	-0.685540	-4.307830	-0.143479
C	-1.120994	-2.948375	-0.043528
H	-3.228324	-3.163420	0.064815
H	-3.233712	3.158136	0.056111
H	3.235802	3.245001	-0.000292
H	3.247327	-3.205893	-0.008504
H	-5.031061	-1.353681	0.193982
H	-5.026394	1.354380	0.190257
H	-1.379190	5.168351	-0.193863
H	1.320470	5.189921	-0.279573
H	4.978283	1.167695	0.490565
H	1.350012	-5.157289	-0.265738
H	-1.349758	-5.160257	-0.181972
H	-0.056091	-1.174807	0.133576
H	-0.033817	1.198317	0.145524
N	4.114781	-0.720592	0.231693
C	1.992741	0.013121	-0.374287
H	1.043417	0.001377	-0.890791

NCP-3H (S₄)

C	-2.413704	-2.431476	0.052454
C	-2.421024	2.444957	0.048579
C	2.438123	2.501232	-0.118189
C	2.455503	-2.478706	-0.095371
N	-1.951037	0.008502	0.076744
C	-2.782636	-1.084166	0.103242
C	-4.181796	-0.676641	0.163397
C	-4.183689	0.674975	0.162703
C	-2.783659	1.086309	0.101520
N	0.000435	2.192498	-0.055684
C	-1.131736	2.962877	-0.046057
C	-0.703499	4.328141	-0.151379
C	0.666362	4.337245	-0.202470
C	1.128204	2.979023	-0.136743
C	2.784433	1.139407	-0.114682
C	4.085004	0.587908	0.256069
C	2.807791	-1.120427	-0.098093
N	0.011395	-2.172983	-0.034796
C	1.143489	-2.956519	-0.120650
C	0.685918	-4.313055	-0.202682
C	-0.685892	-4.307397	-0.156780
C	-1.115519	-2.945821	-0.038997
H	-3.217443	-3.160962	0.066811
H	-3.230300	3.167845	0.066306
H	3.226851	3.244981	-0.044936
H	3.251986	-3.211211	-0.009526
H	-5.022712	-1.357830	0.193348
H	-5.026823	1.353727	0.191293
H	-1.374176	5.175319	-0.187924
H	1.320316	5.193823	-0.290043
H	4.956144	1.176630	0.531236
H	1.342408	-5.166760	-0.298464
H	-1.354656	-5.155240	-0.207432
H	-0.030928	-1.181645	0.174344
H	-0.040935	1.197493	0.134431
N	4.103803	-0.719448	0.267216
C	1.991680	0.004911	-0.376985
H	1.039149	-0.012768	-0.890272

NCP-2H (S₀)

C	-2.439785	-2.394811	-0.044548
C	-2.518912	2.421034	0.056733
C	2.492537	2.414926	0.036899
C	2.450773	-2.398565	-0.043480
N	-2.105672	0.011129	0.024919
C	-2.904987	-1.047744	-0.012096
C	-4.319894	-0.665229	-0.016694
C	-4.339104	0.686594	0.013760
C	-2.943029	1.116975	0.041314
C	-1.148223	2.826989	0.071472
C	-0.664776	4.137856	-0.107673
C	1.120970	2.785677	0.062848
N	2.101943	0.004103	0.007359
C	2.929251	1.111929	0.023624
C	4.329084	0.694610	0.007883
C	4.320874	-0.657971	-0.012123
C	2.909218	-1.051668	-0.015003
N	0.006317	-2.020941	-0.049632
C	1.139343	-2.805120	-0.053187
C	0.678916	-4.183355	-0.059426
C	-0.672902	-4.181517	-0.060452
C	-1.130148	-2.802075	-0.053963
H	-3.186961	-3.181890	-0.058482
H	-3.279552	3.198103	0.031328
H	3.241052	3.203376	0.007776
H	3.198826	-3.184739	-0.053216
H	-5.155920	-1.352627	-0.045910
H	-5.195743	1.349085	0.018828
H	-1.202646	5.065336	-0.246941
H	1.275277	4.902661	-0.245581
H	5.180127	1.364190	0.015113
H	5.162782	-1.338396	-0.031042
H	1.344934	-5.035802	-0.057575
H	-1.341128	-5.032302	-0.059415
H	0.010146	-1.006308	-0.092281
H	-0.008804	0.946262	0.377609
C	-0.009598	2.000751	0.195335
N	0.675414	4.099475	-0.108336

NCP-2H (S₁)

C	-2.458462	-2.397961	-0.051294
C	-2.503331	2.425382	0.030983
C	2.478536	2.433005	0.019119
C	2.466093	-2.390520	-0.042243
N	-2.080084	0.005556	-0.026059
C	-2.898717	-1.078233	-0.023335
C	-4.303940	-0.679218	0.014798
C	-4.306946	0.672824	0.038228
C	-2.903150	1.090523	0.016631
C	-1.158408	2.880998	0.025264
C	-0.668995	4.195891	-0.094547
C	1.139399	2.844619	0.026458
N	2.073559	0.011900	-0.015150
C	2.889289	1.087075	0.015725
C	4.297620	0.681755	0.030475
C	4.303271	-0.670038	0.012410
C	2.900376	-1.079560	-0.015703
N	0.002190	-2.065649	-0.065862
C	1.125324	-2.848055	-0.059964
C	0.693899	-4.199480	-0.059361
C	-0.687244	-4.201948	-0.063005
C	-1.125041	-2.851391	-0.065672
H	-3.213602	-3.178944	-0.050694
H	-3.292413	3.173563	0.025301
H	3.255956	3.191944	-0.007342
H	3.220861	-3.171689	-0.042214
H	-5.147639	-1.357855	0.021861
H	-5.155329	1.345122	0.071056
H	-1.197602	5.132042	-0.192639
H	1.290327	4.957142	-0.188299
H	5.141025	1.360421	0.054113
H	5.151232	-1.343208	0.016184
H	1.359311	-5.051732	-0.051813
H	-1.349380	-5.056841	-0.058485
H	0.001990	-1.048634	-0.090477
H	-0.015854	0.985613	0.276985
C	-0.014680	2.046810	0.123009
N	0.690561	4.148773	-0.088702

NCP-2H (S₂)

C	-2.465324	-2.386534	-0.045297
C	-2.507705	2.436137	0.044854
C	2.488900	2.438482	0.024107
C	2.467532	-2.386640	-0.041171
N	-2.115642	0.021158	0.016296
C	-2.929784	-1.071156	-0.018309
C	-4.336003	-0.675913	-0.024291
C	-4.343733	0.678379	0.003172
C	-2.941248	1.098198	0.029932
C	-1.149935	2.809627	0.069322
C	-0.654170	4.144911	-0.078147
C	1.132686	2.779606	0.058238
N	2.111869	0.019288	0.002550
C	2.931913	1.100848	0.014988
C	4.334747	0.689663	-0.002236
C	4.333834	-0.666293	-0.021624
C	2.930706	-1.067334	-0.020060
N	0.001258	-2.029579	-0.050641
C	1.133639	-2.816756	-0.047229
C	0.688852	-4.175023	-0.041344
C	-0.683862	-4.174752	-0.042704
C	-1.127535	-2.815817	-0.049088
H	-3.206944	-3.179620	-0.061015
H	-3.264429	3.214358	0.008326
H	3.234998	3.226238	-0.017998
H	3.211326	-3.177981	-0.050420
H	-5.177532	-1.356494	-0.050105
H	-5.194659	1.347893	0.007202
H	-1.199147	5.072578	-0.193564
H	1.268045	4.921873	-0.197495
H	5.182246	1.363343	0.002695
H	5.179186	-1.342316	-0.038793
H	1.352464	-5.028988	-0.031698
H	-1.348052	-5.028250	-0.034324
H	0.001697	-1.014831	-0.095459
H	-0.002305	0.931646	0.339646
C	-0.008080	1.987952	0.177819
N	0.670194	4.112098	-0.080395

NCP-2H (S₃)

C	-2.455385	-2.399218	-0.049665
C	-2.511555	2.427070	0.051855
C	2.493937	2.437715	0.026871
C	2.453709	-2.394905	-0.049065
N	-2.112818	0.010727	0.009073
C	-2.925943	-1.066611	-0.017362
C	-4.329549	-0.677616	-0.006287
C	-4.341665	0.679289	0.027027
C	-2.943616	1.103418	0.038582
C	-1.147500	2.824550	0.063221
C	-0.658558	4.151353	-0.107710
C	1.134373	2.797534	0.054126
N	2.108637	0.016694	-0.012960
C	2.935948	1.107172	0.020991
C	4.333377	0.691943	0.025465
C	4.324501	-0.668012	-0.002436
C	2.923682	-1.059003	-0.023946
N	-0.000839	-2.026202	-0.061009
C	1.135456	-2.810542	-0.060118
C	0.682220	-4.183857	-0.060423
C	-0.677040	-4.184652	-0.061068
C	-1.131253	-2.812398	-0.060576
H	-3.196933	-3.192102	-0.059853
H	-3.272232	3.203409	0.023112
H	3.243973	3.223046	-0.011162
H	3.198459	-3.185483	-0.053292
H	-5.169518	-1.360292	-0.024602
H	-5.194719	1.345837	0.043322
H	-1.201843	5.077396	-0.240020
H	1.275711	4.923986	-0.239992
H	5.183820	1.361548	0.047729
H	5.166426	-1.348529	-0.007099
H	1.349331	-5.035542	-0.054597
H	-1.343284	-5.037081	-0.055854
H	-0.003351	-1.010630	-0.101205
H	0.002215	0.949034	0.374189
C	-0.006094	2.003840	0.187839
N	0.677922	4.117113	-0.107359

NCP-2H (S₄)

C	-2.446501	-2.404019	-0.039171
C	-2.507961	2.443780	0.039546
C	2.487291	2.441557	0.026275
C	2.449563	-2.407848	-0.038952
N	-2.117097	0.017639	0.018781
C	-2.925075	-1.060120	-0.017939
C	-4.325725	-0.678549	-0.030094
C	-4.341342	0.685744	-0.002296
C	-2.949576	1.104807	0.028564
C	-1.150553	2.803077	0.067684
C	-0.643480	4.149433	-0.076825
C	1.133898	2.777907	0.063955
N	2.109374	0.009224	0.012014
C	2.939233	1.113212	0.019519
C	4.329524	0.706596	-0.007950
C	4.324646	-0.656906	-0.032145
C	2.920032	-1.051852	-0.020442
N	0.003561	-2.021981	-0.042858
C	1.140638	-2.808285	-0.043444
C	0.673746	-4.194416	-0.040528
C	-0.674770	-4.191415	-0.041300
C	-1.137054	-2.808265	-0.044076
H	-3.189341	-3.195977	-0.050355
H	-3.257472	3.228348	-0.002615
H	3.227820	3.234817	-0.018593
H	3.195758	-3.195622	-0.047645
H	-5.164457	-1.363068	-0.058248
H	-5.195521	1.351429	-0.002261
H	-1.188242	5.077216	-0.191196
H	1.277262	4.922269	-0.185523
H	5.178121	1.378951	-0.008621
H	5.168549	-1.334925	-0.056467
H	1.340534	-5.046130	-0.032876
H	-1.343495	-5.041904	-0.034333
H	0.004219	-1.009135	-0.101329
H	-0.008396	0.927149	0.347231
C	-0.013580	1.983384	0.183056
N	0.675869	4.113879	-0.072802