SUPPORTING INFORMATION

Quantum Chemical Investigation for Enhanced Electrochemical Sensing of Toxic Gases by HexaazaphenH_2

Sabir Ali Siddique[a,b], Muhammad Bilal Ahmed Siddique[c], Ejaz Ahmed[a], Asad Ullah[b], Ali Rauf[d], Muhammad Arif Ali[b], Tariq Mahmood[e]*, Abdul Rauf[b], Muhammad Arshad[b]*

[a] *Centre for Organic Chemistry, School of Chemistry, University of the Punjab, Lahore 54590, Pakistan*

[b] *Institute of Chemistry, The Islamia University of Bahawalpur, Bahawalpur-63100, Pakistan*

[c] *School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China*

[d] *Department of Chemistry and Chemical Engineering, Syed Babar Ali School of Science and Engineering, Lahore University of Management Sciences, Lahore 54792, Pakistan*

[e] *Department of Chemistry, College of Science, University of Bahrain, P.O. Box 32038, Bahrain*

For Correspondence:

Tariq Mahmood (PhD): tmahmood@uob.edu.bh

Muhammad Arshad (PhD): muhammad.arshad@iub.edu.pk

Section-S1

Detailed formulas for calculating the charge-transfer spectrum (CTS)

The general absorption curve for the molecular UV-Vis spectrum can be described by the equation:

$$\varepsilon(E) = c\sum_i f_i G(E - E_i^{ex})$$

where $\varepsilon(E)$ is the molar absorption coefficient at energy E, c is a constant, i sums over all excited states, and f_i and E_i^{ex} represent the oscillator strength and excitation energy of the i-th excited state, respectively. In a similar manner, the charge-transfer spectrum (CTS) of a system is defined as:

$$\varepsilon_{A,B}(E) = \sum_i f_i Q_i^{A,B} G(E - E_i^{ex})$$

Here, Q is obtained through inter-fragment charge transfer (IFCT) analysis, as proposed by Zeyu Liu et al., within the framework of hole-electron analysis [S1–S3]. The term $Q_i^{A,B}$, is defined as $Q_i^{A,B} = \Theta_i^{A,hole}\Theta_i^{B,ele}$, where $\Theta_i^{A,hole}$ represents the contribution of fragment A **(the analyte)** to the hole distribution, and $\Theta_i^{B,ele}$ denotes the contribution of fragment B **(HA)** to the electron distribution. $Q_i^{A,A}$ represents the electron redistribution within fragment A during the i-th electronic excitation, whereas $Q_i^{A,B}$ describes the electron transfer from fragment A to fragment B in the same excitation. When the system is partitioned into only two fragments, A and B, the following condition is fulfilled: $Q_i^{A,A} + Q_i^{A,B} + Q_i^{B,A} + Q_i^{B,B} = 1$ [S3]. In this study, the robust Hirshfeld partitioning method was utilized to derive the Θ terms for the IFCT analysis.

Table S1

The charge-transfer spectrum (CTS) displays the absorption wavelength (λ), oscillator strength (f_o), percentage of electron transfer of HA→Analyte and electron redistribution within HA along with excitation energy (E_x) of analyte@HA Complexes.

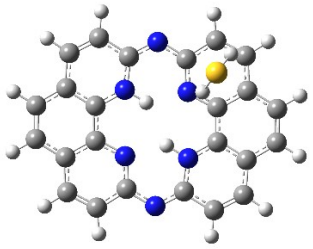
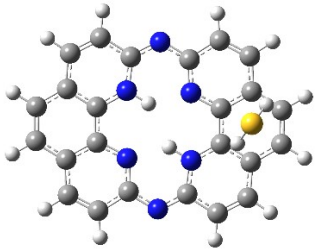
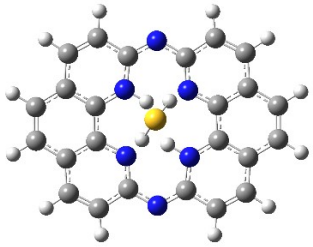
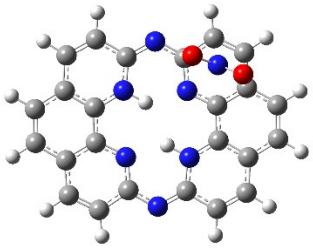
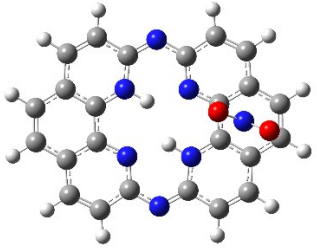
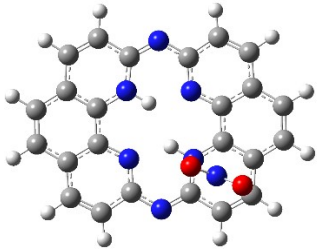
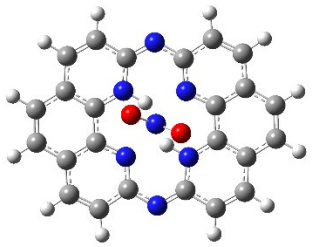
Complex	Excited States	λ (nm)	f_o (au)	Electron transfer of HA → analyte	Electron redistribution within HA	Ex (eV)
HA	$S_0 \rightarrow S_{23}$	261.2	1.1035	0.0 %	100 %	4.75
NO_2@HA	$S_0 \rightarrow S_{40}$	260.8	0.7326	32.3 %	67.2 %	4.75
N_2O@HA	$S_0 \rightarrow S_{23}$	261.7	1.0285	0.6 %	99.4 %	4.74
H_2S@HA	$S_0 \rightarrow S_{23}$	261.9	1.0263	0.8 %	99.2 %	4.73
SO_2@HA	$S_0 \rightarrow S_{37}$	261.7	0.5458	39.9 %	58.30 %	4.74
SO_3@HA	$S_0 \rightarrow S_{30}$	262.9	0.7298	22.8 %	77.2 %	4.72

References

[S1] T. Lu, *Multiwfn manual, version 3.8(dev), Section 3.21.8, available at http://sobereva.com/multiwfn*, 2024, **161**, 082503.

[S2] Z. Liu, T. Lu and Q. Chen, *Carbon*, 2020, **165**, 461–467.

[S3] Z. Liu, X. Wang, T. Lu, A. Yuan and X. Yan, *Carbon*, 2022, **187**, 78–85.

Complexes	Possible Orientations A	B	C	D
H_2S@ HA				
Energy (au)	-1645.397	-1645.397	-1645.397	-1645.397
ZPE	0.3568	0.3568	0.3568	0.3568
N_2O@ HA				
Energy (au)	-1422.64	-1422.64	-1422.64	-1422.64
ZPE	0.3519	0.3519	0.3519	0.3519
NO_2@ HA				
Energy (au)	-1442.981	-1442.981	-1442.981	-1442.981

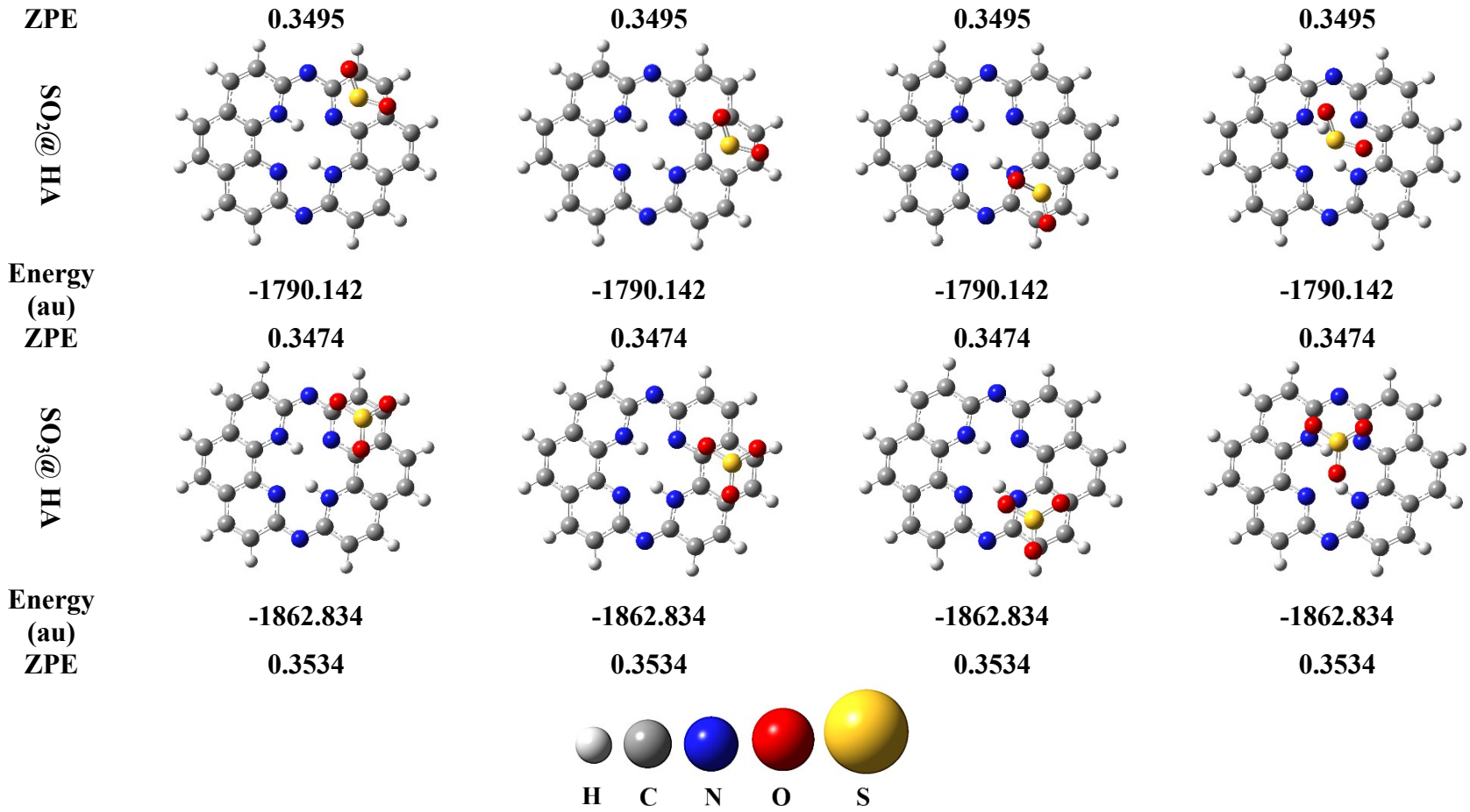


Figure S1: Optimized geometries of all designed complexes at positions A, B, C, and D. The red values represent the stabilization energy (E) in atomic units (au), and the blue values represent the Zero-Point Energy (ZPE) in Hartrees.[1]

[1] This figure shows the optimized geometries of the HA-analyte complexes across different orientations (A, B, C, and D). The stabilization energy (E) and zero-point energy (ZPE) values indicate that the D orientation consistently provides the most stable configuration. This choice is supported by both the total energy and ZPE values, reinforcing the selection of the D orientation as the optimal starting point for further geometry optimization.

Section-S2

Structure Coordinates

HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 1, Point group = C1

Electronic Energy = -1251.216806

	Coordinates (Angstroms)		
Atoms	X	Y	Z
C	-3.624565	2.822933	-0.000268
C	-3.710816	1.387418	-0.000262
C	-2.506323	0.690846	-0.000178
N	-1.324367	1.372910	-0.000203
C	-1.187313	2.726931	-0.000168
C	-2.427810	3.466770	-0.000210
C	-3.687594	-1.439756	0.000080
C	-3.587850	-2.862269	0.000305
C	-2.365265	-3.466185	0.000437
C	-1.167054	-2.673812	0.000436
N	-1.255051	-1.340349	-0.000074
C	-2.470223	-0.738415	-0.000057
C	1.167053	2.673810	0.000532
N	1.255051	1.340348	0.000080
C	2.470223	0.738415	0.000022
C	3.687594	1.439757	0.000093
C	3.587849	2.862269	0.000278
C	2.365263	3.466184	0.000396

N	1.324369	-1.372910	-0.000200
C	1.187314	-2.726931	-0.000110
C	2.427810	-3.466769	-0.000257
C	3.624565	-2.822933	-0.000297
C	3.710817	-1.387418	-0.000259
C	2.506324	-0.690847	-0.000151
N	0.023114	-3.353667	0.000261
N	-0.023116	3.353667	0.000185
C	4.929751	-0.649320	-0.000198
C	4.917915	0.719181	-0.000068
C	-4.929749	0.649321	-0.000201
C	-4.917915	-0.719181	-0.000065
H	-4.546420	3.398262	-0.000302
H	-0.429068	0.870067	0.000070
H	-2.353964	4.547333	-0.000057
H	-4.496267	-3.458646	0.000390
H	-2.256508	-4.544354	0.000541
H	4.496265	3.458647	0.000266
H	2.256507	4.544353	0.000375
H	0.429068	-0.870070	0.000261
H	2.353962	-4.547332	-0.000160
H	4.546420	-3.398262	-0.000376
H	5.870763	-1.191235	-0.000209
H	5.850595	1.275585	-0.000001
H	-5.870762	1.191236	-0.000186
H	-5.850596	-1.275582	0.000052

H2S@HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 1, Point group = C1

Electronic Energy = -1650.599244

Atoms	Coordinates (Angstroms) X	Y	Z
C	-3.622224	2.825868	-0.225884
C	-3.710712	1.390864	-0.242055
C	-2.507571	0.693110	-0.274697
N	-1.325401	1.374134	-0.300636
C	-1.186189	2.726672	-0.266999
C	-2.424462	3.467976	-0.235232
C	-3.689421	-1.436094	-0.254829
C	-3.589562	-2.859166	-0.253480
C	-2.367837	-3.464294	-0.264268
C	-1.168289	-2.673507	-0.273424
N	-1.256436	-1.338334	-0.280244
C	-2.472845	-0.735110	-0.274135
C	1.168581	2.673206	-0.273817
N	1.256742	1.338034	-0.280377
C	2.473156	0.734829	-0.273929
C	3.689727	1.435818	-0.254662
C	3.589856	2.858890	-0.253542
C	2.368125	3.464002	-0.264542
N	1.325697	-1.374412	-0.299859
C	1.186491	-2.726966	-0.266240
C	2.424766	-3.468260	-0.234438
C	3.622529	-2.826153	-0.225109
C	3.711018	-1.391151	-0.241421
C	2.507882	-0.693395	-0.274175

N	0.020313	-3.352250	-0.264188
N	-0.020016	3.351953	-0.264700
C	4.929893	-0.653922	-0.221982
C	4.919111	0.714710	-0.231635
C	-4.929586	0.653646	-0.222516
C	-4.918808	-0.714989	-0.231972
H	-4.542805	3.402474	-0.200321
H	-0.433462	0.869161	-0.331286
H	-2.348738	4.548162	-0.216009
H	-4.498071	-3.455155	-0.241032
H	-2.259958	-4.542483	-0.260752
H	4.498358	3.454890	-0.241087
H	2.260237	4.542191	-0.261144
H	0.433749	-0.869456	-0.330996
H	2.349044	-4.548446	-0.215169
H	4.543106	-3.402759	-0.199434
H	5.870289	-1.196194	-0.198124
H	5.851968	1.270463	-0.216543
H	-5.869981	1.195926	-0.198752
H	-5.851662	-1.270744	-0.216844
S	-0.001880	0.001727	2.957510
H	0.564105	0.787490	2.023675
H	-0.564164	-0.786534	2.023561

NO2@HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 2, Point group = C1

Electronic Energy = -1456.237444

	Coordinates (Angstroms)		
Atoms	X	Y	Z
C	3.650691	-2.789032	-0.277722
C	3.723206	-1.353207	-0.286684
C	2.512944	-0.668129	-0.329610
N	1.338941	-1.361596	-0.369809
C	1.214360	-2.715538	-0.330402
C	2.460154	-3.444132	-0.296770
C	3.672155	1.472899	-0.276772
C	3.558745	2.894444	-0.263719
C	2.330962	3.486860	-0.285064
C	1.140429	2.683587	-0.319518
N	1.241410	1.350255	-0.341535
C	2.462636	0.759895	-0.319735
C	-1.140456	-2.683598	-0.319479
N	-1.241438	-1.350268	-0.341515
C	-2.462661	-0.759909	-0.319715
C	-3.672180	-1.472913	-0.276732
C	-3.558771	-2.894458	-0.263669
C	-2.330988	-3.486873	-0.285020
N	-1.338965	1.361590	-0.369812
C	-1.214386	2.715529	-0.330412
C	-2.460179	3.444123	-0.296768
C	-3.650716	2.789020	-0.277707
C	-3.723229	1.353193	-0.286663
C	-2.512966	0.668117	-0.329599
N	-0.054929	3.352206	-0.320721
N	0.054902	-3.352217	-0.320704
C	-4.934001	0.603795	-0.246823

C	-4.908684	-0.764615	-0.244045
C	4.933978	-0.603809	-0.246859
C	4.908660	0.764602	-0.244090
H	4.577527	-3.355428	-0.247827
H	0.439897	-0.867123	-0.392948
H	2.395747	-4.525134	-0.279969
H	4.461102	3.499161	-0.233741
H	2.211499	4.563805	-0.272456
H	-4.461128	-3.499173	-0.233677
H	-2.211523	-4.563818	-0.272408
H	-0.439914	0.867130	-0.392977
H	-2.395770	4.525125	-0.279966
H	-4.577553	3.355413	-0.247802
H	-5.879684	1.136545	-0.216086
H	-5.835303	-1.330121	-0.212460
H	5.879662	-1.136559	-0.216128
H	5.835279	1.330110	-0.212516
O	-1.030288	0.378898	2.746795
N	0.000074	-0.000065	2.276000
O	1.030534	-0.378697	2.746840

N2O@HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 1, Point group = C1

Electronic Energy = -1435.825712

Coordinates (Angstroms)

Atoms	X	Y	Z

C	-3.680031	2.771778	-0.266384
C	-3.749087	1.335588	-0.269797
C	-2.537249	0.653754	-0.312585
N	-1.365485	1.350292	-0.363182
C	-1.243439	2.704125	-0.322154
C	-2.491164	3.429766	-0.288091
C	-3.688869	-1.490188	-0.238687
C	-3.570819	-2.911257	-0.214729
C	-2.341165	-3.499564	-0.234965
C	-1.152742	-2.693031	-0.277700
N	-1.257713	-1.359933	-0.303435
C	-2.481602	-0.773862	-0.287896
C	1.111670	2.675995	-0.313702
N	1.216239	1.342727	-0.326078
C	2.440318	0.756703	-0.322949
C	3.647808	1.473455	-0.300179
C	3.530019	2.894470	-0.288576
C	2.300072	3.482861	-0.296103
N	1.322976	-1.367334	-0.355744
C	1.201773	-2.720828	-0.310013
C	2.449693	-3.446376	-0.289855
C	3.638820	-2.788327	-0.290680
C	3.707674	-1.352373	-0.306128
C	2.495389	-0.670982	-0.333319
N	0.043576	-3.359625	-0.284576
N	-0.085265	3.342642	-0.311932
C	4.916908	-0.599134	-0.285167
C	4.887258	0.768978	-0.284797
C	-4.957560	0.582758	-0.221388
C	-4.927712	-0.785488	-0.209453

H	-4.608204	3.336006	-0.236507
H	-0.465865	0.857234	-0.382299
H	-2.429526	4.510961	-0.272952
H	-4.471120	-3.518757	-0.178858
H	-2.218129	-4.576034	-0.216568
H	4.430672	3.502299	-0.272598
H	2.177324	4.559473	-0.286930
H	0.423049	-0.874639	-0.366415
H	2.388293	-4.527461	-0.267690
H	4.567343	-3.352465	-0.271582
H	5.864602	-1.128926	-0.267106
H	5.812372	1.337615	-0.268167
H	-5.904872	1.112694	-0.191697
H	-5.852424	-1.353811	-0.172237
O	1.193686	-0.403413	2.631404
N	0.121213	0.108028	2.628510
N	-0.895365	0.593231	2.629602

SO2@HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 1, Point group = C1

Electronic Energy = -1799.757981

Coordinates (Angstroms)

Atoms	X	Y	Z
C	-3.697382	2.689452	-0.473867
C	-3.786497	1.256388	-0.388599
C	-2.586349	0.553882	-0.425769

N	-1.406367	1.228685	-0.551263
C	-1.265384	2.581377	-0.597680
C	-2.500964	3.326440	-0.569566
C	-3.762708	-1.564087	-0.186490
C	-3.661718	-2.982217	-0.072024
C	-2.439957	-3.586964	-0.076552
C	-1.242522	-2.801420	-0.195246
N	-1.331916	-1.472552	-0.319528
C	-2.547904	-0.870034	-0.314028
C	1.087208	2.521457	-0.646367
N	1.175314	1.188027	-0.549936
C	2.394229	0.587495	-0.529134
C	3.608774	1.288067	-0.584241
C	3.507480	2.707889	-0.682923
C	2.285589	3.310183	-0.717431
N	1.248556	-1.515018	-0.373556
C	1.111686	-2.861755	-0.237444
C	2.350797	-3.599701	-0.176334
C	3.547904	-2.959253	-0.240606
C	3.634944	-1.529656	-0.366206
C	2.431050	-0.835287	-0.426164
N	-0.054552	-3.481764	-0.164237
N	-0.099138	3.200508	-0.666381
C	4.852293	-0.793509	-0.425756
C	4.838909	0.571026	-0.534735
C	-5.002520	0.525614	-0.261584
C	-4.990251	-0.840150	-0.167949
H	-4.616265	3.268744	-0.449662
H	-0.519117	0.717795	-0.598842
H	-2.423399	4.405459	-0.618527

H	-4.568275	-3.573676	0.023320
H	-2.329689	-4.661140	0.013971
H	4.415407	3.303135	-0.726424
H	2.175182	4.385719	-0.787185
H	0.353123	-1.017330	-0.433245
H	2.276543	-4.675424	-0.075046
H	4.469367	-3.532871	-0.191113
H	5.793928	-1.332233	-0.380764
H	5.770862	1.126676	-0.577934
H	-5.941605	1.070104	-0.237277
H	-5.921147	-1.390866	-0.070472
S	0.252406	0.603407	2.334787
O	-0.220344	1.958884	2.565104
O	1.633228	0.296712	2.673282

SO3@HA

opt wb97xd/6-31+g(d,p) geom=connectivity

Charge = 0, Multiplicity = 1, Point group = C1

Electronic Energy = -1874.916598

Coordinates (Angstroms)

Atoms	X	Y	Z
C	3.296519	-3.237276	-0.312971
C	3.454941	-1.815505	-0.464372
C	2.291909	-1.049971	-0.417475
N	1.080878	-1.662059	-0.278398
C	0.875185	-2.998616	-0.149616
C	2.072878	-3.806357	-0.157562

C	3.564261	0.982888	-0.818395
C	3.527100	2.394495	-1.044417
C	2.342694	3.063753	-1.045803
C	1.115229	2.367582	-0.767888
N	1.154356	1.055696	-0.451181
C	2.332951	0.367403	-0.559782
C	-1.470419	-2.815090	-0.059769
N	-1.494833	-1.488511	-0.226804
C	-2.678634	-0.830204	-0.254710
C	-3.926740	-1.457394	-0.111810
C	-3.895906	-2.871516	0.067671
C	-2.704715	-3.534587	0.092268
N	-1.438689	1.199083	-0.571571
C	-1.231793	2.532033	-0.702915
C	-2.423847	3.336474	-0.738325
C	-3.653627	2.764200	-0.623377
C	-3.814776	1.347605	-0.461522
C	-2.649110	0.587839	-0.436094
N	-0.030063	3.092421	-0.814111
N	-0.318487	-3.555259	-0.032654
C	-5.067127	0.682036	-0.314255
C	-5.118957	-0.674741	-0.147094
C	4.698179	-1.159336	-0.678202
C	4.749524	0.197070	-0.864605
H	4.184835	-3.862714	-0.329425
H	0.213386	-1.115283	-0.261820
H	1.943811	-4.875951	-0.046564
H	4.456611	2.923625	-1.235433
H	2.280496	4.127082	-1.243426
H	-4.830322	-3.413609	0.184695

H	-2.647528	-4.608397	0.225992
H	-0.583990	0.639671	-0.528008
H	-2.292583	4.405248	-0.852225
H	-4.542235	3.389032	-0.646534
H	-5.979644	1.269984	-0.334056
H	-6.075906	-1.175700	-0.034080
H	5.606614	-1.753216	-0.710256
H	5.698731	0.690219	-1.051091
S	0.897314	1.164650	2.186186
O	0.839123	-0.270677	2.315607
O	-0.325747	1.928468	2.165434
O	2.164653	1.842122	2.310512