

Benchmarking DFT-based excited-state methods for intermolecular charge-transfer excitations - Supporting Information

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1 Charge-Transfer descriptors

In Figure 1 the number of identified ICT states is plotted against the assignment threshold using the D_{CT} , d^{EMD} and S_{+-} descriptors for the IMOM and MOM methods. The system under investigation is the ammonia-fluorine dimer, the XCF is LRC- ω PBE and the basis is def2-TZVP. The D_{CT} and d^{EMD} descriptors produce a clearly identifiable plateau, selecting 22 ICT excitations for IMOM and 21 ICT excitations for MOM. The S_{+-} descriptor does exhibit such a plateau structure, making this descriptor unsuitable for the reliable identification of ICT excitations since the dependence on the chosen threshold is very large. In the inset, the C_+ and C_- ellipsoids produced using the IMOM and MOM densities at 10 Å separation are displayed. The ellipsoids are elongated along the direction where the charge is transferred, due to polarization of the electron density in the excited state. This effect is also present in the reference density (see Figure 2 in the main text, panel C).

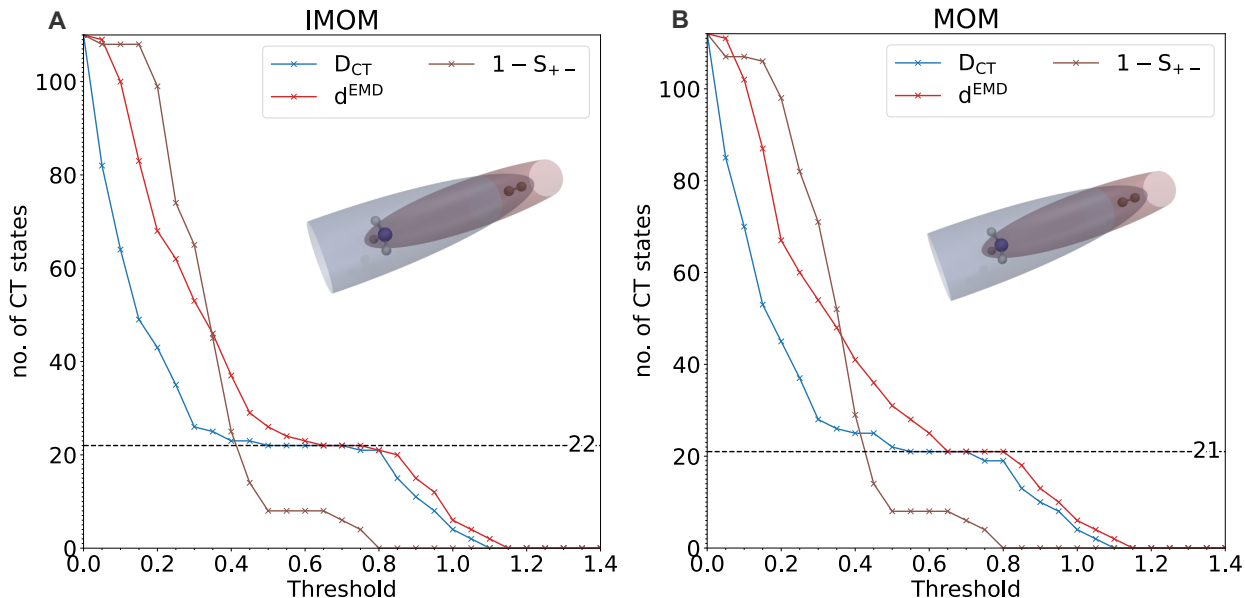


Figure 1: Number of identified CT states vs. assignment threshold for the IMOM (panel A), and MOM (panel B) methods. For a definition of the assignment threshold, see the main text. Inset: iso-surface plot of the normalized C_+ and C_- ellipsoids produced by Multiwfn, using IMOM and MOM densities at 10 Å separation. The isovalue is 0.0001 for C_+ and -0.0001 for C_- .

2 Reference excitation energies and xyz structures

Table 1: DOIs of reference ICT excitation energies and xyz structures from the literature used in this benchmark study.

Dimer	Reference exc. energy	XYZ structure source
acetone-fluorine (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
pyrazine-fluorine (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
acetone-nitromethane (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
ammonia-pyrazine (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
pyrrole-pyrazine (H-bond)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
pyrrole-pyrazine (stacked)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
ammonia-fluorine (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
ammonia-oxygen-difluoride (3 Å)	10.1021/acs.jctc.0c00154	10.1021/acs.jctc.0c00154
guanine-thymine (5'-TG-3')	10.1021/acs.jctc.0c00973	10.1021/acs.jctc.0c00973

Table 1: DOIs of reference ICT excitation energies and xyz structures from the literature used in this benchmark study.

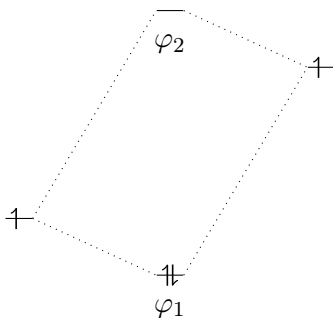
Dimer	Reference exc. energy	XYZ structure source
guanine-thymine (5'-GT-3')	10.1021/acs.jctc.0c00973	10.1021/acs.jctc.0c00973
ammonia-fluorine (6 Å)	10.1021/jp066479k	10.1021/jp066479k
benzene-tetracyanoethylene	10.1021/j100658a012	10.1021/ja8087482
toluene-tetracyanoethylene	10.1021/j100658a012	10.1021/ja8087482
o-xylene-tetracyanoethylene	10.1021/j100658a012	10.1021/ja8087482
naphthalene-tetracyanoethylene	10.1021/j100658a012	10.1021/ja8087482
anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-cyano)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-chloro)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-carbo-methoxy)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-methyl)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-nitro)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9.10-dimethyl)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-formyl)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
(9-formyl 10-chloro)anthracene-tetracyanoethylene	10.1139/v84-436	10.1021/ja8087482
ammonia-nitrous acid (3.7, 6.1, 8.6, 11, 13.5, 15.9, 18.4, 23.3 and 25.8 Å)	10.1021/acs.jctc.5b00456	10.1021/acs.jctc.5b00456
beryllium-fluorine (3.5, 4.25, 5, 8, 10 Å)	this work	10.1063/1.4928736
ammonia-fluorine (3.5, 4.25, 5, 8, 10 Å)	this work	10.1021/acs.jctc.0c00154
tetrafluor-ethylene-ethylene (3.5, 4.25, 5, 8, 10 Å)	this work	10.1021/acs.jctc.5b00456

The xyz structures for the beryllium-fluorine, ammonia-fluorine, and tetrafluor-ethylene-ethylene dimers were prepared by shifting one of the dimers in the structure indicated in the references.

3 Discussion of the singlet-triplet energy gap in ICT excitations

Consider a system of two atoms, A and B, positioned at a large separation distance and two electrons, 1 and 2. Consider further a set of two localized MOs $\{\varphi_1, \varphi_2\}$, such that one is centered on atom A and another is centered on atom B.

We start by defining the wavefunction for the electronic ground state, which consists of a Slater determinant constructed from the doubly-occupied φ_1 molecular orbital.



$$\begin{aligned} \Psi_{\text{GS}}(1, 2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [\varphi_g(1)\alpha(1)\varphi_g(2)\beta(2) - \varphi_g(2)\alpha(2)\varphi_g(1)\beta(1)] \end{aligned}$$

By exciting one electron from φ_1 to φ_2 the following singly-excited determinants D_1 to D_4 can be constructed:

φ_2	+	+	+	+
φ_1	+	+	+	+
	D_1	D_2	D_3	D_4

Since D_2 and D_4 are not spin-separable (they are not eigenfunctions of the spin operator \hat{S}), their normalized linear combinations are the lowest excited singlet wave function or part of the excited triplet manifold, respectively

$$\begin{aligned}\Psi_{T_1} &= \frac{1}{\sqrt{2}} (D_2 + D_4) \\ \Psi_{S_1} &= \frac{1}{\sqrt{2}} (D_2 - D_4)\end{aligned}$$

One can factor out symmetric and anti-symmetric spin functions, respectively. The three triplet microstates (D_1 , D_3 and $D_2 + D_4$) are characterised by the spatial function

$$\Psi_{T_1}^{\text{spatial}}(1, 2) = \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)] .$$

and hence, they have the same energy. The singlet state $D_2 - D_4$ (S_1) has the following spatial function

$$\Psi_{S_1}^{\text{spatial}}(1, 2) = \frac{1}{\sqrt{2}} [\varphi_1(1)\varphi_2(2) + \varphi_1(2)\varphi_2(1)]$$

The energy expectation value can be calculated as

$$\langle \Psi^* | \hat{H} | \Psi \rangle = E$$

with \hat{H} being the standard quantum-chemical Coulomb Hamiltonian. Using standard notation for Coulomb- and exchange integrals, we evaluate the energies of singlet and triplet determinants to

$$E_{S_1} = \varepsilon_1 + \varepsilon_2 + J_{12} + K_{12}$$

and

$$E_{T_1} = \varepsilon_1 + \varepsilon_2 + J_{12} - K_{12} .$$

The singlet-triplet energy gap is simply a function of the exchange integral

$$\Delta E_{ST} = 2K_{12} .$$

Since K_{12} is given by

$$K_{12} = \langle \varphi_1^*(1)\varphi_2(1) | \frac{1}{r_{12}} | \varphi_2^*(2)\varphi_1(2) \rangle ,$$

we see that this term vanishes when the molecular orbitals do not overlap which is the case for localized fragment orbitals at large separation distances.

In the special case of inter-molecular CT this means that $\Delta E_{ST} = 0$, meaning the singlet and triplet states are degenerate.

The same is true for a many-electron Hamiltonian and wave function which is numerically confirmed by a computation of excitation energies as shown in Fig. 2.

Here, the 20 lowest-lying singlet and triplet excited states were computed for the ammonia-fluorine dimer at various separation distances using the TDA method, LRC- ω PBE XCF, and def2-SVP basis set. The ICT states were selected by comparing the D_{CT} descriptor to the donor-acceptor distance R_{DA} , as explained in the manuscript. TDA produces identical excitation energies for all singlet and triplet states for all ICT excitations. The same holds true for the IMOM method. In Figure 3, the 5th-lowest-lying ICT state was computed by using a spin-broken determinant (panel A), to approximate the singlet wavefunction, and a triplet determinant (panel B). Converged calculations show no significant difference for the singlet and triplet energy at each distance.

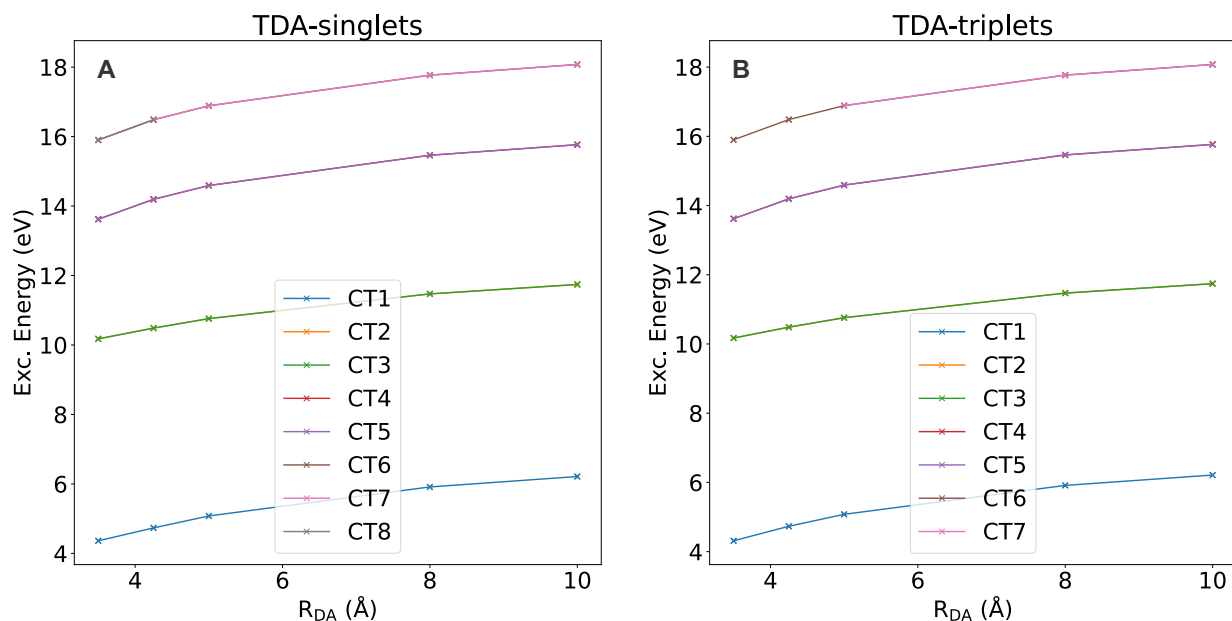


Figure 2: Excitation energies of the ICT states in the ammonia-fluorine dimer at various separation distances. The ICT states were selected among the 20 lowest-lying singlet (panel A) and triplet (panel B) excited states.

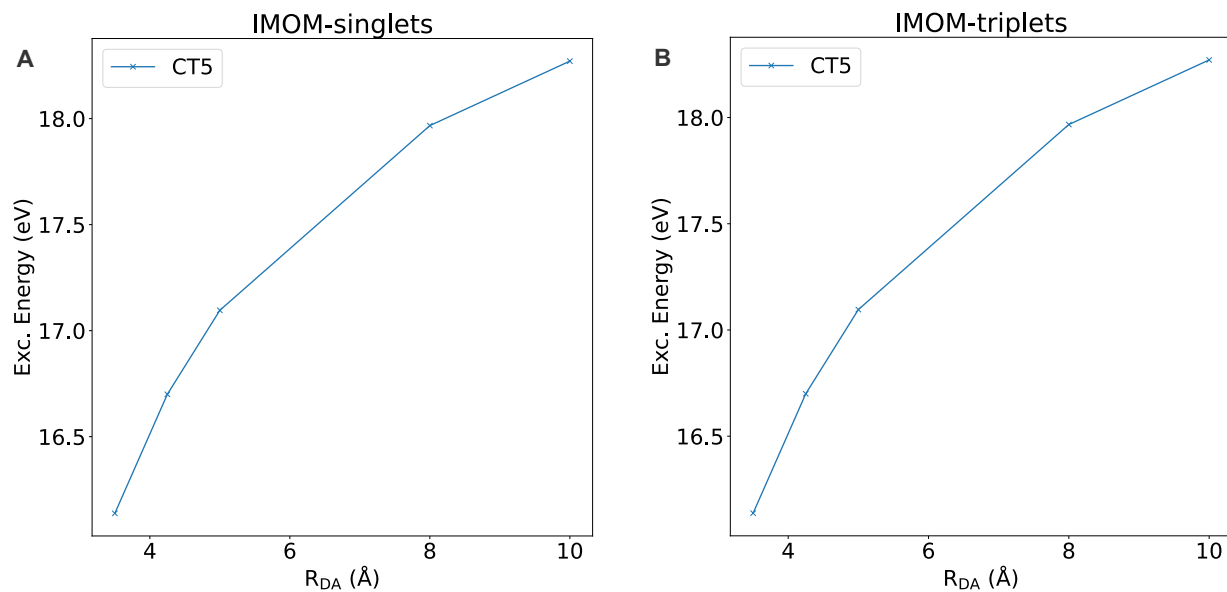


Figure 3: Excitation energies of the 5th-lowest-lying ICT state in the ammonia-fluorine dimer at various separation distances using IMOM. The ICT states were computed by using the ground-state MOs guess and the dominant configurations from the TDA calculations. Panel A shows the energy computed for a spin-broken determinant, whereas panel B shows the energy for a triplet determinant.

4 Calculation of a large supramolecular system

As mentioned in section 3, we tested CPU times on a supramolecular system previously investigated by Clever *et al.*.

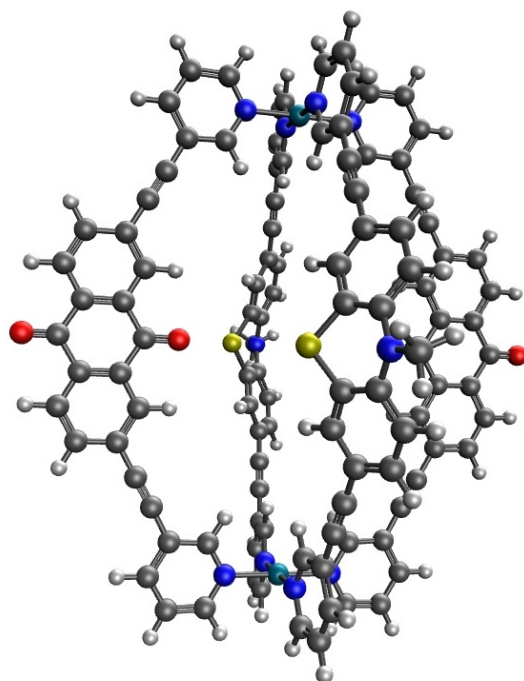


Figure 4: Balls-and-sticks representation of the supramolecular system computed to test the CPU times.

The system has structure:

C	3.48032	-0.39189	7.93804
C	2.26390	-0.39500	8.58776
C	1.06926	-0.36448	7.86904
C	3.52028	-0.35910	6.53832
C	2.32900	-0.33072	5.81305
C	1.10365	-0.33234	6.46822
C	-1.40847	-0.28485	6.40577
C	-1.44502	-0.31693	7.80654
C	-2.67419	-0.30167	8.46499
C	-2.59883	-0.23765	5.69055
C	-3.82489	-0.22052	6.35572
C	-3.85585	-0.25341	7.75564
H	4.40175	-0.41473	8.49924
H	2.21014	-0.42020	9.66600
H	2.33953	-0.30654	4.73302
H	-2.55482	-0.21405	4.61135
H	-4.80424	-0.24092	8.27031
H	-2.67508	-0.32773	9.54454
C	-0.13277	-0.29926	5.65381
C	-0.20789	-0.36667	8.62287
O	-0.10225	-0.28285	4.43777
O	-0.23870	-0.40614	9.83253
C	4.75932	-0.35666	5.86837
C	-5.02803	-0.17158	5.62492
C	-6.06435	-0.12539	5.00302
C	5.82672	-0.34851	5.29970
C	7.07949	-0.34766	4.66124
C	-7.28242	-0.07377	4.30257
C	7.16920	-0.33154	3.26557
C	8.27498	-0.36617	5.39416
C	9.47808	-0.36850	4.71420

C	9.47299	-0.35420	3.32703
C	-7.30110	-0.05169	2.90428
C	-9.60399	0.02227	2.84999
C	-8.51303	-0.04466	4.97454
C	-9.67947	0.00407	4.23510
H	8.24433	-0.37864	6.47244
H	10.41388	-0.38215	5.24905
H	-10.64078	0.02775	4.72224
H	-8.53710	-0.06057	6.05294
N	8.33602	-0.33587	2.62767
N	-8.43356	-0.00529	2.20866
H	10.40099	-0.35729	2.75887
H	6.26618	-0.31480	2.65661
H	-6.36873	-0.07243	2.34128
H	-10.50153	0.06004	2.23607
C	-3.47486	-0.19946	-7.11604
C	-2.26014	-0.25025	-7.76706
C	-1.06446	-0.26914	-7.04968
C	-3.51180	-0.16694	-5.71626
C	-2.31943	-0.18640	-4.99244
C	-1.09603	-0.23688	-5.64886
C	1.41522	-0.30073	-5.58836
C	1.44968	-0.33252	-6.98913
C	2.67800	-0.37452	-7.64801
C	2.60650	-0.31185	-4.87370
C	3.83188	-0.35361	-5.53914
C	3.86097	-0.38491	-6.93911
H	-4.39701	-0.18480	-7.67638
H	-2.20868	-0.27649	-8.84540
H	-2.32741	-0.16170	-3.91245
H	2.56369	-0.28698	-3.79454
H	4.80862	-0.41701	-7.45435
H	2.67736	-0.39873	-8.72763

C	0.14105	-0.25537	-4.83508
C	0.21097	-0.32356	-7.80484
O	0.11232	-0.23436	-3.61923
O	0.23923	-0.35725	-9.01466
C	-4.74804	-0.11429	-5.04363
C	5.03471	-0.36303	-4.80663
C	6.06570	-0.36927	-4.17399
C	-5.80896	-0.06789	-4.46431
C	-7.05999	-0.01730	-3.82494
C	7.28283	-0.38007	-3.47053
C	-7.15135	-0.01403	-2.42902
C	-8.25403	0.03067	-4.55932
C	-9.45698	0.07779	-3.88111
C	-9.45400	0.07580	-2.49371
C	7.30092	-0.36002	-2.07188
C	9.60516	-0.39631	-2.01498
C	8.51451	-0.40945	-4.14091
C	9.68096	-0.41725	-3.40017
H	-8.22167	0.03000	-5.63763
H	-10.39125	0.11517	-4.41754
H	10.64271	-0.43953	-3.88655
H	8.53882	-0.42536	-5.21931
N	-8.31858	0.03081	-1.79299
N	8.43379	-0.36834	-1.37515
H	-10.38271	0.11126	-1.92706
H	-6.24968	-0.04909	-1.81835
H	6.36783	-0.33634	-1.50978
H	10.50346	-0.40205	-1.40029
Pd	8.38579	-0.34790	0.62061
Pd	-8.37786	0.01537	0.20230
C	3.69648	6.93224	1.79916
C	2.49471	7.60224	1.85174
C	1.36286	7.14779	1.15908

C	3.81143	5.73819	1.08140
C	2.67899	5.23960	0.42915
C	1.49122	5.93821	0.45691
C	-1.19582	5.98404	0.41941
C	-1.04633	7.19213	1.11827
C	-2.18566	7.70417	1.75620
C	-2.40764	5.33067	0.35468
C	-3.54276	5.88004	0.96003
C	-3.40886	7.07864	1.66767
H	4.55040	7.32128	2.33122
H	2.43487	8.49197	2.45633
H	2.73596	4.32160	-0.13557
H	-2.48073	4.41146	-0.20616
H	-4.26830	7.50959	2.15702
H	-2.11414	8.60806	2.33656
C	5.02573	5.04255	1.01640
C	-4.78144	5.23605	0.84592
C	-5.84515	4.66604	0.73114
C	6.06834	4.42776	0.95195
C	7.28373	3.73514	0.88263
C	-7.08704	4.03361	0.59468
C	7.30565	2.34639	0.69727
C	8.51971	4.39374	1.00411
C	9.68456	3.65808	0.92670
C	9.61073	2.28287	0.74699
C	-7.16795	2.65063	0.38375
C	-9.47324	2.70132	0.32153
C	-8.29411	4.75067	0.66984
C	-9.48833	4.07546	0.52340
H	8.54323	5.46208	1.15094
H	10.64649	4.13780	1.00695
H	-10.42837	4.60114	0.56646
H	-8.27216	5.81636	0.83492

N	8.43773	1.65254	0.64055
N	-8.32867	2.01525	0.25982
H	10.50817	1.67033	0.68472
H	6.37328	1.79117	0.59739
H	-6.26032	2.05112	0.31839
H	-10.39553	2.13541	0.20467
N	0.16991	7.85136	1.18918
S	0.14925	5.28136	-0.48847
C	0.17959	9.28741	1.43236
C	-3.76030	-7.26338	1.61159
C	-2.56143	-7.93095	1.72551
C	-1.39693	-7.47450	1.09085
C	-3.84092	-6.07018	0.88782
C	-2.67800	-5.56999	0.29284
C	-1.49165	-6.26592	0.38172
C	1.19414	-6.30563	0.48293
C	1.01111	-7.51328	1.17452
C	2.11660	-8.02239	1.87154
C	2.40664	-5.65016	0.47981
C	3.50982	-6.19695	1.14366
C	3.34152	-7.39468	1.84554
H	-4.63933	-7.65353	2.10015
H	-2.53026	-8.82013	2.33308
H	-2.70826	-4.65274	-0.27518
H	2.50705	-4.73178	-0.07818
H	4.17546	-7.82333	2.37901
H	2.01672	-8.92577	2.44848
C	-5.05129	-5.37587	0.76258
C	4.75353	-5.55474	1.09091
C	5.82424	-4.98966	1.02986
C	-6.09193	-4.76572	0.64463
C	-7.30160	-4.07154	0.51588
C	7.07372	-4.36181	0.95571

C	-7.31086	-2.68253	0.33172
C	-8.54366	-4.72725	0.57355
C	-9.70124	-3.98849	0.43765
C	-9.61516	-2.61324	0.26364
C	7.16924	-2.97998	0.74406
C	9.47455	-3.03683	0.79637
C	8.27349	-5.08181	1.09333
C	9.47542	-4.41029	1.00368
H	-8.57739	-5.79571	0.71751
H	-10.66719	-4.46589	0.46803
H	10.41066	-4.93835	1.09509
H	8.24052	-6.14680	1.26108
N	-8.43678	-1.98567	0.21819
N	8.33644	-2.34802	0.67568
H	-10.50665	-1.99831	0.15633
H	-6.37310	-2.12982	0.28030
H	6.26750	-2.37846	0.63123
H	10.40291	-2.47378	0.72301
N	-0.20558	-8.17537	1.18251
S	-0.10403	-5.60723	-0.49410
C	-0.22422	-9.61153	1.42435
H	-1.23393	-9.96463	1.39769
H	0.20025	-9.81702	2.38482
H	0.34733	-10.10800	0.66821
H	-0.82412	9.65797	1.42030
H	0.74888	9.77467	0.66855
H	0.62113	9.48456	2.38686