Gold(I)-Containing Light-Emitting Molecules with an Inverted Singlet-Triplet Gap

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Electronic Supplementary Information

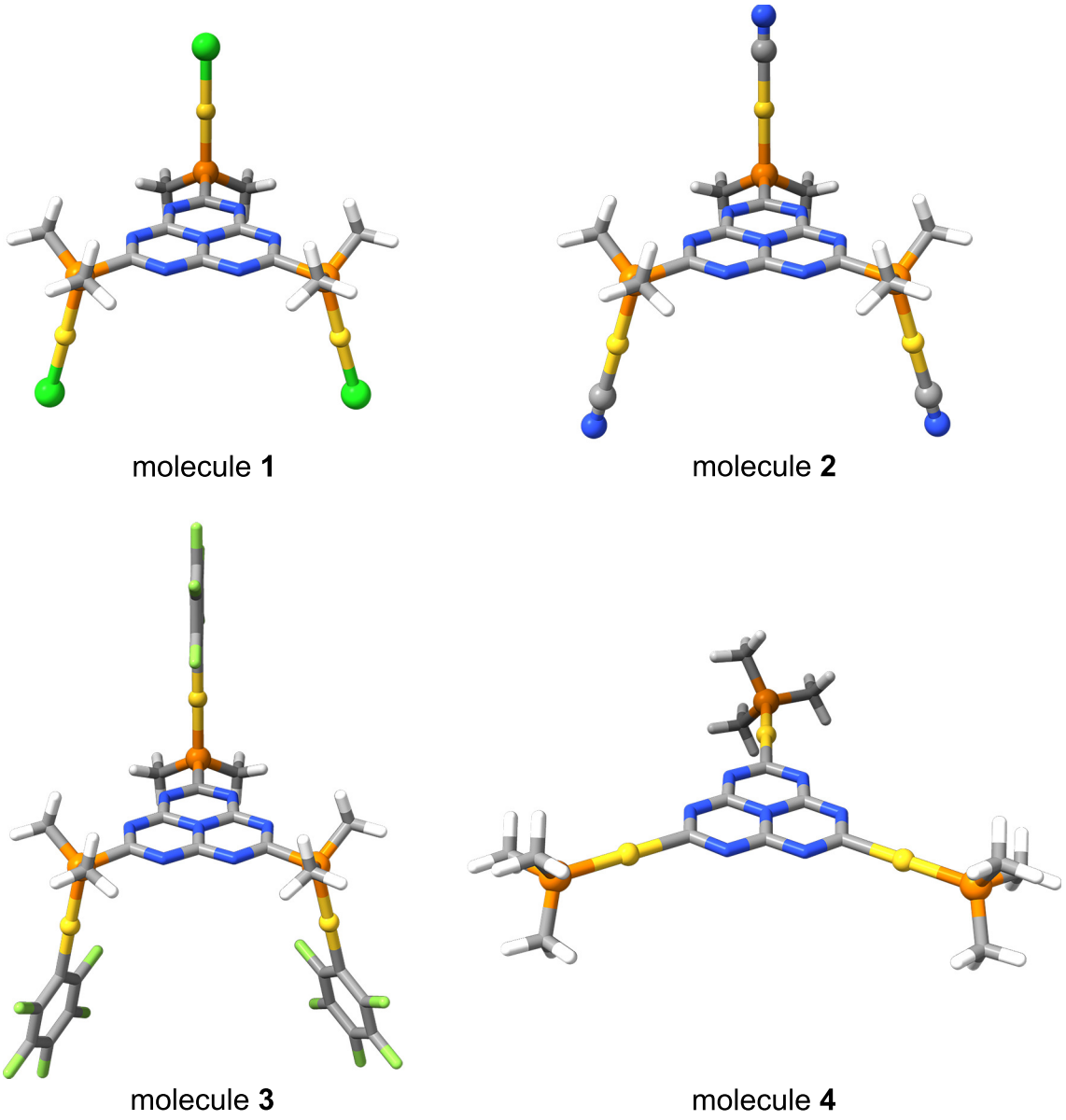

Figure S1: Structure of molecules **1-4** (DFT/PBE0-D3(BJ)/def2-TZVP level of theory). Colour code: C, grey; H, white; Au, yellow; Cl, green; F, light green; N, blue; P, orange.

Table S1: Selected bond distances (in Å) and angles (in °) of heptazine, 2,4,6-tris(diphenylphosphino)heptazine, and molecules **1-4**

Model	C–N	C–N[9b]	C–P	Au–P(C)	Au–X
Heptazine[a]	1.305(4)-1.369(4)	1.378(3)-1.397(3)	-	-	-
2,4,6-tris(diphenylphosphino)heptazine[b]	1.328(3)-1.341(2)	1.391(3)-1.394(3)	1.834(2)-1.841(2)	-	-
1 (X = Cl)	1.32-1.33	1.39	1.83	2.22-2.23	2.26-2.27
2 (X = CN)	1.32-1.33	1.39	1.83	2.27-2.28	1.99-2.00
3 (X = C_6F_5)	1.32-1.33	1.39	1.83	2.28	2.05
4 (X = PMe_3)	1.33-1.34	1.39	-	2.30	2.05

[a] R. S. Hosmane, M. A. Rossman and N. J. Leonard, *J. Am. Chem. Soc.*, 1982, **104**, 5497–5499

[b] C. Posern, U. Böhme and E. Kroke, *Z. Anorg. All. Chem.*, 2018, **644**, 121–126

Table S2: First singlet-to-singlet vertical excitation energies at the TD-DFT/PBE0-D3(BJ)/def2-TZVP and TD-DFT/ωB97X-D/def2-TZVP levels of theory for molecules **1-4** (energies are given in eV)

Molecule	irrep[a]	$E(S_1 \leftarrow S_0)$ ($f \cdot 10^4$)	Contributions (%)	
		PBE0 functional		
1	a''	2.702 (0.200)	64 a'' → 83 a'	(78.4)
			63 a'' → 83 a'	(18.7)
2	a''	3.000 (3.502)	57 a'' → 80 a'	(91.1)
3	a	2.281 (0.125)	242 a → 243 a	(99.4)
4	a	2.951 (0.005)	134 a → 135 a	(97.0)
		ωB97X-D functional		
1	a''	3.174 (0.509)	60 a'' → 83 a'	(93.4)
2	a''	3.171 (0.447)	57 a'' → 80 a'	(83.2)
			58 a'' → 80 a'	(5.1)
3	a	3.187(0.160)	233 a → 243 a	(95.1)
4	a	3.173 (0.002)	134 a → 135 a	(87.6)
			134 a → 141 a	(9.6)

[a] Irreducible representation

Table S3: First singlet-to-triplet vertical excitation energies at the TD-DFT/PBE0-D3(BJ)/def2-TZVP and TD-DFT/ωB97X-D/def2-TZVP levels of theory for molecules **1-4** (energies are given in eV)

Molecule	irrep[a]	$E(T_1 \leftarrow S_0)$	Contributions (%)	
		PBE0 functional		
1	a''	2.652	63 a'' → 83 a'	(74.4)
			64 a'' → 83 a'	(20.6)
2	a''	2.760	57 a'' → 80 a'	(92.7)
3	a	2.278	242 a → 243 a	(99.3)
4	a	2.736	134 a → 135 a	(96.1)
		ωB97X-D functional		
1	a''	2.934	60 a'' → 83 a'	(93.1)
2	a''	2.928	57 a'' → 80 a'	(83.0)
			58 a'' → 80 a'	(5.0)
3	a	2.948	233 a → 243 a	(94.7)
4	a	2.956	134 a → 135 a	(86.9)
			134 a → 141 a	(9.7)

[a] Irreducible representation

Table S4: Spin contamination of the ΔSCF calculations using the PBE0 and ωB97X-D functionals

	PBE0		ωB97X-D	
Molecule	S_1	T_1	S_1	T_1
1	1.11	2.01	1.16	2.02
2	1.12	2.02	1.16	2.02
3	1.08	-[a]	1.16	2.02

[a] The ΔSCF calculation did not converge

1 Cartesian coordinates of molecule 1.

C	0.7925856	-6.9323107	-1.7660438
P	2.1606248	-6.5123949	-2.9120869
C	-0.2445015	-8.4995372	-0.5128682
C	-0.8562813	-6.1648812	-0.4263985
C	-2.5442005	-5.5741532	0.9528847
C	-2.0112289	-7.7687565	0.9626019
C	-1.3663296	-9.9294529	0.8283864
N	-1.0338844	-7.4774336	0.0109666
N	-2.1639003	-9.0186344	1.3693323
N	-0.4317701	-9.7418313	-0.0932696
N	0.6738712	-8.2071406	-1.4214721
N	0.0782506	-5.9052491	-1.3264869
N	-1.6299809	-5.2095400	0.0646635
N	-2.7674944	-6.7895227	1.4332326
P	-1.5214628	-11.6237600	1.5114344
P	-3.7094710	-4.2672418	1.4936048
Au	-5.4195761	-4.2754939	0.0681876
Au	3.9292902	-5.8888054	-1.7164383
Au	-0.2975304	-11.7632801	3.3632334
C	-1.0352338	-12.6886260	0.1346599
H	-1.6801743	-12.5305903	-0.7310145
H	-0.0034751	-12.4657688	-0.1339502
H	-1.1017073	-13.7269902	0.4618107
C	-2.6924987	-2.7739130	1.5360952
H	-1.8660222	-2.8830343	2.2400031
H	-2.2990594	-2.5904542	0.5370911
H	-3.3219993	-1.9337886	1.8317036
C	1.4344668	-5.2446201	-3.9785636
H	0.5682497	-5.6327399	-4.5167628
H	1.1332436	-4.4005510	-3.3593150
H	2.1927817	-4.9127597	-4.6886064
C	2.3467357	-7.9989513	-3.9226932
H	2.6174955	-8.8318696	-3.2751657
H	1.4213825	-8.2331513	-4.4510546
H	3.1506822	-7.8296908	-4.6400930
C	-3.3068304	-11.8252925	1.7207690
H	-3.6642018	-11.0618634	2.4107878
H	-3.8276312	-11.7304865	0.7666076
H	-3.4967325	-12.8099269	2.1494736
C	-4.0778941	-4.7015121	3.2087813
H	-4.5284760	-5.6929894	3.2291112
H	-3.1717131	-4.6992901	3.8164621
H	-4.7907706	-3.9772227	3.6045941
Cl	-7.1544598	-4.2949300	-1.3900528
Cl	5.7399103	-5.2337915	-0.5247107
Cl	0.9273851	-11.9288494	5.2605525

2 Cartesian coordinates of molecule 2.

C	-0.1209681	-0.9994638	-0.9569529
C	2.0635738	-0.6957620	-1.4435599
C	1.2228542	0.6844875	0.1338074
C	0.2267059	1.9703606	1.7004227
C	-1.1047840	0.4292221	0.7241078
C	-2.2950302	-1.1497488	-0.3660827
N	0.0007577	0.0356652	-0.0299435
N	-2.2630246	-0.1858223	0.5430787
N	-1.2933921	-1.5939465	-1.1121414
N	0.9375737	-1.3593989	-1.6648887
N	2.2606688	0.3050460	-0.5969018
N	1.3200338	1.6701057	1.0139219
N	-0.9717642	1.4124568	1.5995068
P	-3.9425757	-1.8680677	-0.7216607
P	0.3936059	3.2402673	3.0120485
P	3.5297139	-1.3078270	-2.3583482
C	-4.7814222	-1.8591237	0.8786256
H	-4.2445410	-2.4701826	1.6055259
H	-4.8398880	-0.8322669	1.2375168
H	-5.7915484	-2.2477923	0.7437882
C	-1.1348963	4.1966553	2.8641763
H	-1.2147077	4.6607849	1.8800975
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C	4.5981938	0.1426658	-2.4942802
H	4.0938954	0.9543280	-3.0202996
H	4.8729327	0.4730030	-1.4933219
H	5.5015424	-0.1437441	-3.0344670
C	2.8791625	-1.6442721	-4.0125334
H	2.0891284	-2.3899283	-3.9303990
H	2.4824905	-0.7372788	-4.4710424
H	3.6850128	-2.0465573	-4.6275281
C	-3.5906461	-3.5917573	-1.1340872
H	-2.9253663	-3.6163870	-1.9963313
H	-3.1209832	-4.1070614	-0.2950955
H	-4.5280048	-4.0857652	-1.3927726
C	1.7382390	4.2974429	2.4305664
H	2.6458842	3.7006990	2.3492743
H	1.5021413	4.7355101	1.4599217
H	1.8974265	5.0882307	3.1648662
Au	-4.8415528	-0.5768096	-2.3671154
Au	4.3726012	-3.1026571	-1.2453277
Au	0.7055714	2.1798231	4.9991689
C	0.9540944	1.2576587	6.7505038
N	1.0887883	0.7225886	7.7660152
C	5.1049366	-4.6934962	-0.2902255
N	5.5226739	-5.6208605	0.2585912
C	-5.5767768	0.5894060	-3.8096140
N	-5.9834495	1.2772112	-4.6447808

3 Cartesian coordinates of molecule 3.

C	0.4215848	-0.6344752	-1.4907473
C	2.5008935	-0.1495015	-0.7538542
C	0.8320692	1.0239229	0.2158635
C	-0.9513242	2.1200331	1.0627810
C	-1.4279925	0.5605619	-0.4993464
C	-1.7232208	-1.0231973	-2.0825802
N	-0.0582006	0.3136149	-0.5889324
N	-2.2595775	-0.1281500	-1.2641244
N	-0.4372446	-1.3004832	-2.2481522
N	1.7254915	-0.8512121	-1.5696515
N	2.1284306	0.7738125	0.1216322
N	0.3616839	1.9352708	1.0524423
N	-1.8650799	1.4803145	0.3463412
P	-2.9160653	-2.0687398	-2.9971291
P	-1.5610497	3.5078647	2.0887488
P	4.2804511	-0.5801794	-0.7456849
C	-2.0284892	-2.5352456	-4.5012962
H	-1.7451337	-1.6560338	-5.0815044
H	-1.1340529	-3.0904300	-4.2214861
H	-2.6747367	-3.1802859	-5.0980249
C	-0.4613214	3.5066816	3.5240013
H	-0.5326187	2.5669815	4.0735443
H	0.5617862	3.6503192	3.1786933
H	-0.7380104	4.3372107	4.1745955
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H	4.8717338	1.7047436	-1.3154914
H	4.7635786	1.4370627	0.4427779
H	6.1776491	0.8460937	-0.4532355
C	4.6140402	-1.0877433	-2.4487904
H	3.9849752	-1.9445290	-2.6870398
H	4.4085859	-0.2774753	-3.1497087
H	5.6610707	-1.3843538	-2.5226646
C	-4.2075391	-0.9005877	-3.4904290
H	-4.6308999	-0.4536258	-2.5916075
H	-3.8065673	-0.1176139	-4.1358135
H	-4.9893730	-1.4489260	-4.0172069
C	-3.1811901	2.9474156	2.6636106
H	-3.8099421	2.7520735	1.7957749
H	-3.0938272	2.0398467	3.2626291
H	-3.6325647	3.7415972	3.2595396
Au	-1.5042442	5.3308132	0.7224340
Au	-3.5502855	-3.7468546	-1.5947587
Au	4.5923899	-2.1455475	0.8779087
C	-1.4213236	6.9188641	-0.5733334
C	-0.9423340	6.7721531	-1.8621725
C	-1.8364560	8.1898451	-0.2200707
C	-0.8718507	7.8191196	-2.7649651
C	-1.7848150	9.2674886	-1.0886220
C	-1.2978579	9.0768721	-2.3712414
C	4.8573419	-3.5426147	2.3550951
C	4.0548818	-3.5694656	3.4812454
C	5.8422887	-4.5109390	2.2854394
C	4.2081868	-4.5015924	4.4934121
C	6.0327474	-5.4630750	3.2726653
C	5.2068543	-5.4552430	4.3846340
C	-4.1281106	-5.2303305	-0.3026465

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C    -4.1010019   -5.0477019    1.0680554
C    -4.5696332   -6.4642537   -0.7443127
C    -4.4882341   -6.0273032    1.9664888
C    -4.9664922   -7.4737824    0.1164726
C    -4.9242466   -7.2497966    1.4827415
F    -3.6863149   -3.8819680    1.5842199
F    -4.4493711   -5.8152052    3.2781593
F    -5.3002941   -8.2020979    2.3247020
F    -5.3858881   -8.6478982   -0.3439365
F    -4.6291774   -6.7277535   -2.0562272
F     3.0743823   -2.6678112    3.6312862
F     3.4174736   -4.4965828    5.5618269
F     5.3717965   -6.3573577    5.3417786
F     6.9899948   -6.3795811    3.1718366
F     6.6658746   -4.5585996    1.2301345
F    -0.5177824    5.5734323   -2.2919796
F    -0.4046318    7.6382432   -3.9971551
F    -1.2396694   10.0943169   -3.2192548
F    -2.1926602   10.4754842   -0.7142208
F    -2.3150086    8.4241131    1.0081581
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4 Cartesian coordinates of molecule 4 (S_0 geometry).

C	-0.0223868	-1.3895448	-0.0009576
C	2.2665614	-1.3586142	-0.0007087
C	1.2180368	0.6763406	-0.0004191
C	0.0466891	2.6431511	-0.0001259
C	-1.1912799	0.7176154	-0.0006942
C	-2.3089365	-1.2802102	-0.0011788
N	0.0014476	0.0014530	-0.0006905
N	-2.3437835	0.0584436	-0.0009687
N	-1.1917598	-2.0184431	-0.0011443
N	1.1247161	-2.0581437	-0.0009542
N	2.3472804	-0.0219768	-0.0004581
N	1.2234222	2.0040243	-0.0001705
N	-1.1512244	2.0447607	-0.0003888
Au	0.0825934	4.6930553	0.0004563
Au	4.0247717	-2.4131897	-0.0010814
Au	-4.1023605	-2.2737246	-0.0016964
P	-6.1171781	-3.3927850	-0.0020308
P	5.9997648	-3.6011389	-0.0006706
P	0.1195443	6.9974637	0.0016887
C	1.7778401	7.7438652	-0.0448317
H	1.7247294	8.8352473	-0.0417045
H	2.3492642	7.4057740	0.8208739
H	2.2986424	7.4084141	-0.9428899
C	-0.7362771	7.7787055	-1.4009853
H	-1.7800921	7.4614215	-1.4076493
H	-0.6880698	8.8686540	-1.3402884
H	-0.2771497	7.4472897	-2.3335355
C	-0.6544302	7.7751549	1.4530574
H	-0.1426942	7.4413562	2.3569284
H	-0.6095589	8.8652492	1.3924443
H	-1.6962333	7.4579668	1.5186589
C	7.5053753	-2.5970649	-0.1857508
H	7.5570546	-1.8723428	0.6281104
H	8.4037471	-3.2189982	-0.1764237
H	7.4564402	-2.0443780	-1.1251202
C	6.3150314	-4.5620256	1.5118558
H	5.4997341	-5.2706938	1.6646429
H	7.2612869	-5.1048413	1.4490488
H	6.3407229	-3.8874086	2.3688947
C	6.1504941	-4.8393869	-1.3251199
H	7.1033785	-5.3710387	-1.2672614
H	5.3304246	-5.5543899	-1.2443022
H	6.0708404	-4.3432095	-2.2934969
C	-6.3674976	-4.5207852	-1.4074513
H	-5.5714521	-5.2667709	-1.4164330
H	-7.3359190	-5.0233420	-1.3475340
H	-6.3100612	-3.9551205	-2.3385805
C	-6.4038068	-4.4553730	1.4467829
H	-7.3706683	-4.9607325	1.3852886
H	-5.6086961	-5.1997111	1.5101961
H	-6.3698210	-3.8475971	2.3521775
C	-7.5919061	-2.3285557	-0.0450893
H	-8.5110104	-2.9194830	-0.0428372
H	-7.5837567	-1.6667229	0.8221982
H	-7.5618239	-1.7076631	-0.9416803

5 Cartesian coordinates of molecule 4 (S_1 geometry).

C	1.3851072	-0.0015812	0.2359577
C	1.3338405	2.3042258	0.2324567
C	-0.6911842	1.2003286	0.2359577
C	-2.6624383	0.0030269	0.2324567
C	-0.6939230	-1.1987474	0.2359577
C	1.3285978	-2.3072527	0.2324567
N	0.0000000	-0.0000000	-0.0293533
N	-0.0201488	-2.3299986	0.3329374
N	2.0254806	-1.1522524	0.3316570
N	2.0279124	1.1475499	0.3329374
N	-0.0148604	2.3302438	0.3316570
N	-2.0077635	1.1824487	0.3329374
N	-2.0106201	-1.1779914	0.3316570
Au	-4.6950581	0.0059681	0.1013877
Au	2.3526975	4.0630556	0.1013877
Au	2.3423606	-4.0690236	0.1013877
P	3.4837413	-6.0513054	-0.0459855
P	3.4987136	6.0426611	-0.0459855
P	-6.9824549	0.0086443	-0.0459855
C	3.4142347	-6.8745763	-1.6660389
H	3.9756489	-7.8119785	-1.6606855
H	2.3730480	-7.0759883	-1.9215941
H	3.8261032	-6.2084368	-2.4252820
C	-7.6606750	0.4804742	-1.6660389
H	-8.7531962	0.4629763	-1.6606855
H	-7.3145097	1.4828743	-1.9215941
H	-7.2897156	-0.2092841	-2.4252820
C	4.2464404	6.3941021	-1.6660389
H	4.7775474	7.3490022	-1.6606855
H	4.9414617	5.5931140	-1.9215941
H	3.4636124	6.4177210	-2.4252820
C	2.9232593	-7.3445669	1.1020550
H	1.8686908	-7.5547916	0.9186348
H	3.5038988	-8.2622754	0.9819114
H	3.0221019	-6.9828189	2.1263394
C	-7.8222111	1.1406666	1.1020550
H	-7.4769869	2.1590621	0.9186348
H	-8.9072898	1.0966723	0.9819114
H	-7.5583494	0.8741924	2.1263394
C	4.8989518	6.2039002	1.1020550
H	5.4033910	7.1656031	0.9819114
H	4.5362476	6.1086264	2.1263394
H	5.6082961	5.3957295	0.9186348
C	5.2661867	-5.9318401	0.2883931
H	5.7531625	-6.9060968	0.2031596
H	5.7185926	-5.2358379	-0.4192714
H	5.4169431	-5.5364158	1.2937524
C	2.5040308	7.5265715	0.2883931
H	2.0862052	7.4594182	1.2937524
H	3.1042740	8.4354332	0.2031596
H	1.6750723	7.5703654	-0.4192714
C	-7.7702175	-1.5947314	0.2883931
H	-7.5031483	-1.9230024	1.2937524
H	-8.8574365	-1.5293365	0.2031596
H	-7.3936649	-2.3345275	-0.4192714

6 Cartesian coordinates of molecule 4 (T_1 geometry).

C	1.3926675	-0.0019652	0.0933578
C	1.3356990	2.3059695	0.1010576
C	-0.6946318	1.2070680	0.0933578
C	-2.6648776	0.0037645	0.1010576
C	-0.6980356	-1.2051028	0.0933578
C	1.3291786	-2.3097340	0.1010576
N	-0.0000000	0.0000000	-0.0680534
N	-0.0249090	-2.3395309	0.1530375
N	2.0353229	-1.1539346	0.1527261
N	2.0385477	1.1481937	0.1530375
N	-0.0183248	2.3396087	0.1527261
N	-2.0136388	1.1913373	0.1530375
N	-2.0169982	-1.1856740	0.1527261
Au	-4.7009897	0.0066758	0.0427476
Au	2.3562762	4.0678386	0.0427476
Au	2.3447134	-4.0745144	0.0427476
P	3.4878618	-6.0591557	-0.0207383
P	3.5034518	6.0501548	-0.0207383
P	-6.9913137	0.0090009	-0.0207383
C	3.4499634	-6.9313704	-1.6159505
H	4.0098528	-7.8686745	-1.5710965
H	2.4138386	-7.1395557	-1.8862837
H	3.8778946	-6.2887530	-2.3865664
C	-7.7277245	0.4779293	-1.6159505
H	-8.8193984	0.4617028	-1.5710965
H	-7.3899559	1.4793323	-1.8862837
H	-7.3851672	-0.2139788	-2.3865664
C	4.2777611	6.4534411	-1.6159505
H	4.8095456	7.4069717	-1.5710965
H	4.9761173	5.6602234	-1.8862837
H	3.5072725	6.5027318	-2.3865664
C	2.9057786	-7.3178302	1.1546910
H	1.8554055	-7.5355392	0.9562339
H	3.4896868	-8.2378945	1.0749041
H	2.9831817	-6.9245573	2.1691700
C	-7.7903162	1.1424370	1.1546910
H	-7.4536711	2.1609413	0.9562339
H	-8.8790694	1.0967898	1.0749041
H	-7.4884334	0.8787675	2.1691700
C	4.8845376	6.1753932	1.1546910
H	5.3893825	7.1411047	1.0749041
H	4.5052517	6.0457898	2.1691700
H	5.5982656	5.3745979	0.9562339
C	5.2635688	-5.9288629	0.3439589
H	5.7519531	-6.9051154	0.2980069
H	5.7296220	-5.2547053	-0.3759385
H	5.3952728	-5.5026086	1.3393670
C	2.5027615	7.5228157	0.3439589
H	2.0677624	7.4237477	1.3393670
H	3.1040288	8.4338953	0.2980069
H	1.6858973	7.5893508	-0.3759385
C	-7.7663303	-1.5939528	0.3439589
H	-7.4630353	-1.9211390	1.3393670
H	-8.8559820	-1.5287798	0.2980069
H	-7.4155193	-2.3346455	-0.3759385