Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION

On the structure of the $Au_{18}(SR)_{14}$ cluster

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PART I.

The following methodology was used to obtain the initial structures for the $Au_{18}(SCH_3)_{14}$ cluster isomers.

First, a prolate Au_8 core of the $Au_{18}(SCH_3)_{14}$ cluster is dictated by the electron shell model, where it is established that the electronic stability of $Au_{18}(SCH_3)_{14}$ corresponds to a shell-closing electron count of 4, being this a magic number in the non-spherical (cylindrical) model.

Second, by applying the algorithm proposed by Jiang, (D. Jiang, *Chem. Eur. J.*, 2011, **17**, 12289-12293), based on the *staple fitness concept*, we have found that an Au_8 cluster core with an initial D_{2d} symmetry can be covered with 2 dimer and 2 trimer motifs in two ways or combinations. However, one of these combinations results in isomers with higher energy by 1.33 eV, which reduce the possibilities to only one combination. Once the Au_8 core is covered with two dimer and two trimer motifs, it is possible by means of permutations between these motifs, and by using different orientations of the methyl CH_3 groups, to obtain different structural isomers.

We have found that when the methyl groups are arranged in a *trans* orientation, the energy increases resulting in less stable isomers. The energy difference between **Iso1**, with the methyl groups in *cis* and *trans* orientation, and an isomer with all its methyl groups arranged in a *trans* orientation is of 0.14 eV.

PART II.

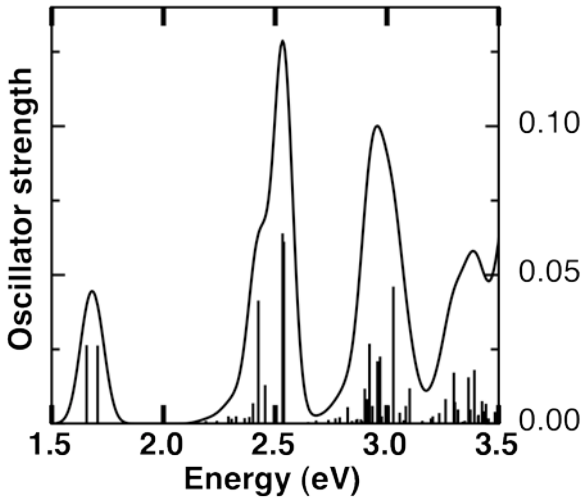

Figure S1. Calculated absorption spectrum for $Au_{12}(SCH_3)_9^+$ cluster in good agreement with the calculations reported in Figure 7 of the Reference: D. Jiang, R. L. Whetten, W. Luo, S. Dai, *J. Phys. Chem. C* 2009, **113**, 17291-17295.

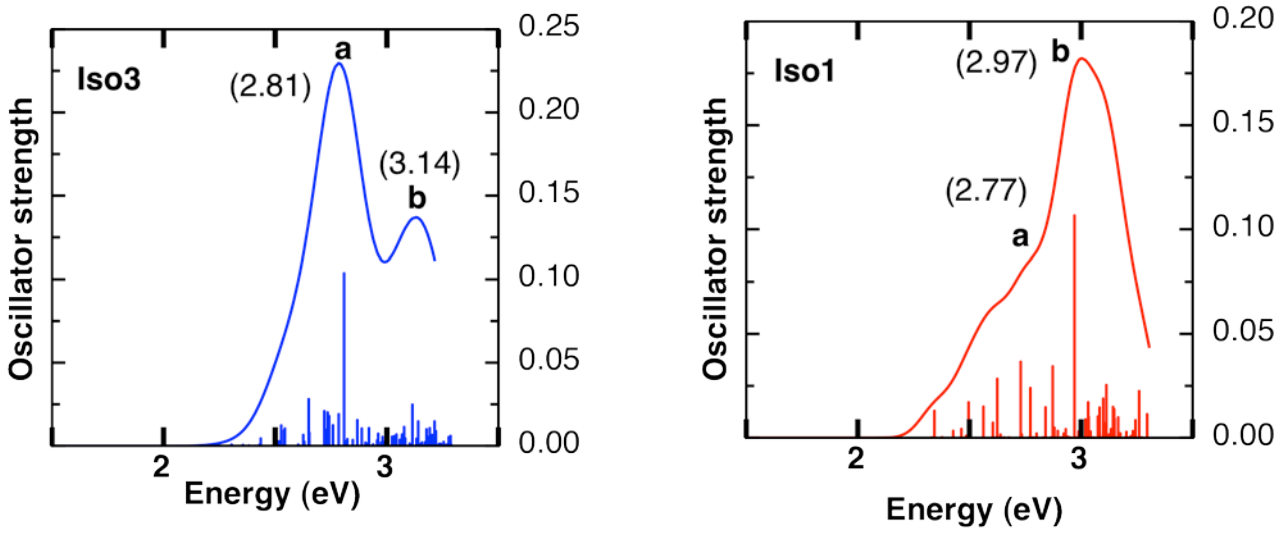

Figure S2. Calculated absorption spectra for Iso 1 and Iso 3 of the $Au_{20}(SCH_3)_{16}$ cluster in good agreement with the calculations reported in Figure 2 of the Reference: Y. Pei, Y. Gao, N. Shao and X. C. Zeng, *J. Am. Chem. Soc*. 2009, **131**, 13619-13621.

PART III.

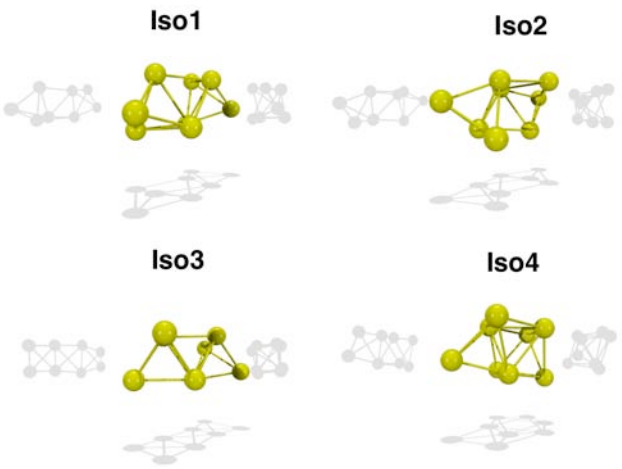

Figure S3. Au_8 cores with projections on Cartesian planes of **Iso1-Iso4**.

PART IV.

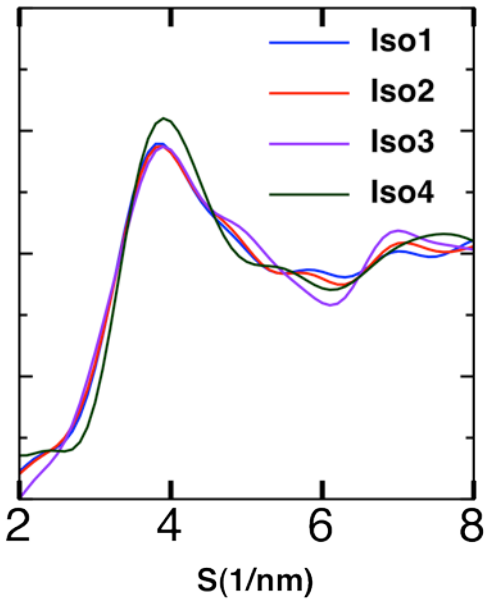

Figure S4. Simulated XRD patterns of **Iso1-Iso4**.

The calculated XRD`s curves where obtained with the program provided by Dr. Yong Pei.

PART V.

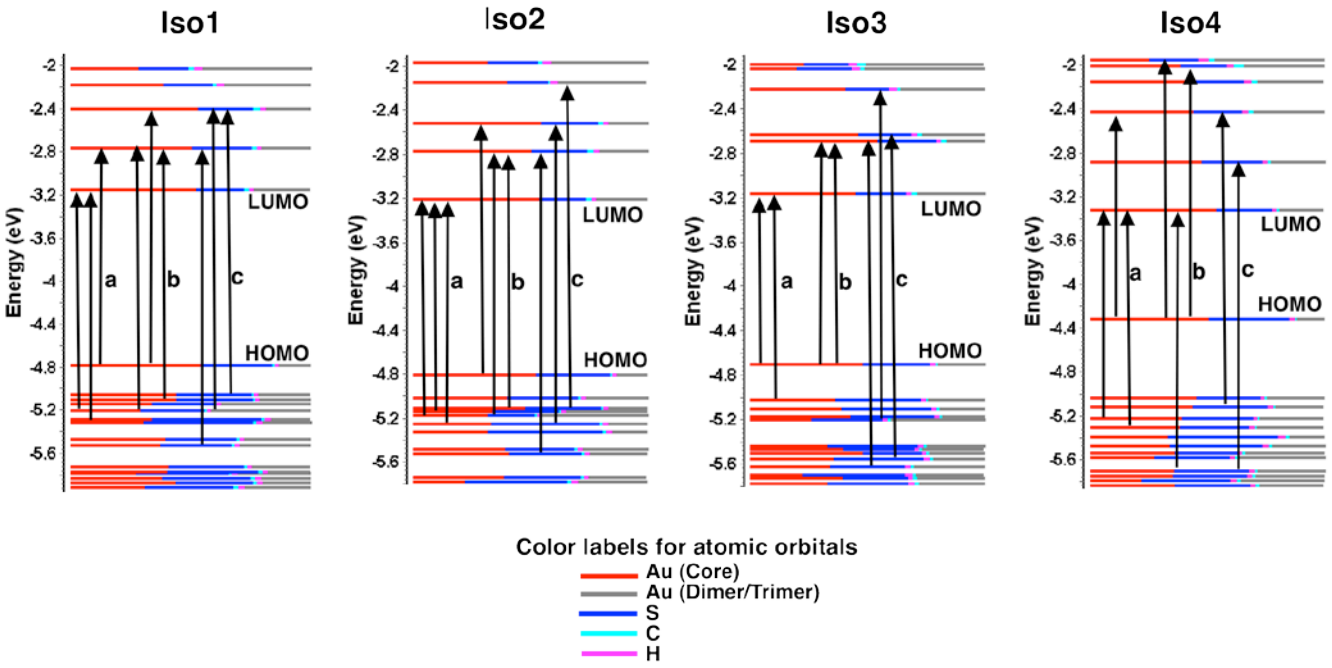

Figure S5. Kohn-Sham molecular orbital (MO) energies and the atomic orbital components in each MO for **Iso1-Iso4**. The electronic transitions of the three major peaks displayed in Figure 3 are depicted. A similar analysis of the Kohn-Sham orbital energy levels diagrams was used by Zhu et al. (Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. *J. Am. Chem. Soc*. **2008**, *130*, 5883) in the discussion of the optical absorption spectrum of the $Au_{25}(SH)_{18}^-$ cluster and by Pei et al. (Pei, Y.; Gao, Y.; Shao, N; Zeng, X. C. *J. Am. Chem. Soc*. **2009**, *131*, 13619) in the corresponding discussion of the $Au_{20}(SCH_3)_{16}$ cluster.

PART VI.

Table S1. Excitation energy, oscillator strength, electronic transitions and their weights for peaks **a-c** for **Iso1-Iso4.**

Isomer	Peak	E (eV)	Oscillator strength	from	to	weight
Iso1		1.7268	0.0073	HOMO	LUMO	0.91
	a	2.5434	0.0333	H-4	L+1	0.46
				HOMO	L+2	0.20
				H-2	L+1	0.09
	b	2.1431	0.0263	H-4	LUMO	0.77
				H-5	LUMO	0.05
				HOMO	L+1	0.03
	c	2.8784	0.0253	H-8	L+1	0.44
				H-4	L+2	0.16
				H-1	L+2	0.03
Iso2		1.7068	0.0077	HOMO	LUMO	0.91
	a	2.0664	0.0567	H-4	LUMO	0.71
				H-3	LUMO	0.13
				H-5	LUMO	0.02
	b	2.4986	0.0411	HOMO	L+2	0.21
				H-4	L+1	0.19
				H-2	L+1	0.19
	c	2.8320	0.0238	H-8	L+1	0.41
				H-5	L+2	0.23
				H-1	L+3	0.04
Iso3	**a**	1.7156	0.025	HOMO	LUMO	0.84
				H-1	LUMO	0.03
	b	2.1692	0.0646	HOMO	L+1	0.69
				HOMO	L+2	0.14
	c	2.9980	0.0275	H-9	L+1	0.28
				H-4	L+3	0.17
				H-8	L+2	0.09
Iso4		1.1218	0.124	HOMO	LUMO	0.87
	a	1.9622	0.0142	H-3	LUMO	0.63
				HOMO	L+2	0.25
				H-4	LUMO	0.03
	b	2.4162	0.0212	HOMO	L+5	0.40
				H-9	LUMO	0.28
				HOMO	L+4	0.05
	c	2.7948	0.0317	H-2	L+2	0.30
				HOMO	L+9	0.11
				H-9	L+1	0.10

Table S2. Relative contributions (in percentage) of the atomic orbitals to each molecular orbital involved in the excitations giving rise to peaks **a,b,c** of **Iso1**-**Iso4**. Au(0) stands for Au atoms forming the Au_8 core and Au(1) denotes Au atoms in the dimer and trimer motifs.

Isomer	Au(0)	Au(1)	S	peak
Iso1				
L+3	0.39	0.36	0.20	
L+2	0.53	0.19	0.23	
L+1	0.51	0.21	0.25	a,c
LUMO	**0.53**	0.23	0.20	b
HOMO	**0.54**	0.13	0.30	
H-1	0.44	0.22	0.31	
H-2	0.44	0.21	0.32	
H-3	0.34	**0.37**	0.26	
H-4	0.29	**0.42**	0.27	a, b
H-8	0.37	0.30	0.29	c
Iso2				
L+3	0.40	0.38	0.18	
L+2	0.55	0.17	0.24	b
L+1	0.50	0.21	0.24	c
LUMO	**0.54**	0.22	0.20	a
HOMO	0.53	0.13	**0.32**	b
H-1	0.40	0.27	0.30	
H-2	0.48	0.17	0.32	
H-3	0.34	0.35	0.28	
H-4	0.32	0.46	0.20	a
H-8	0.41	0.24	0.31	c
Iso3				
L+3	0.41	0.36	0.18	
L+2	0.46	0.27	0.23	
L+1	0.54	0.16	0.25	b,c
LUMO	**0.45**	0.30	0.22	a
HOMO	**0.48**	0.21	0.29	a,b
H-1	0.36	0.24	0.36	
H-2	0.39	0.20	0.38	
H-3	0.43	0.18	0.35	
H-4	0.26	**0.40**	0.30	
H-9	**0.34**	0.30	0.32	c
Iso4				
L+3	0.43	0.28	0.23	b
L+2	0.44	0.30	0.21	c
L+1	0.47	0.23	0.26	
LUMO	**0.54**	0.19	0.24	a
HOMO	**0.51**	0.12	0.34	
H-1	0.46	0.25	0.27	b
H-2	0.44	0.21	0.32	c
H-3	0.39	0.27	0.31	a
H-4	0.38	0.29	0.30	

PART VII.

Relaxed Cartesian coordinates of **Iso1**-**Iso4**.

Coordinates **Iso1**.

Au	0.903002	-1.246443	-1.004471
Au	3.310683	0.212339	-0.797967
Au	-1.106306	0.952543	-1.275478
Au	-3.752390	0.290432	-0.700204
Au	-1.785353	-1.403732	0.231558
Au	-1.985298	1.179363	1.333707
Au	1.094320	1.018331	0.682526
Au	2.369124	-1.420238	1.316515
Au	-4.744223	-2.474958	0.001152
Au	4.878473	-0.028017	2.573415
Au	-2.140253	-2.538873	-2.573471
Au	-4.046795	-0.404047	2.984792
Au	2.213347	2.519409	-2.510872
S	-0.046496	2.127612	-3.128511
C	-0.813715	3.803884	-3.037033
H	-0.353265	4.441017	-3.806193
H	-1.888789	3.689218	-3.240865
S	5.845134	2.076889	2.105075
C	7.650298	1.730148	1.916761
H	7.829718	0.936495	1.180676
H	8.036836	1.425775	2.899959
S	4.525489	3.100639	-2.336215
C	4.484984	4.948867	-2.283563
H	4.100092	5.304199	-3.250459
H	3.846732	5.313889	-1.468801
S	0.194413	-2.550169	-2.963489
C	0.454167	-1.441846	-4.416340
H	1.538382	-1.288813	-4.522449
H	-0.045704	-0.473714	-4.283652
S	-5.221333	-2.354418	2.333676
C	-6.986011	-1.805341	2.368897
H	-7.257628	-1.610362	3.416429
H	-7.131401	-0.899884	1.766157
S	-2.871914	1.587626	3.584521
C	-1.514073	1.046228	4.713795
H	-1.034401	0.129243	4.348790
H	-4.099256	4.859541	2.236470
S	-4.498075	-2.792540	-2.348761
C	-4.711587	-4.619307	-2.556756
H	-4.052754	-5.175354	-1.878096
H	-4.472391	-4.868767	-3.600737
S	3.855121	-2.106346	3.122225
C	2.945759	-1.733140	4.687287
H	2.406714	-0.779998	4.613906
H	2.235698	-2.553761	4.866091
H	-7.601304	-2.625955	1.972456
H	-5.763160	-4.862639	-2.346809
H	8.141272	2.660540	1.597137
H	0.063616	-1.952368	-5.308753
H	-0.676956	4.246140	-2.039735
H	-1.939544	0.878719	5.714005
H	3.674567	-1.691274	5.509529
H	5.515481	5.305451	-2.141697
Au	0.888690	-3.976578	0.521899
Au	3.937447	-2.887801	-1.258624
S	2.838440	-4.859321	-0.531715
C	3.867569	-5.435466	0.888729
H	4.004708	-4.637613	1.630978

H	4.841604	-5.755022	0.490851
S	5.036568	-0.944519	-2.109025
C	6.580321	-0.847394	-1.102356
H	7.031794	0.140438	-1.282981
H	7.265485	-1.638183	-1.441971
S	-1.218819	-3.445965	1.478186
C	-0.814971	-2.776694	3.149731
H	-1.748256	-2.375420	3.575710
H	-0.059530	-1.981576	3.076042
H	3.355487	-6.294632	1.346149
H	6.362728	-0.968445	-0.031686
H	-0.443211	-3.601095	3.776396
Au	-1.184237	4.012295	0.877064
Au	-4.455432	3.286583	-0.703076
S	0.783517	3.154453	1.889406
C	2.119731	4.236951	1.220842
H	1.953766	5.259762	1.589540
H	3.080738	3.853765	1.596597
S	-3.107729	5.104475	-0.008013
C	-3.960286	5.684964	1.526607
H	-0.773837	1.858764	4.752243
H	-4.934160	6.102667	1.233720
S	-5.802047	1.427334	-1.355212
C	-5.723642	1.412589	-3.202428
H	-6.027891	0.410962	-3.539050
H	-4.708636	1.628859	-3.558593
H	-6.428110	2.166112	-3.583463
H	-3.338629	6.471100	1.978890
H	2.124297	4.219872	0.121556
Au	5.110285	2.492856	-0.115221

Coordinates of **Iso2.**

Au	-2.279770	1.335453	-1.342726
Au	1.844317	1.374019	-0.223724
Au	1.814982	-1.223029	-1.390407
Au	-1.092087	-1.111958	-0.544069
Au	-3.313833	-0.161747	0.830147
Au	1.236007	-0.917850	1.336123
Au	3.827836	-0.437351	0.444092
Au	-0.853591	1.172741	1.034621
Au	-5.207862	-2.379346	0.171549
S	-6.165695	-1.816371	-1.925347
Au	-4.860477	0.041881	-2.590115
S	-3.582581	1.919481	-3.302812
S	-4.466626	-3.067085	2.323523
Au	-2.128705	-2.588083	2.383209
S	0.201935	-2.552398	2.844547
Au	4.434498	-3.446650	0.291049
S	5.942831	-1.633602	0.673795
S	2.942504	-5.231450	-0.136076
Au	1.042957	-4.081786	-0.993823
S	-0.931309	-3.149259	-1.928182
Au	-4.104301	2.906087	0.969820
S	-2.932732	4.842384	0.261822
Au	-0.921033	3.933573	-0.643386
S	1.177507	3.321875	-1.570780
S	-5.318557	0.980055	1.694065
Au	4.883354	2.337330	0.215643
S	5.510672	2.182065	-2.076581
Au	4.010545	0.514781	-2.855667
S	2.544448	-1.163344	-3.717870
S	4.483217	2.593866	2.549783
Au	2.108271	2.652292	2.549364
S	-0.240098	2.877615	2.715336
C	7.117727	1.275030	-1.976035
H	7.864106	1.958162	-1.545480
H	7.411725	0.999521	-2.998954
H	7.021508	0.375559	-1.352782
C	1.207099	-0.174719	-4.524793
H	0.350966	-0.847106	-4.682167
H	1.583060	0.185059	-5.493836
H	0.906700	0.674730	-3.897023
C	4.946358	4.352165	2.890759
H	6.039122	4.437129	2.802488
H	4.637088	4.589928	3.918929
H	4.459003	5.037131	2.185568
C	-0.646770	2.163311	4.367911
H	-1.737097	2.023049	4.411822
H	-0.337137	2.879212	5.143369
H	-0.139032	1.203639	4.522594
C	2.272199	4.698254	-1.007292
H	3.300310	4.455732	-1.317370
H	2.230664	4.809411	0.084884
H	1.941632	5.625409	-1.498065
C	-3.871925	5.372830	-1.237903
H	-3.338690	6.226298	-1.681544
H	-4.874371	5.689227	-0.915345
H	-3.948158	4.555862	-1.967915
C	-5.116696	0.955224	3.529455
H	-5.388779	-0.050895	3.880957
H	-5.797578	1.700970	3.965133
H	-4.081630	1.179552	3.817476
C	-2.601535	1.273280	-4.729162
H	-1.790225	1.988257	-4.929066
H	-3.265989	1.211664	-5.603167
H	-2.182768	0.284594	-4.503295

C	-7.760214	-1.029505	-1.414553
H	-8.407838	-1.817654	-1.004398
H	-8.223738	-0.597390	-2.312961
H	-7.590174	-0.249196	-0.661706
C	-4.501902	-4.914897	2.257559
H	-5.553370	-5.226066	2.174928
H	-4.073024	-5.297557	3.194956
H	-3.931182	-5.294583	1.400519
C	0.305321	-1.889020	4.563350
H	1.366747	-1.713047	4.792170
H	-0.100867	-2.644130	5.252173
H	-0.257757	-0.953048	4.667244
C	6.234981	-1.648560	2.498595
H	6.594196	-0.650830	2.789538
H	7.005156	-2.402472	2.717109
H	5.312652	-1.882527	3.044846
C	2.381083	-5.700506	1.563088
H	3.251551	-6.089072	2.110929
H	1.628783	-6.495508	1.456179
H	1.945741	-4.841010	2.090589
C	-2.258607	-4.242315	-1.253881
H	-3.229141	-3.782784	-1.497982
H	-2.166486	-4.341904	-0.163287
H	-2.174154	-5.226050	-1.738594

Coordinates of **Iso3.**

Au	-2.397111	0.943793	0.900587
Au	1.848625	1.180837	0.754427
Au	3.834411	-0.706158	1.261473
Au	-0.489788	-1.143181	0.852614
Au	-2.480010	-1.047533	-1.066326
Au	1.947627	-1.252524	-0.761207
Au	3.884777	0.708631	-1.195851
Au	-0.451259	0.923425	-1.081278
Au	-4.122587	-3.383972	0.737832
S	-5.884214	-2.330055	1.927178
Au	-4.896058	-0.219487	2.290300
S	-3.805734	1.853685	2.693359
S	-2.549858	-4.824186	-0.296525
Au	-0.795419	-3.574417	-1.310979
S	1.105304	-2.783843	-2.490354
Au	5.031941	-2.323610	-1.034390
S	5.703058	-0.440889	-2.369652
S	4.401414	-4.214137	0.278062
Au	2.464834	-3.323340	1.375790
S	0.473142	-2.660104	2.513398
Au	-4.150857	3.338633	-0.616673
S	-2.300308	4.809869	-0.428403
Au	-0.818736	3.552779	0.946423
S	0.693892	2.535307	2.467014
S	-6.155268	2.087328	-0.810674
Au	-5.183903	0.188039	-1.823331
S	-4.176919	-1.786648	-2.681712
Au	2.425910	3.197787	-1.457137
S	4.140176	4.255862	-0.159190
Au	4.848669	2.385492	1.154519
S	5.581114	0.518697	2.485443
S	0.769531	2.149261	-2.815626
C	5.516771	4.502273	-1.366329
H	5.202456	5.276370	-2.081130
H	6.398456	4.846642	-0.806840
H	5.742357	3.568720	-1.897081
C	4.847765	0.847201	4.147081
H	4.994032	-0.056181	4.757551
H	5.381219	1.691736	4.607231
H	3.775311	1.072044	4.070357
C	-0.346024	3.513297	-3.361645
H	0.196865	4.123768	-4.098353
H	-1.225397	3.054846	-3.838010
H	-0.667847	4.135651	-2.516869
C	1.857563	3.908619	2.885101
H	2.739424	3.472984	3.378690
H	2.174000	4.452646	1.985983
H	1.346951	4.594753	3.577043
C	-2.942640	6.075664	0.757566
H	-2.111286	6.745881	1.019887
H	-3.732985	6.645716	0.248118
H	-3.344553	5.598268	1.660507
C	-7.064233	2.932929	-2.181889
H	-7.941600	2.318966	-2.431944
H	-7.394027	3.914420	-1.811818
H	-6.428373	3.059088	-3.066828
C	-3.487027	-1.266782	-4.316576
H	-2.769919	-2.038272	-4.632852
H	-4.312261	-1.211680	-5.041207
H	-2.981806	-0.294937	-4.246303
C	-2.802691	1.524763	4.212386
H	-1.945947	2.214602	4.204509
H	-3.438745	1.715774	5.089152

H	-2.440669	0.488939	4.231124
C	-7.189703	-2.028343	0.655983
H	-7.565191	-3.006510	0.322883
H	-7.999096	-1.461729	1.138375
H	-6.793444	-1.462215	-0.198917
C	-1.724159	-5.620557	1.152244
H	-2.486616	-6.195909	1.697154
H	-0.952215	-6.302072	0.766000
H	-1.269176	-4.872910	1.815300
C	0.455974	-1.693341	-3.827526
H	1.306832	-1.140100	-4.250733
H	0.001732	-2.329804	-4.601316
H	-0.281011	-0.983395	-3.426747
C	7.256423	0.125020	-1.544093
H	8.043109	-0.616995	-1.744161
H	7.541298	1.090730	-1.987629
H	7.114770	0.239592	-0.461576
C	3.664494	-5.353044	-0.977942
H	4.490071	-5.746043	-1.588999
H	3.174566	-6.178249	-0.441487
H	2.940733	-4.830622	-1.618038
C	1.050504	-1.547138	3.866082
H	0.157630	-1.174463	4.389199
H	1.671618	-2.132983	4.559038
H	1.621221	-0.703100	3.454358

Coordinates of **Iso4.**

Au	-0.050303	1.193178	-0.962370
Au	-2.614664	-0.458677	-0.900923
Au	1.552655	-1.177702	-1.805525
Au	2.859741	0.893563	-0.556071
Au	0.993302	1.049661	1.669588
Au	2.447734	-1.508972	0.844206
Au	-0.363011	-1.137088	0.537837
Au	-1.873087	1.410482	1.098712
Au	-4.104091	-0.533859	2.287966
Au	-1.602389	-2.778372	-3.062480
S	0.622920	-2.324614	-3.731958
C	1.425748	-3.989203	-3.697781
H	1.045592	-4.572291	-4.549292
H	2.510606	-3.840309	-3.802596
S	-4.545825	-2.836777	1.963945
C	-6.390635	-2.936896	2.055140
H	-6.865908	-2.228116	1.365434
H	-6.688640	-2.710248	3.089122
S	-3.860452	-3.423754	-2.691717
C	-3.812653	-5.262851	-2.868672
H	-3.586337	-5.495215	-3.919528
H	-3.053865	-5.710351	-2.213712
H	1.576174	-3.423412	5.911745
S	-3.651193	1.752311	2.779799
C	-2.802276	1.652555	4.418577
H	-1.943124	0.970205	4.377736
H	-2.459745	2.664778	4.678874
H	-6.686905	-3.965205	1.802008
H	1.218788	-4.518610	-2.759338
H	-3.525429	1.305975	5.170743
H	-4.807293	-5.653424	-2.609086
Au	-1.669593	4.479794	0.487495
Au	-3.972841	2.366915	-1.609413
S	-3.665977	4.558659	-0.798260
C	-4.960718	4.708607	0.512142
H	-4.859859	3.911218	1.260757
H	-5.942609	4.650084	0.021026
S	-4.329099	0.210546	-2.524071
C	-5.953448	-0.262704	-1.782685
H	-6.119626	-1.328589	-1.999662
H	-6.737078	0.343608	-2.260716
S	0.255607	5.101924	1.725993
C	-0.032279	4.429465	3.418631
H	0.839090	4.684538	4.039344
H	-0.172056	3.340688	3.393737
H	-4.842639	5.692985	0.987834
H	-5.955199	-0.097412	-0.696850
H	-0.926704	4.925536	3.822777
Au	1.128526	-3.467201	2.612835
Au	2.577474	-1.022931	3.893142
S	-0.813578	-3.450485	1.271748
C	-0.292544	-4.529983	-0.127922
H	-0.339254	-5.575745	0.210186
H	-1.000938	-4.362137	-0.956151
S	3.098498	-3.358221	3.966545
C	2.541983	-3.875479	5.653519
H	3.309156	-3.560686	6.375610
S	1.896614	1.236978	3.939047
C	3.473991	2.184266	3.799557

H	3.220670	3.236972	3.602504
H	4.100641	1.804065	2.982517
H	4.006114	2.099104	4.758418
H	2.456663	-4.971736	5.657479
H	0.725023	-4.276935	-0.453995
Au	-4.104611	-3.064335	-0.355533
Au	2.086028	3.865687	0.866550
S	4.116362	2.879227	0.115596
C	4.564791	3.749001	-1.450095
H	4.894165	4.768209	-1.201094
H	3.718685	3.780173	-2.149416
H	5.393070	3.189677	-1.909248
H	3.334677	-1.551682	-4.940611
Au	2.459014	1.236530	-3.479690
Au	4.666472	-1.101165	-1.803236
S	0.290672	2.181446	-3.210634
C	0.572319	3.966138	-2.838602
H	0.960949	4.458142	-3.742091
H	-0.402077	4.400008	-2.566382
S	4.612463	0.222094	-3.806847
C	4.260560	-0.998091	-5.147982
H	5.114661	-1.686970	-5.216571
S	4.756602	-2.393377	0.216861
C	5.930107	-1.441175	1.275373
H	5.897529	-1.884991	2.281810
H	5.645314	-0.381313	1.327594
H	6.944050	-1.537607	0.860211
H	4.154620	-0.440329	-6.089746
H	1.269283	4.094854	-1.997489