Supporting Information for

Automatic Construction of the Initial Orbitals for Efficient Generalized Valence Bond Calculations of Large Systems

Qingchun Wang,† Jingxiang Zou,† Enhua Xu,‡ Peter Pulay,*,¶ Shuhua Li*,†

†School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, Nanjing University, 210023, P. R. China

‡Graduate School of Science, Technology, and Innovation, Kobe University, Nada-ku, Kobe 657-8501, Japan

¶Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, United States

shuhua@nju.edu.cn; pulay@uark.edu.

Contents

1. The detail of Kuhn-Munkres (KM) algorithm ---------- S2
2. **Table S1** UB3LYP and UHF energies of polyacenes ---------- S7
3. **Table S2** Singlet GVB energies of polyacenes from two schemes ---------- S8
4. **Table S3** GVB energies of hexacene using PM localized orbitals to construct the initial GVB guess ---------- S8
5. **Figure S1** GVB orbitals of the singlet heptacene ---------- S9
6. Selected GVB CI coefficients of singlet polyacenes ---------- S10

7. Cartesian coordinates of singlet polyacenes ---------- S13

8. Cartesian coordinates of triplet polyacenes ---------- S22

9. **Table S4** Singlet energies of two forms of $\{[Cu(NH_3)]_2O_2\}^{2+}$ ---------- S26

10. Cartesian coordinates of two forms of $\{[Cu(NH_3)]_2O_2\}^{2+}$ ---------- S26

1. The KM pairing algorithm

In the construction of initial orbitals for GVB calculations, matching the occupied orbitals with the virtual orbitals one by one is a crucial step. The orbital pair assignment problem is mathematically similar to the assignment problem previously introduced by Kuhn[1] and later developed by Munkres.[2] In their solution, the weighted biparticle graph G(E,V) is defined to contain two subsets, X and Y, and satisfies $X \cup Y=V$ with $X \cap Y=\varnothing$ and $E \subseteq X \times Y$. A feasible labeling l_i (called top-label) will be assigned to each vertex in the biparticle graph G. In addition, the equality subgraph is defined to contain a set of lines connecting two vertices, which satisfies $l_i + l_j = W_{ij},\ i \in X,\ j \in Y$. According to the KM algorithm, a maximum weight matching corresponds to perfect matching of equality subgraph. So a maximum weight matching can be found when the equality subgraph is extended gradually until it reaches perfect matching when the top-labels are modified and edges are joined equality subgraph continuously. In this way, an optimization problem of finding a max-weight matching is transformed into a combinatorial one of finding a perfect matching, which can be solved by the Hungarian algorithm.[1] In our case, the active (occupied and virtual) orbitals are these vertices in bipartite graph, and the localized occupied orbitals set O and localized virtual orbitals set V correspond to the two disjoint

subsets X and Y. The transition-dipole-like integrals, W_{ia}, between a localized occupied orbitals $\{\phi_i, i \in O\}$ and a localized virtual orbitals $\{\phi_a, a \in V\}$ are taken as the weight, which are a measure of spatial vicinity between two orbitals.

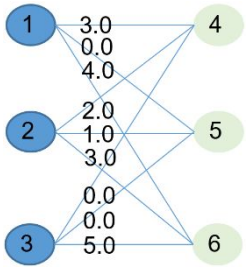
$$W_{ia} = \left|\langle \phi_i \mid \hat{r} \mid \phi_a \rangle\right|^2 = \left[\left|\langle \phi_i \mid x \mid \phi_a \rangle\right|^2 + \left|\langle \phi_i \mid \mathrm{y} \mid \phi_a \rangle\right|^2 + \left|\langle \phi_i \mid \mathrm{z} \mid \phi_a \rangle\right|^2 \right] \tag{1}$$

Where $\langle \phi_i \mid \hat{r} \mid \phi_a \rangle$ is the standard MO-based dipole integral. By maximizing the sum of weights between all pairs of orbitals, we can match the occupied orbitals with the virtual orbitals one by one.

$$W = \sum_{i,a \in P} W_{ia} \tag{2}$$

Assume that the transition-dipole-like integral between three occupied orbitals $\{\phi_i, i = 1,2,3\}$ and three virtual orbitals $\{\phi_a, a = 4,5,6\}$ and the corresponding bipartite graph are listed as follows.

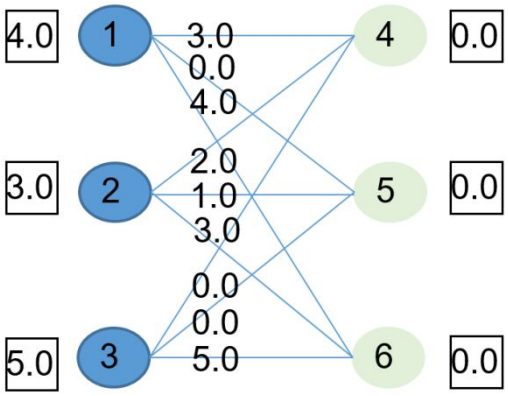
		virtual orbitals		
		4	5	6
occupied orbitals	1	3.0	0.0	4.0
	2	2.0	1.0	3.0
	3	0.0	0.0	5.0



The KM algorithm can be described as the following four steps:

Step 1: Initializing the top-labels for all active orbital. For occupied orbitals, the top-labels are taken as the maximum weight of the orbital. For virtual orbitals, the initial values are zero.

$$\begin{cases} l_i = \max(W_{ia}) & i \in O \\ l_a = 0 & a \in V \end{cases} \tag{3}$$



As shown in the above figure, $l_i + l_a \geq W_{ia},\ i \in O,\ a \in V$, and $\sum_{k=1}^{6} l_k = 12$ is the maximum value of the weights that can be obtained.

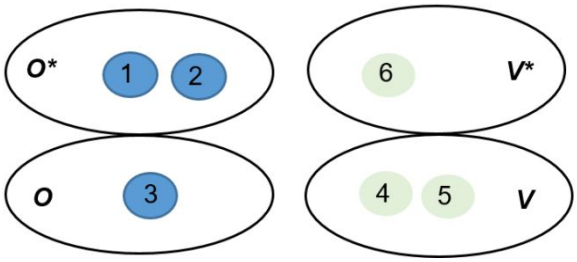
Step 2: Using Hungarian algorithm to find the perfect matching. Starting from the occupied orbital ϕ_1, each occupied orbital is matched with a virtual orbital in turn. The principle of matching here is that matching the occupied orbital ϕ_i with the virtual orbital ϕ_a if $l_i + l_a = W_{ia},\ i \in O,\ a \in V$. Otherwise, the top-labels will be modified and re-assigned as follows:

First of all, for the occupied orbital ϕ_1, $l_1 + l_6 = 4.0 = W_{16}$, so occupied orbital ϕ_1 is matched with the virtual orbital ϕ_6.

Next, for the occupied orbital ϕ_2, $l_2 + l_6 = 3.0 = W_{26}$, but the virtual orbital ϕ_6 has been matched with the occupied orbital ϕ_1, hence the matching is unsuccessful.

Step 3: If the matching is not successful, the corresponding top-label will be modified and

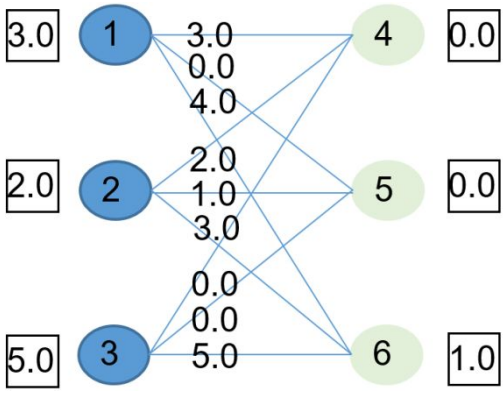
re-assigned. In order to ensure that the sum of weight is as large as possible, each modification of the top-label is supposed to be as small as possible. Let O and O^* (V and V^*) represent unpaired and paired occupied (virtual) orbital subsets, respectively. Up to now, paired occupied orbitals are ϕ_1, ϕ_2 and the paired virtual orbital is ϕ_6, while the unpaired occupied orbital is ϕ_3 and unpaired virtual orbital are ϕ_4, ϕ_5.



To ensure that the modification of the top-labels is as small as possible, they are modified as follows.

$$\begin{aligned} l_i &= l_i - d,\ i \in O^* \\ l_a &= l_a + d,\ a \in V^* \end{aligned} \tag{4}$$

where $d = \min(l_i + l_a - W_{ia}),\ i \in O^*,\ a \in V$. Hence the top-labels will be modified as follows.

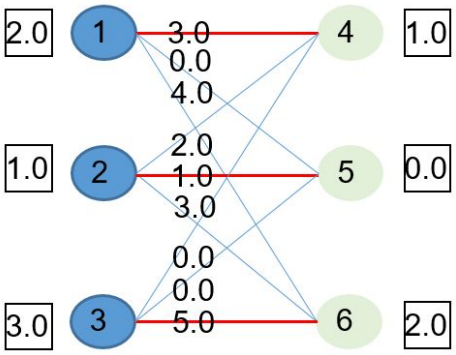


One can find $\sum_{k=1}^{6} l_k = 11$ after this modification, and the sum of all top-labels is only

reduced by 1.0.

Now rematch the occupied orbitals with the virtual orbitals. For the occupied orbital ϕ_1, $l_1 + l_6 = 4.0 = W_{16}$, so the occupied orbital ϕ_1 is still matched with the virtual orbital ϕ_6. For the occupied orbital ϕ_2, $l_2 + l_4 = 2.0 = W_{24}$, so the occupied orbital ϕ_2 is now matched with the virtual orbital ϕ_4.

Step 4: Repeat **Step 2** and **3** until all occupied orbitals are matched successfully, that is, prefect matching of equality subgraph is found, $\sum l_i + l_a = \sum W_{ia},\ i \in O,\ a \in V$. And the final matching result are $1 \leftarrow 4,\ 2 \leftarrow 5,\ 3 \leftarrow 6$, the sum of weight between all paired orbitals is $W = \sum W_{ia} = W_{14} + W_{25} + W_{36} = 9.0$.



With the above procedure, one can easily achieve the automatic pairing between active occupied orbitals and active virtual orbitals.

REFERENCES

(1) Kuhn, H. W., The Hungarian method for the assignment problem. *Naval Research Logistics Quarterly* **1955,** *2*, 83-97.
(2) Munkres, J., Algorithms for the Assignment and Transportation Problems. *J. Soc. Ind. Appl. Math.* **1957,** *5*, 32-38.

2. Table S1 UB3LYP and UHF energies of polyacenes

Size	S=0, UB3LYP/6-31G(d)[a]		S=0, UHF/cc-pVDZ[a]		S=1, UHF/cc-pVDZ[a]	
	Elec E (E_h)	<S**2>	Elec E (E_h)	<S**2>	Elec E (E_h)	<S**2>
1	-232.248650	0	-230.725694	0.447	-230.599621	2.348
2	-385.892705	0	-383.399050	1.096	-383.289450	2.613
3	-539.530486	0	-536.071581	1.773	-535.980006	2.836
4	-693.165812	0	-688.744688	2.424	-688.657616	2.911
5	-846.799944	0	-841.418199	3.060	-841.333571	3.712
6	-1000.433682	0.262	-994.093398	3.706	-994.009908	4.069
7	-1154.069426	0.796	-1146.769747	4.358	-1146.687941	4.963
8	-1307.706243	1.075	-1299.444679	4.991	-1299.363160	5.412
9	-1461.343238	1.260	-1452.119225	5.621	-1452.037605	6.260
10	-1614.980131	1.418	-1604.793743	6.252	-1604.711498	6.717

‘1’ means benzene, ‘2’ means naphthalene, etc.

Size	UHF S-T Gap (kcal/mol)
1	79.11
2	68.77
3	57.46
4	54.64
5	53.11
6	52.39

7	51.33
8	51.15
9	51.22
10	51.61

a: All values are computed based on singlet geometries optimized at UB3LYP/6-31G(d) level.

The vertical S-T gaps at the UHF/cc-pVDZ level tend to be constant for longer polyacenes, which are far away from the results of GVB-BCPT2, SF-CCSD and GAS-PDFT methods.

3. Table S2 Singlet GVB energies (E_h) of polyacenes from two schemes
(Both schemes started with Boys localized orbitals)

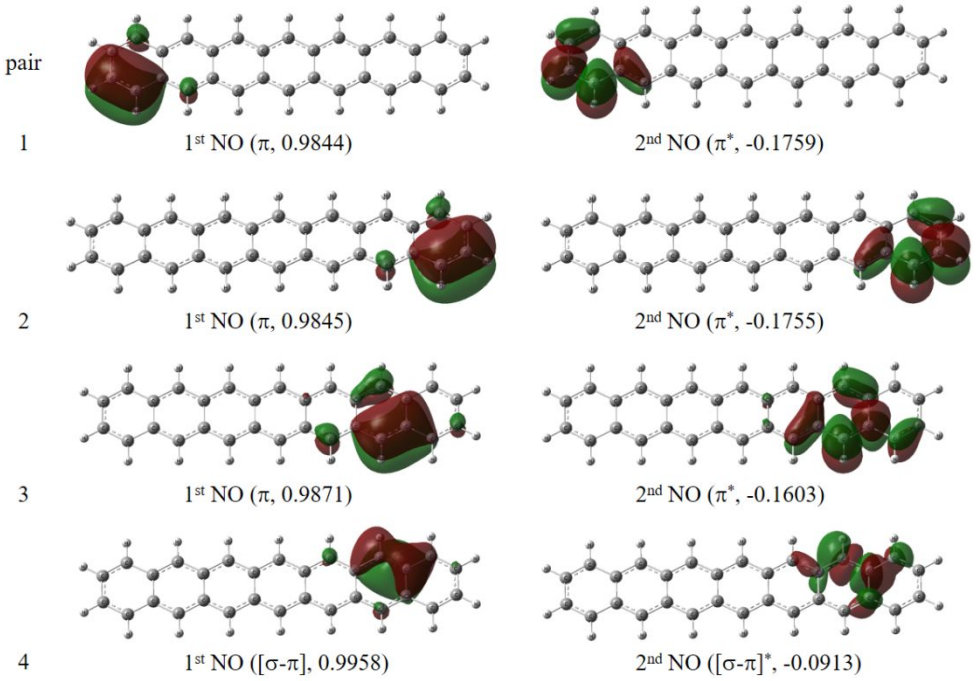
Size	Active space GVB(*n*)	Scheme I	Scheme II
1	15	-230.919494	-230.919494
2	24	-383.706239	-383.706239
3	33	-536.480241	-536.480241
4	42	-689.252703	-689.252703
5	51	-842.018728	-842.018728
6	60	-994.781710	-994.781710
7	69	-1147.537575	-1147.536859
8	78	-1300.293338	-1300.294400
9	87	-1453.051816	-1453.051865
10	96	-1605.810345	-1605.812021

4. Table S3 GVB energies of hexacene using PM localized orbitals to construct the initial GVB guess

Spin multiplicity	**Scheme I**	**Scheme II**
Singlet	-994.775987	-994.775987
Triplet[a]	-994.690770	-994.690770

a: calculated using the ground-state geometry optimized at the UB3LYP/6-31G(d) level.

5. Figure S1 GVB orbitals of the singlet heptacene



(a)

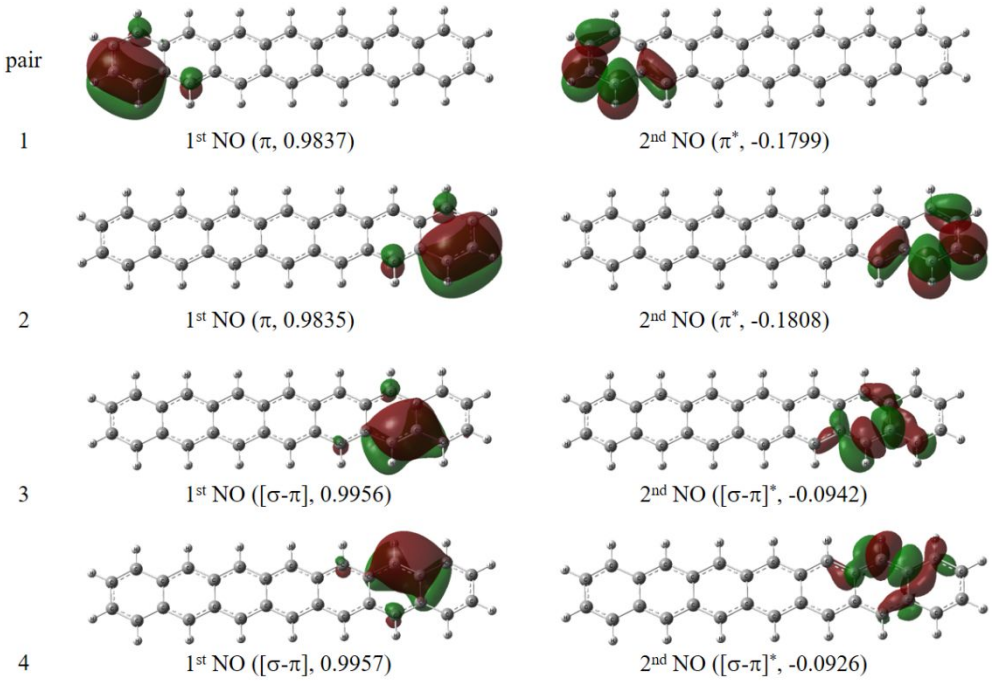


Figure S1. (a) GVB orbitals in four GVB pairs for the singlet heptacene. The initial GVB orbitals are obtained with **Scheme I** and the Boys localization method; (b) GVB orbitals in four GVB pairs for the singlet heptacene. The initial GVB orbitals are obtained with **Scheme II** and the Boys localization method. CI coefficients for two orbitals (first and second natural orbitals) in several GVB pairs are included in the parenthesis. The indices on the left of orbitals are shown schematically.

6. Selected GVB CI coefficients of singlet polyacenes

The Cartesian cc-pVDZ basis set is employed in GVB calculations of polyacenes. The Boys localized orbitals are used as GVB initial orbitals in all GVB calculations here.

benzene, GVB(15)

pair	orbital 1	orbital 2
1	0.9960	-0.0894
2	0.9960	-0.0892
3	0.9960	-0.0892
4	0.9960	-0.0890
5	0.9960	-0.0890
6	0.9960	-0.0889
7	0.9961	-0.0885
8	0.9961	-0.0885
9	0.9961	-0.0885
10	0.9961	-0.0885
11	0.9961	-0.0885

12 0.9961 -0.0885
13 0.9979 -0.0643
14 0.9979 -0.0642
15 0.9979 -0.0642

naphthalene, GVB(24), only the top 4 pairs are shown.

pair	orbital 1	orbital 2
1	0.9874	-0.1583
2	0.9874	-0.1583
3	0.9874	-0.1583
4	0.9874	-0.1583

anthracene, GVB(33), only the top 4 pairs are shown.

pair	orbital 1	orbital 2
1	0.9848	-0.1739
2	0.9848	-0.1739
3	0.9861	-0.1662
4	0.9861	-0.1662

tetracene, GVB(42), only the top 4 pairs are shown.

pair	orbital 1	orbital 2
1	0.9843	-0.1765
2	0.9843	-0.1765
3	0.9843	-0.1765
4	0.9843	-0.1765

pentacene, GVB(51), only the top 4 pairs are shown.

pair	orbital 1	orbital 2
1	0.9837	-0.1797
2	0.9837	-0.1797
3	0.9841	-0.1776
4	0.9841	-0.1776

hexacene, GVB(60), only the top 4 pairs are shown.

pair	orbital 1	orbital 2
1	0.9836	-0.1801
2	0.9836	-0.1801
3	0.9836	-0.1801
4	0.9836	-0.1801

heptacene, GVB(69), Scheme I, only the top 6 pairs are shown.

pair orbital 1 orbital 2
1 0.9834 -0.1813
2 0.9836 -0.1804
3 0.9844 -0.1759
4 0.9845 -0.1755
5 0.9863 -0.1651
6 0.9871 -0.1603

heptacene, GVB(69), Scheme II, only the top 4 pairs are shown.
pair orbital 1 orbital 2
1 0.9835 -0.1809
2 0.9835 -0.1808
3 0.9837 -0.1799
4 0.9837 -0.1799

octacene, GVB(78), Scheme I, only the top 4 pairs are shown.
pair orbital 1 orbital 2
1 0.9835 -0.1807
2 0.9835 -0.1807
3 0.9835 -0.1807
4 0.9835 -0.1807

octacene, GVB(78), Scheme II, only the top 6 pairs are shown.
pair orbital 1 orbital 2
1 0.9835 -0.1811
2 0.9837 -0.1797
3 0.9837 -0.1797
4 0.9844 -0.1761
5 0.9859 -0.1673
6 0.9863 -0.1651

nonacene, GVB(87), Scheme I, only the top 6 pairs are shown.
pair orbital 1 orbital 2
1 0.9834 -0.1816
2 0.9835 -0.1812
3 0.9844 -0.1760
4 0.9844 -0.1757
5 0.9860 -0.1667
6 0.9864 -0.1645

nonacene, GVB(87), Scheme II, only the top 7 pairs are shown.

pair orbital 1 orbital 2
1 0.9834 -0.1813
2 0.9842 -0.1773
3 0.9842 -0.1773
4 0.9843 -0.1763
5 0.9857 -0.1685
6 0.9864 -0.1646
7 0.9870 -0.1607

decacene, GVB(96), Scheme I, only the top 6 pairs are shown
pair orbital 1 orbital 2
1 0.9834 -0.1816
2 0.9834 -0.1816
3 0.9844 -0.1760
4 0.9844 -0.1760
5 0.9860 -0.1666
6 0.9860 -0.1666

decacene, GVB(96), Scheme II, only the top 6 pairs are shown
pair orbital 1 orbital 2
1 0.9834 -0.1813
2 0.9837 -0.1797
3 0.9837 -0.1797
4 0.9843 -0.1763
5 0.9857 -0.1684
6 0.9857 -0.1683

7. Cartesian coordinates of singlet polyacenes

benzene

C	-1.06282200	-0.90590700	0.00000500
C	0.25326800	-1.37324900	0.00006800
C	1.31599300	-0.46745000	-0.00005500
C	1.06274500	0.90599500	0.00000800
C	-0.25315300	1.37326700	0.00006100
C	-1.31603300	0.46734500	-0.00005700
H	-1.88970100	-1.61101400	-0.00006600
H	0.45015400	-2.44198100	0.00007800
H	2.34003700	-0.83107500	-0.00015400
H	1.88979600	1.61088900	0.00000700
H	-0.45028500	2.44194700	0.00001800
H	-2.33999500	0.83122400	-0.00006300

naphthalene

C	2.43347515	-0.70849336	0.00000605
C	1.24468049	-1.40245308	-0.00001220
C	-0.00000466	-0.71652844	-0.00000430
C	0.00000955	0.71654145	-0.00001020
C	1.24469900	1.40245764	-0.00000420
C	2.43349188	0.70846924	0.00001351
H	-1.24174558	-2.48973815	-0.00002207
H	3.37792042	-1.24517662	0.00000642
H	1.24172273	-2.48974029	-0.00001289
C	-1.24469564	-1.40244925	0.00000316
C	-1.24468726	1.40245041	-0.00001109
H	1.24176424	2.48975332	0.00001146
H	3.37794597	1.24514408	0.00002004
C	-2.43347991	0.70848723	0.00000048
C	-2.43348853	-0.70848078	0.00001378
H	-1.24173989	2.48973619	-0.00001745
H	-3.37792656	1.24517316	0.00002778
H	-3.37794173	-1.24515809	0.00001685

anthracene

C	3.66067900	0.71314600	-0.00001700
C	2.47953000	1.40703600	0.00004600
C	1.22392300	0.72262400	0.00003000
C	1.22392400	-0.72262500	0.00002200
C	2.47953200	-1.40703600	-0.00002500

C	3.66068100	-0.71314200	-0.00006100
C	0.00000000	1.40337700	0.00002400
C	0.00000100	-1.40337800	0.00002800
C	-1.22392200	-0.72262600	0.00002400
C	-1.22392400	0.72262400	0.00000600
C	-2.47953000	1.40703700	-0.00002700
H	-2.47686500	2.49457900	-0.00006700
C	-3.66068000	0.71314500	-0.00005500
C	-3.66068000	-0.71314300	-0.00000700
C	-2.47953100	-1.40703700	0.00002900
H	-0.00000600	2.49174700	0.00004600
H	4.60736000	1.24665700	-0.00004400
H	2.47686200	2.49457900	0.00009700
H	2.47686600	-2.49457800	-0.00002700
H	4.60735600	-1.24666200	-0.00011900
H	-0.00000400	-2.49174900	0.00004700
H	-4.60735700	1.24666200	-0.00009100
H	-4.60735700	-1.24666000	-0.00002300
H	-2.47686900	-2.49458000	0.00007400

tetracene

C	-3.71114100	1.40931000	0.00000000
C	-4.88886600	0.71537900	0.00000000
C	-4.88886700	-0.71537900	0.00000000
C	-3.71114100	-1.40931000	0.00000000
C	-2.45052400	-0.72589300	0.00000000
C	-1.23538500	-1.40634300	0.00000000
C	0.00000000	-0.72614400	0.00000000
C	1.23538500	-1.40634300	0.00000000
C	2.45052400	-0.72589300	0.00000000
C	3.71114100	-1.40931000	0.00000000
C	4.88886700	-0.71537900	0.00000000
C	4.88886700	0.71538000	0.00000000
C	3.71114100	1.40931000	0.00000000
C	2.45052400	0.72589300	0.00000000
C	1.23538400	1.40634300	0.00000000
C	0.00000000	0.72614300	0.00000000
C	-1.23538500	1.40634300	0.00000000
C	-2.45052400	0.72589300	0.00000000
H	-3.70882600	2.49682900	-0.00000100
H	-5.83642800	1.24728800	-0.00000100

H	-5.83642800	-1.24728700	0.00000000
H	-3.70882700	-2.49682900	0.00000000
H	-1.23521400	-2.49457000	0.00000000
H	1.23521300	-2.49457000	0.00000000
H	3.70882600	-2.49683000	-0.00000100
H	5.83642800	-1.24728800	-0.00000100
H	5.83642800	1.24728800	0.00000000
H	3.70882600	2.49683000	0.00000000
H	1.23521300	2.49457000	0.00000000
H	-1.23521300	2.49457000	0.00000000

pentacene

C	-6.11791400	-0.71658900	-0.00000100
C	-6.11791300	0.71659000	-0.00000500
C	-4.94181600	1.41055700	-0.00000400
C	-3.67862900	0.72768000	0.00000000
C	-3.67862900	-0.72768000	0.00000200
C	-4.94181600	-1.41055700	0.00000300
C	-2.46766600	-1.40789000	0.00000300
C	-1.22644800	-0.72852500	0.00000200
C	-1.22644800	0.72852500	0.00000100
C	-2.46766600	1.40789000	-0.00000100
C	0.00000000	1.40851800	0.00000100
C	1.22644800	0.72852500	0.00000100
C	1.22644800	-0.72852500	0.00000100
C	0.00000000	-1.40851900	0.00000100
C	2.46766600	-1.40788900	-0.00000200
C	3.67862900	-0.72767900	-0.00000200
C	3.67862900	0.72768000	0.00000100
C	2.46766600	1.40789000	0.00000300
C	4.94181600	1.41055700	0.00000300
C	6.11791400	0.71659000	0.00000000
C	6.11791400	-0.71659000	-0.00000300
C	4.94181600	-1.41055700	-0.00000400
H	-7.06597000	-1.24758700	0.00000100
H	-7.06596900	1.24758800	-0.00000800
H	-4.93957400	2.49805900	-0.00000600
H	-4.93957400	-2.49806000	0.00000800
H	-2.46759700	-2.49608200	0.00000500
H	-2.46759800	2.49608200	-0.00000200
H	0.00000000	2.49659900	0.00000000

H	0.00000000	-2.49659900	0.00000000
H	2.46759800	-2.49608100	-0.00000300
H	2.46759700	2.49608100	0.00000600
H	4.93957400	2.49805900	0.00000600
H	7.06597000	1.24758800	0.00000000
H	7.06596900	-1.24758800	-0.00000400
H	4.93957400	-2.49805900	-0.00000700

hexacene

C	-7.35065400	0.71575600	0.00000000
C	-7.35065500	-0.71575600	-0.00000100
C	-6.17304400	-1.40989000	-0.00000100
C	-4.91162500	-0.72716200	0.00000000
C	-4.91162500	0.72716200	0.00000000
C	-6.17304400	1.40989000	0.00000000
C	-3.69852900	1.40795300	0.00000000
C	-2.45763200	0.72937700	0.00000000
C	-2.45763200	-0.72937700	0.00000000
C	-3.69852900	-1.40795300	0.00000000
C	-1.23213500	-1.40969700	0.00000000
C	0.00000000	-0.73061900	0.00000100
C	0.00000000	0.73061800	0.00000000
C	-1.23213500	1.40969700	0.00000000
C	1.23213500	1.40969700	0.00000000
C	2.45763100	0.72937700	0.00000100
C	2.45763100	-0.72937700	0.00000100
C	1.23213500	-1.40969700	0.00000100
C	3.69852800	-1.40795300	0.00000000
C	4.91162500	-0.72716200	0.00000000
C	4.91162500	0.72716200	0.00000000
C	3.69852900	1.40795300	0.00000000
C	6.17304400	1.40989000	0.00000000
C	7.35065500	0.71575600	-0.00000100
C	7.35065500	-0.71575600	-0.00000100
C	6.17304400	-1.40989000	-0.00000100
H	-8.29826900	1.24750000	-0.00000100
H	-8.29826900	-1.24749900	0.00000000
H	-6.17101500	-2.49739000	0.00000000
H	-6.17101500	2.49739000	0.00000000
H	-3.69897400	2.49612200	0.00000000
H	-3.69897400	-2.49612200	0.00000000

H	-1.23252900	-2.49771300	0.00000100
H	-1.23252900	2.49771300	-0.00000100
H	1.23252900	2.49771300	-0.00000100
H	1.23252900	-2.49771300	0.00000100
H	3.69897400	-2.49612200	0.00000000
H	3.69897400	2.49612200	0.00000100
H	6.17101500	2.49739000	0.00000000
H	8.29827000	1.24750000	-0.00000100
H	8.29827000	-1.24750000	-0.00000100
H	6.17101500	-2.49739000	0.00000000

heptacene

C	-8.58789300	-0.71364100	0.00045300
C	-8.58789800	0.71362900	0.00036100
C	-7.40676600	1.40799400	0.00015100
C	-6.14991600	0.72500100	-0.00000200
C	-6.14991200	-0.72500200	0.00015100
C	-7.40675900	-1.40800000	0.00036600
C	-4.93012200	-1.40657300	0.00011000
C	-3.69512000	-0.72828000	-0.00009400
C	-3.69512200	0.72828600	-0.00026200
C	-4.93012800	1.40657600	-0.00017000
C	-2.46278800	1.40914900	-0.00039500
C	-1.23286500	0.73100100	-0.00029800
C	-1.23286400	-0.73099400	-0.00023600
C	-2.46278700	-1.40914200	-0.00018000
C	-0.00000100	-1.41010300	-0.00040100
C	1.23286400	-0.73099800	-0.00027300
C	1.23286200	0.73100200	-0.00016900
C	-0.00000100	1.41010700	-0.00034400
C	2.46278800	1.40914900	0.00004100
C	3.69512100	0.72828500	0.00002000
C	3.69512000	-0.72828300	-0.00015800
C	2.46278600	-1.40914600	-0.00022000
C	4.93012200	-1.40657400	-0.00004600
C	6.14991400	-0.72500200	0.00012700
C	6.14991800	0.72500100	0.00025600
C	4.93012800	1.40657500	0.00023000
C	7.40676600	1.40799500	0.00021500
C	8.58789800	0.71363000	0.00030600
C	8.58789500	-0.71363900	0.00026200

C	7.40676000	-1.40800000	0.00007900
H	-9.53454300	-1.24702600	0.00058100
H	-9.53455000	1.24701000	0.00046000
H	-7.40466500	2.49548500	0.00011400
H	-7.40465200	-2.49549100	0.00042300
H	-4.93091600	-2.49472800	0.00016200
H	-4.93092500	2.49473100	-0.00018900
H	-2.46365800	2.49712700	-0.00046800
H	-2.46365700	-2.49712100	-0.00023700
H	-0.00000300	-2.49804200	-0.00053000
H	-0.00000100	2.49804600	-0.00042900
H	2.46365900	2.49712800	0.00012000
H	2.46365600	-2.49712400	-0.00019900
H	4.93091700	-2.49472800	-0.00005600
H	4.93092500	2.49473000	0.00026200
H	7.40466600	2.49548500	0.00013500
H	9.53455100	1.24701000	0.00031900
H	9.53454500	-1.24702400	0.00029100
H	7.40465600	-2.49549000	-0.00003100

octacene

C	9.82180700	-0.71304900	-0.00028600
C	9.82180600	0.71305000	-0.00028500
C	8.63986900	1.40746600	-0.00019400
C	7.38431500	0.72425100	-0.00009900
C	7.38431500	-0.72425100	-0.00010000
C	8.63987000	-1.40746600	-0.00019400
C	6.16231500	-1.40597700	-0.00001400
C	4.93007100	-0.72767100	0.00005900
C	4.93007100	0.72767100	0.00006000
C	6.16231500	1.40597700	-0.00001400
C	3.69403100	1.40859500	0.00012100
C	2.46770800	0.73080300	0.00016500
C	2.46770800	-0.73080300	0.00016500
C	3.69403100	-1.40859500	0.00012100
C	1.23074400	-1.40981400	0.00019300
C	0.00000000	-0.73186800	0.00020100
C	0.00000000	0.73186700	0.00020100
C	1.23074400	1.40981400	0.00019400
C	-1.23074400	1.40981400	0.00019300
C	-2.46770800	0.73080300	0.00016500

C	-2.46770800	-0.73080300	0.00016500
C	-1.23074400	-1.40981400	0.00019200
C	-3.69403200	-1.40859500	0.00012100
C	-4.93007100	-0.72767000	0.00006000
C	-4.93007100	0.72767100	0.00005900
C	-3.69403100	1.40859500	0.00012200
C	-6.16231500	1.40597800	-0.00001500
C	-7.38431500	0.72425100	-0.00010000
C	-7.38431500	-0.72425100	-0.00009900
C	-6.16231500	-1.40597700	-0.00001400
C	-8.63986900	-1.40746600	-0.00019300
C	-9.82180600	-0.71305000	-0.00028500
C	-9.82180700	0.71304900	-0.00028600
C	-8.63986900	1.40746600	-0.00019400
H	10.76825800	-1.24680300	-0.00036000
H	10.76825800	1.24680300	-0.00036000
H	8.63750900	2.49497000	-0.00019600
H	8.63750900	-2.49497000	-0.00019600
H	6.16318300	-2.49415700	-0.00001800
H	6.16318300	2.49415700	-0.00001700
H	3.69509800	2.49661000	0.00011200
H	3.69509800	-2.49661000	0.00011300
H	1.23111900	-2.49778900	0.00018500
H	1.23111900	2.49778900	0.00018700
H	-1.23111900	2.49778900	0.00018400
H	-1.23112000	-2.49778900	0.00018300
H	-3.69509800	-2.49661000	0.00011500
H	-3.69509800	2.49661000	0.00011400
H	-6.16318300	2.49415700	-0.00002000
H	-6.16318300	-2.49415700	-0.00001900
H	-8.63750800	-2.49497000	-0.00019400
H	-10.76825700	-1.24680300	-0.00036000
H	-10.76825800	1.24680300	-0.00036200
H	-8.63750900	2.49497000	-0.00019600

nonacene

C	12.28574200	-0.71317500	0.00000000
C	12.28574200	0.71317500	0.00000000
C	11.10396800	1.40757900	0.00000000
C	9.84822200	0.72425700	0.00000000
C	9.84822200	-0.72425700	0.00000000

C	11.10396800	-1.40757900	0.00000000
C	8.62648900	-1.40590100	0.00000000
C	7.39460800	-0.72734100	0.00000000
C	7.39460800	0.72734100	0.00000000
C	8.62648900	1.40590100	0.00000000
C	6.15771200	1.40824900	0.00000000
C	4.93387900	0.73023600	0.00000000
C	4.93387900	-0.73023600	0.00000000
C	6.15771200	-1.40824900	0.00000000
C	3.69326200	-1.40926000	0.00000000
C	2.46798600	-0.73153800	0.00000000
C	2.46798600	0.73153800	0.00000000
C	3.69326200	1.40926000	0.00000000
C	1.23090500	1.40935600	0.00000000
C	0.00000000	0.73182500	0.00000000
C	0.00000000	-0.73182500	0.00000000
C	1.23090500	-1.40935600	0.00000000
C	-1.23090500	-1.40935600	0.00000000
C	-2.46798600	-0.73153800	0.00000000
C	-2.46798600	0.73153800	0.00000000
C	-1.23090500	1.40935600	0.00000000
C	-3.69326200	1.40926000	0.00000000
C	-4.93387900	0.73023600	0.00000000
C	-4.93387900	-0.73023600	0.00000000
C	-3.69326200	-1.40926000	0.00000000
C	-6.15771200	-1.40824900	0.00000000
C	-7.39460800	-0.72734100	0.00000000
C	-7.39460800	0.72734100	0.00000000
C	-6.15771200	1.40824900	0.00000000
C	-8.62648900	1.40590100	0.00000000
C	-9.84822200	0.72425700	0.00000000
C	-9.84822200	-0.72425700	0.00000000
C	-8.62648900	-1.40590100	0.00000000
C	-11.10396800	-1.40757900	0.00000000
C	-12.28574200	-0.71317500	0.00000000
C	-12.28574200	0.71317500	0.00000000
C	-11.10396800	1.40757900	0.00000000
H	13.23222800	-1.24689200	0.00000000
H	13.23222800	1.24689200	0.00000000
H	11.10184600	2.49509100	0.00000000
H	11.10184600	-2.49509100	0.00000000

H	8.62727700	-2.49409200	0.00000000
H	8.62727700	2.49409200	0.00000000
H	6.15870800	2.49629400	0.00000000
H	6.15870800	-2.49629400	0.00000000
H	3.69374400	-2.49728700	0.00000000
H	3.69374400	2.49728700	0.00000000
H	1.23102300	2.49739300	0.00000000
H	1.23102300	-2.49739300	0.00000000
H	-1.23102300	-2.49739300	0.00000000
H	-1.23102300	2.49739300	0.00000000
H	-3.69374400	2.49728700	0.00000000
H	-3.69374400	-2.49728700	0.00000000
H	-6.15870800	-2.49629400	0.00000000
H	-6.15870800	2.49629400	0.00000000
H	-8.62727700	2.49409200	0.00000000
H	-8.62727700	-2.49409200	0.00000000
H	-11.10184600	-2.49509100	0.00000000
H	-13.23222800	-1.24689200	0.00000000
H	-13.23222800	1.24689200	0.00000000
H	-11.10184600	2.49509100	0.00000000

decacene

C	12.28574200	-0.71317500	0.00000000
C	12.28574200	0.71317500	0.00000000
C	11.10396800	1.40757900	0.00000000
C	9.84822200	0.72425700	0.00000000
C	9.84822200	-0.72425700	0.00000000
C	11.10396800	-1.40757900	0.00000000
C	8.62648900	-1.40590100	0.00000000
C	7.39460800	-0.72734100	0.00000000
C	7.39460800	0.72734100	0.00000000
C	8.62648900	1.40590100	0.00000000
C	6.15771200	1.40824900	0.00000000
C	4.93387900	0.73023600	0.00000000
C	4.93387900	-0.73023600	0.00000000
C	6.15771200	-1.40824900	0.00000000
C	3.69326200	-1.40926000	0.00000000
C	2.46798600	-0.73153800	0.00000000
C	2.46798600	0.73153800	0.00000000
C	3.69326200	1.40926000	0.00000000
C	1.23090500	1.40935600	0.00000000

C	0.00000000	0.73182500	0.00000000
C	0.00000000	-0.73182500	0.00000000
C	1.23090500	-1.40935600	0.00000000
C	-1.23090500	-1.40935600	0.00000000
C	-2.46798600	-0.73153800	0.00000000
C	-2.46798600	0.73153800	0.00000000
C	-1.23090500	1.40935600	0.00000000
C	-3.69326200	1.40926000	0.00000000
C	-4.93387900	0.73023600	0.00000000
C	-4.93387900	-0.73023600	0.00000000
C	-3.69326200	-1.40926000	0.00000000
C	-6.15771200	-1.40824900	0.00000000
C	-7.39460800	-0.72734100	0.00000000
C	-7.39460800	0.72734100	0.00000000
C	-6.15771200	1.40824900	0.00000000
C	-8.62648900	1.40590100	0.00000000
C	-9.84822200	0.72425700	0.00000000
C	-9.84822200	-0.72425700	0.00000000
C	-8.62648900	-1.40590100	0.00000000
C	-11.10396800	-1.40757900	0.00000000
C	-12.28574200	-0.71317500	0.00000000
C	-12.28574200	0.71317500	0.00000000
C	-11.10396800	1.40757900	0.00000000
H	13.23222800	-1.24689200	0.00000000
H	13.23222800	1.24689200	0.00000000
H	11.10184600	2.49509100	0.00000000
H	11.10184600	-2.49509100	0.00000000
H	8.62727700	-2.49409200	0.00000000
H	8.62727700	2.49409200	0.00000000
H	6.15870800	2.49629400	0.00000000
H	6.15870800	-2.49629400	0.00000000
H	3.69374400	-2.49728700	0.00000000
H	3.69374400	2.49728700	0.00000000
H	1.23102300	2.49739300	0.00000000
H	1.23102300	-2.49739300	0.00000000
H	-1.23102300	-2.49739300	0.00000000
H	-1.23102300	2.49739300	0.00000000
H	-3.69374400	2.49728700	0.00000000
H	-3.69374400	-2.49728700	0.00000000
H	-6.15870800	-2.49629400	0.00000000
H	-6.15870800	2.49629400	0.00000000

H	-8.62727700	2.49409200	0.00000000
H	-8.62727700	-2.49409200	0.00000000
H	-11.10184600	-2.49509100	0.00000000
H	-13.23222800	-1.24689200	0.00000000
H	-13.23222800	1.24689200	0.00000000
H	-11.10184600	2.49509100	0.00000000

8. Cartesian coordinates of triplet polyacenes

naphthalene

C	2.48798600	-0.68148000	0.00000000
C	1.23859200	-1.40078900	0.00000100
C	0.00005100	-0.72537800	0.00000000
C	-0.00017400	0.72538000	0.00000000
C	1.23757600	1.40115000	0.00000000
C	2.48791200	0.68194500	-0.00000100
H	-1.24577400	-2.48782900	0.00000100
H	3.41942700	-1.24034200	-0.00000100
H	1.24707400	-2.48750100	0.00000100
C	-1.23757600	-1.40110600	0.00000000
C	-1.23859000	1.40074800	0.00000100
H	1.24580100	2.48786300	-0.00000100
H	3.41912400	1.24115000	-0.00000200
C	-2.48793900	0.68155500	0.00000000
C	-2.48786200	-0.68202400	-0.00000100
H	-1.24704700	2.48747000	0.00000100
H	-3.41938400	1.24040800	0.00000100
H	-3.41907800	-1.24122300	-0.00000200

anthracene

C	3.70521200	-0.69161100	0.00000100
C	2.48010100	-1.39592400	0.00000200
C	1.25483000	-0.72060000	0.00000100
C	1.25483000	0.72060000	0.00000000
C	2.48010100	1.39592400	-0.00000100
C	3.70521200	0.69161100	0.00000000
C	0.00000000	-1.40635000	0.00000100
C	0.00000000	1.40635000	0.00000000
C	-1.25483000	0.72060000	0.00000000
C	-1.25483000	-0.72060000	0.00000000
C	-2.48010100	-1.39592400	-0.00000100
H	-2.48352800	-2.48336000	-0.00000100

C	-3.70521300	-0.69161100	-0.00000200
C	-3.70521300	0.69161100	-0.00000200
C	-2.48010100	1.39592400	-0.00000100
H	0.00000000	-2.49383400	0.00000300
H	4.64104600	-1.24328900	0.00000100
H	2.48352800	-2.48336000	0.00000400
H	2.48352800	2.48336000	-0.00000100
H	4.64104600	1.24328900	-0.00000200
H	0.00000000	2.49383400	0.00000000
H	-4.64104600	-1.24328900	-0.00000300
H	-4.64104600	1.24328900	-0.00000300
H	-2.48352800	2.48336000	-0.00000100

tetracene

C	-3.71608300	1.39748900	0.00000000
C	-4.92556100	0.69863700	0.00000000
C	-4.92556100	-0.69863700	0.00000000
C	-3.71608300	-1.39748900	0.00000000
C	-2.48655400	-0.71755600	0.00000000
C	-1.23104000	-1.40477500	0.00000000
C	0.00000000	-0.73086900	0.00000000
C	1.23104000	-1.40477500	0.00000000
C	2.48655400	-0.71755600	0.00000000
C	3.71608300	-1.39748900	0.00000000
C	4.92556100	-0.69863700	0.00000000
C	4.92556100	0.69863700	0.00000000
C	3.71608300	1.39748900	0.00000000
C	2.48655400	0.71755600	0.00000000
C	1.23104000	1.40477500	0.00000000
C	0.00000000	0.73086900	0.00000000
C	-1.23104000	1.40477500	0.00000000
C	-2.48655400	0.71755600	0.00000000
H	-3.71628200	2.48506200	0.00000000
H	-5.86499200	1.24438900	0.00000000
H	-5.86499200	-1.24438900	0.00000000
H	-3.71628300	-2.48506200	0.00000100
H	-1.23534500	-2.49265600	0.00000000
H	1.23534500	-2.49265600	-0.00000100
H	3.71628200	-2.48506200	0.00000000
H	5.86499200	-1.24438900	0.00000000
H	5.86499200	1.24438900	0.00000100

H	3.71628300	2.48506200	0.00000100
H	1.23534500	2.49265600	0.00000000
H	-1.23534500	2.49265600	-0.00000100

pentacene

C	4.94820600	0.26612200	0.12752000
C	4.73247100	1.64484800	-0.05283600
C	3.44100700	2.14102600	-0.14945700
C	2.32417800	1.28023900	-0.06954100
C	2.54424200	-0.12613200	0.11450100
C	3.87033500	-0.60267000	0.20945800
C	1.41565500	-0.99177700	0.19468700
C	0.10741900	-0.52163700	0.10102700
C	-0.11636500	0.90840000	-0.08599100
C	0.98534400	1.75770400	-0.16486700
C	-1.44948500	1.37987400	-0.18036900
C	-2.57444200	0.52163700	-0.10102700
C	-2.35065800	-0.90840000	0.08599100
C	-1.01753800	-1.37987400	0.18036900
C	-3.45236700	-1.75770500	0.16486600
C	-4.79120100	-1.28023900	0.06954200
C	-5.01126500	0.12613200	-0.11450000
C	-3.88267700	0.99177700	-0.19468500
C	-6.33735700	0.60267000	-0.20945600
C	-7.41522900	-0.26612200	-0.12751900
C	-7.19949300	-1.64484800	0.05283600
C	-5.90803000	-2.14102600	0.14945700
H	5.96173500	-0.11814800	0.20251200
H	5.57992200	2.32183500	-0.11643600
H	3.27300500	3.20650700	-0.28867800
H	4.03592500	-1.66852600	0.34864500
H	1.58642000	-2.05738700	0.33390500
H	0.82215000	2.82452000	-0.30397500
H	-1.61645200	2.44579600	-0.31943000
H	-0.85057100	-2.44579600	0.31942900
H	-3.28917300	-2.82452000	0.30397400
H	-4.05344200	2.05738700	-0.33390300
H	-6.50294700	1.66852600	-0.34864200
H	-8.42875700	0.11814800	-0.20251000
H	-8.04694500	-2.32183500	0.11643600
H	-5.74002800	-3.20650700	0.28867800

hexacene

C	-7.37328100	0.70706500	-0.00000100
C	-7.37328100	-0.70706400	-0.00000100
C	-6.18088100	-1.40250300	0.00000000
C	-4.93803700	-0.71905500	0.00000000
C	-4.93803600	0.71905400	0.00000000
C	-6.18088100	1.40250300	0.00000000
C	-3.69716100	1.40279800	0.00000000
C	-2.47917400	0.72741600	0.00000000
C	-2.47917400	-0.72741600	0.00000000
C	-3.69716100	-1.40279800	0.00000000
C	-1.22917900	-1.40803900	0.00000100
C	0.00000000	-0.73363900	0.00000100
C	0.00000000	0.73363900	0.00000000
C	-1.22917900	1.40803900	0.00000100
C	1.22917800	1.40803900	0.00000000
C	2.47917400	0.72741600	0.00000100
C	2.47917400	-0.72741600	0.00000000
C	1.22917800	-1.40803900	0.00000000
C	3.69716100	-1.40279800	0.00000000
C	4.93803700	-0.71905400	0.00000000
C	4.93803700	0.71905400	0.00000000
C	3.69716100	1.40279800	0.00000000
C	6.18088100	1.40250300	0.00000000
C	7.37328100	0.70706400	-0.00000100
C	7.37328100	-0.70706500	-0.00000100
C	6.18088100	-1.40250300	0.00000000
H	-8.31696600	1.24564800	-0.00000200
H	-8.31696600	-1.24564800	0.00000000
H	-6.17897400	-2.49006500	0.00000000
H	-6.17897400	2.49006500	0.00000000
H	-3.69973500	2.49101300	0.00000000
H	-3.69973500	-2.49101300	0.00000000
H	-1.23135100	-2.49599200	0.00000100
H	-1.23135100	2.49599200	0.00000100
H	1.23135100	2.49599200	0.00000000
H	1.23135100	-2.49599200	0.00000000
H	3.69973500	-2.49101300	0.00000000
H	3.69973500	2.49101300	0.00000000
H	6.17897400	2.49006500	0.00000000

H	8.31696600	1.24564800	-0.00000100
H	8.31696600	-1.24564800	0.00000000
H	6.17897400	-2.49006500	0.00000000

9. Table S4 Singlet energies (E_h) of two forms of $\{[Cu(NH_3)]_2O_2\}^{2+}$

basis sets: Cartesian cc-pVTZ for Cu and O atoms; Cartesian cc-pVDZ for N and H atoms.

Species	UHF <S**2>	UHF	GVB(16)	CASSCF(4,4)	CASSCF(4,4)-NEVPT2
bis	1.972	-3539.617296	-3539.779994	-3539.607233	-3542.324940
per	1.003	-3539.588258	-3539.800928	-3539.620771	-3542.363778

10. Cartesian coordinates of two forms of $\{[Cu(NH_3)]_2O_2\}^{2+}$

bis

Cu	0.000000	1.400000	0.000000
Cu	0.000000	-1.400000	0.000000
O	0.000000	0.000000	1.150000
O	0.000000	0.000000	-1.150000
N	0.000000	3.400000	0.000000
N	0.000000	-3.400000	0.000000
H	-0.939693	3.742020	0.000000
H	0.939693	-3.742020	0.000000
H	0.469846	3.742020	0.813798
H	-0.469846	-3.742020	-0.813798
H	0.469846	3.742020	-0.813798
H	-0.469846	-3.742020	0.813798

per

Cu	0.00000000	1.80000000	0.00000000
Cu	0.00000000	-1.80000000	0.00000000
O	0.00000000	0.00000000	0.70000000
O	0.00000000	0.00000000	-0.70000000
N	0.00000000	3.80000000	0.00000000
N	0.00000000	-3.80000000	0.00000000
H	-0.93969300	4.14202000	0.00000000
H	0.93969300	-4.14202000	0.00000000
H	0.46984600	4.14202000	0.81379800
H	-0.46984600	-4.14202000	-0.81379800
H	0.46984600	4.14202000	-0.81379800
H	-0.46984600	-4.14202000	0.81379800