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Supporting Information

Relativity or Aromaticity? A First-Principles Perspective to Chemical Shifts in Osmabenzene and Osmapentalene Derivatives

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Table S1. Contributions of dia- (D) and paramagnetic (P) ring currents into the net ring current of molecules **1** and **2** at scalar (1c) and fully relativistic (4c) level in $nA.T^{-1}$. MICI is obtained via integration of currents passing a rectangular plane perpendicular to the selected bonds marked in **Scheme 2**.

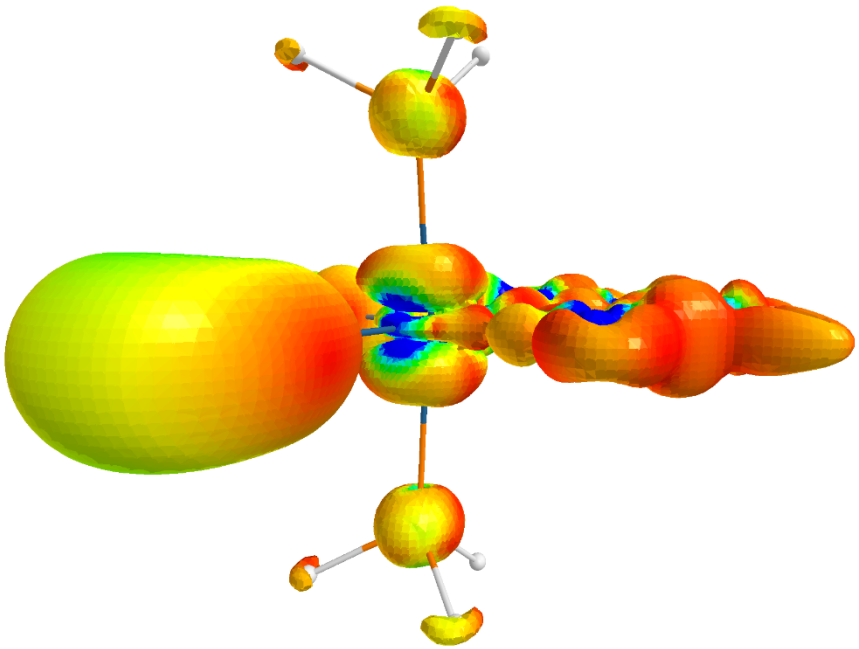
Molecule	$1c_D$	$1c_P$	$1c_{Net}$	$4c_D$	$4c_P$	$4c_{Net}$
1	13.10	-7.04	6.06	13.09	-7.08	6.01
2	13.29	-2.44	10.85	13.13	-2.42	10.70

Table S2. NMR chemical shifts and spin-orbit contribution to magnetic shielding for LA in **1** and **2** in ppm.

1	$\delta(^{13}C)$	σ_{SO} (^{13}C)		$\delta(^{1}H)$	σ^{SO} (^{1}H)
C1	235.7	24.0	H6	12.8	-1.8
C2	133.5	0.3	H7	7.6	-0.1
C3	152.3	-5.0	H8	8.3	-1.1
C4	126.2	-3.4	H9	7.3	-0.2
C5	253.9	29.4	H10	16.2	-3.3
2					
C1	227.0	26.2	H8	13.9	-2.2
C2	160.7	-12.4	H9	8.3	-0.2
C3	154.4	-0.2	H10	9.6	-0.9
C4	191.8	8.6	H11	9.6	-1.0
C5	154.4	-0.2	H12	8.3	-0.2
C6	160.7	-12.4	H13	13.9	-2.2
C7	227.0	26.2			

Table S3. Principal components of SO contribution to NMR chemical shielding tensor, $\boldsymbol{\sigma}^{SO}$, for C1, C5, H6 and H10 in compound **1,** C1 – C4 and H8 in **2** and their projection to Cartesian axes, in ppm.

1						
C1	33.1	3.0	35.8	33.1	3.0	35.8
C5	24.0	13.7	50.5	13.7	24.0	50.5
H6	-1.6	-2.0	-1.7	-1.6	-1.7	-2.0
H10	-3.2	0.5	-7.1	-7.1	-3.2	0.5
2						
C1	23.3	6.3	48.9	23.3	6.3	48.9
C2	-10.6	-2.6	-23.8	-10.6	-2.6	-23.8
C3	-2.4	-0.2	1.8	-2.4	-0.2	1.8
C4	26.0	1.8	-1.8	26.0	1.8	-1.8
H8	-2.0	-0.9	-3.6	-2.0	-3.6	-0.9



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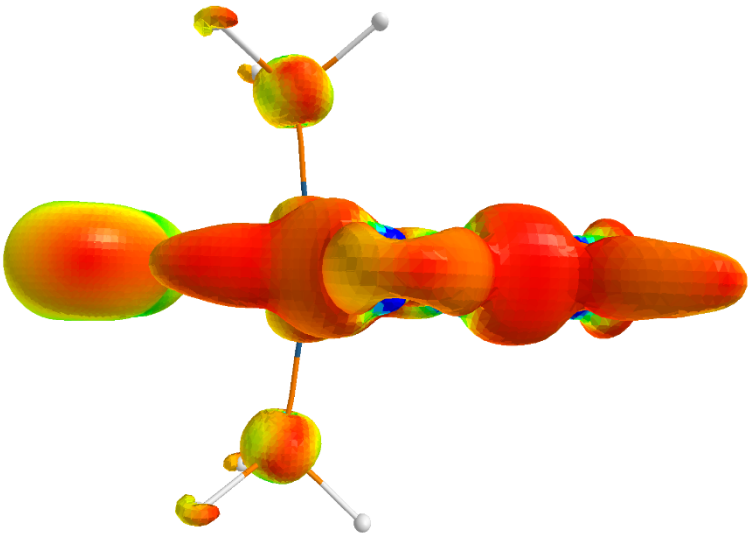

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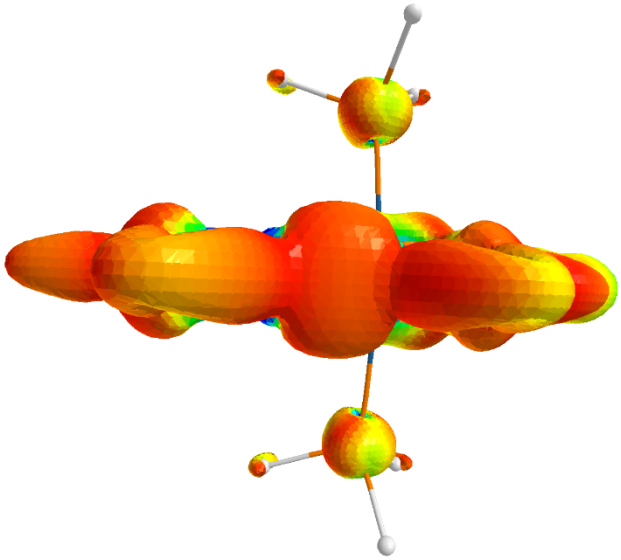

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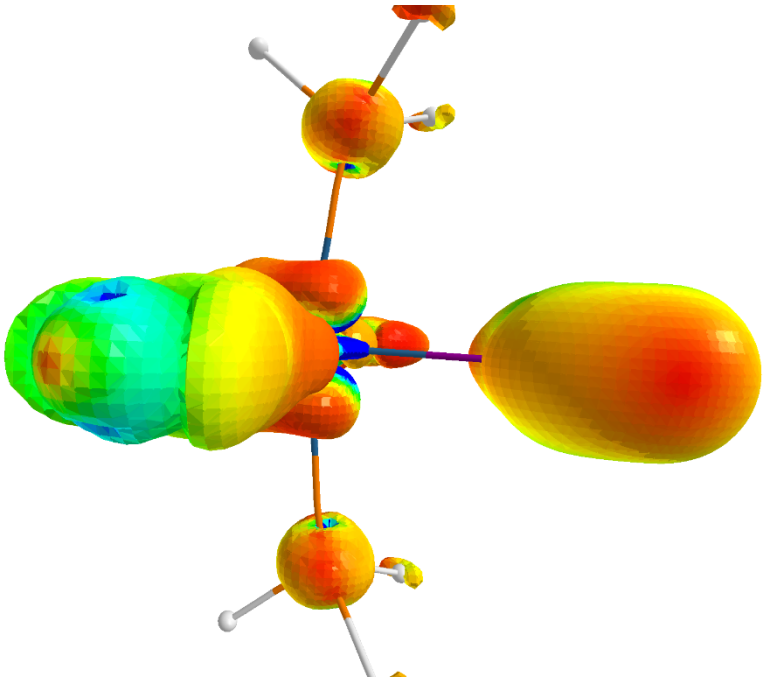

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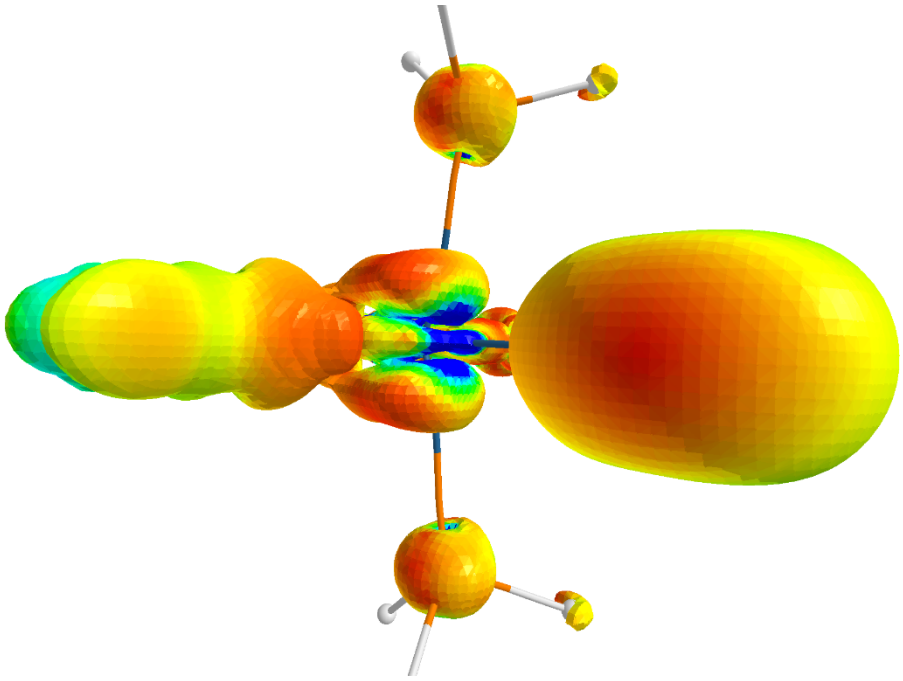

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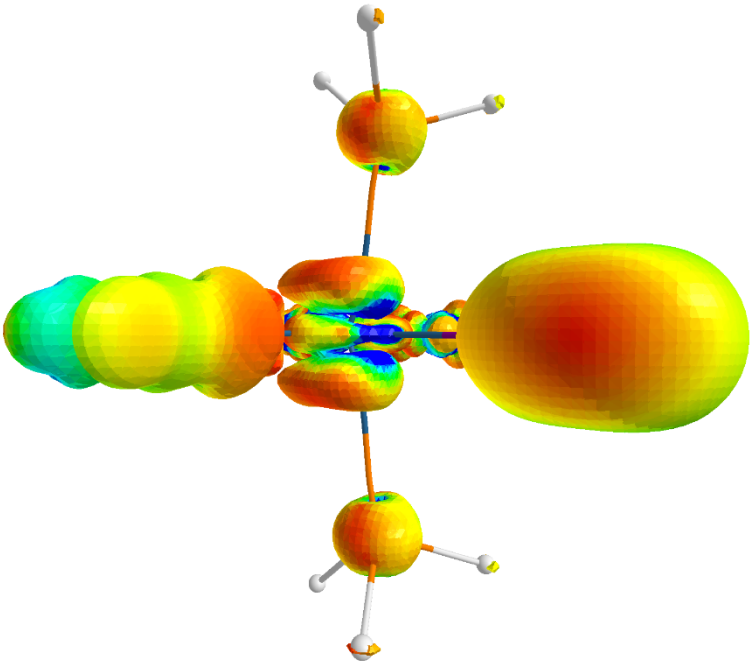

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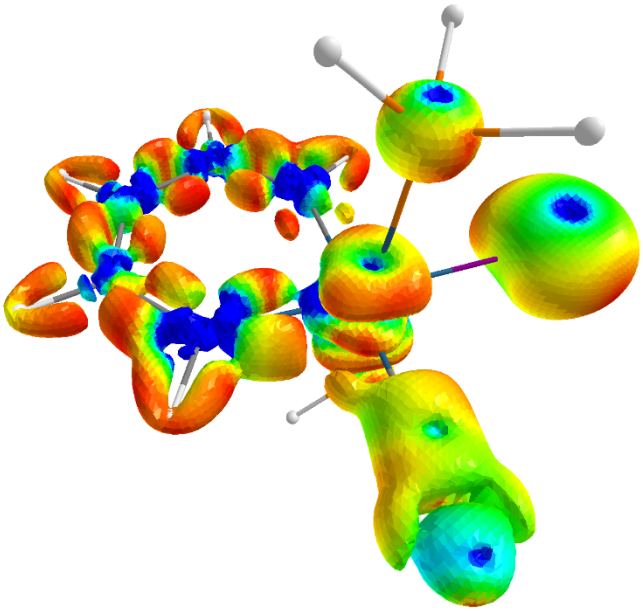

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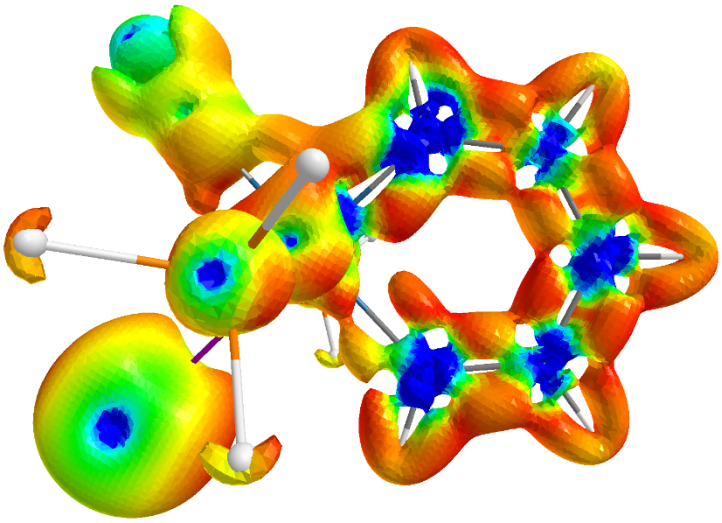

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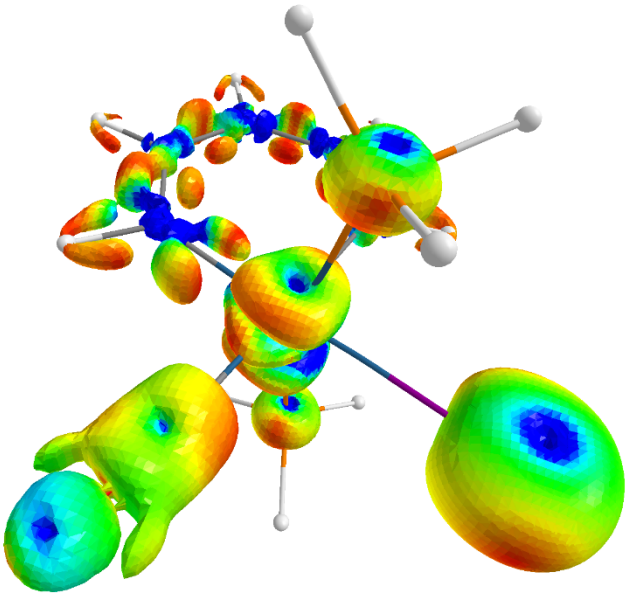

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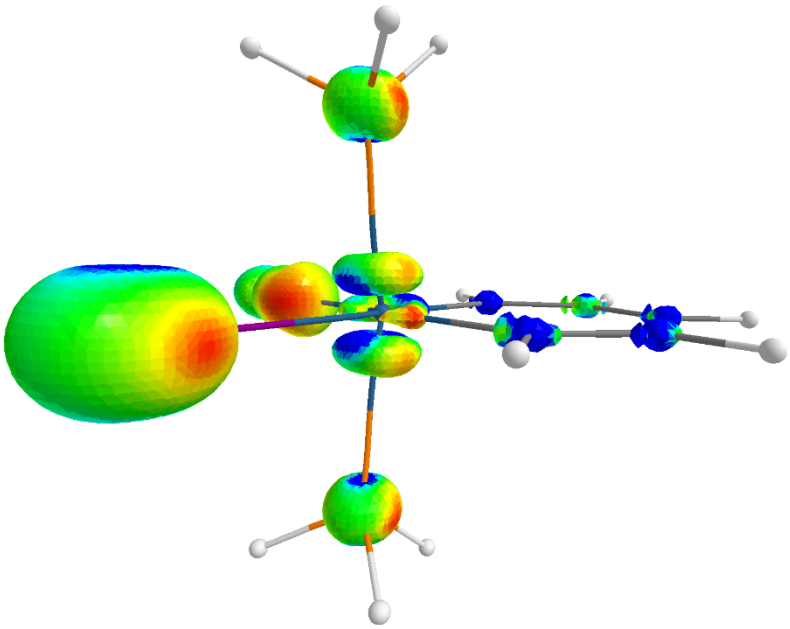

j = 0.001 au

Figure S1. Isosurface of current density at different cutoffs and from different angles for a magnetic field applied perpendicular to the ring plane of molecule **1**. To make the nodal plane more visible, false colors have been added to the isosurface. False colors are generated by highlighting the current intensity on j = 0.0005 au isosurface of perpendicular magnetic field for a second field that is applied along the ring plane of the molecule.

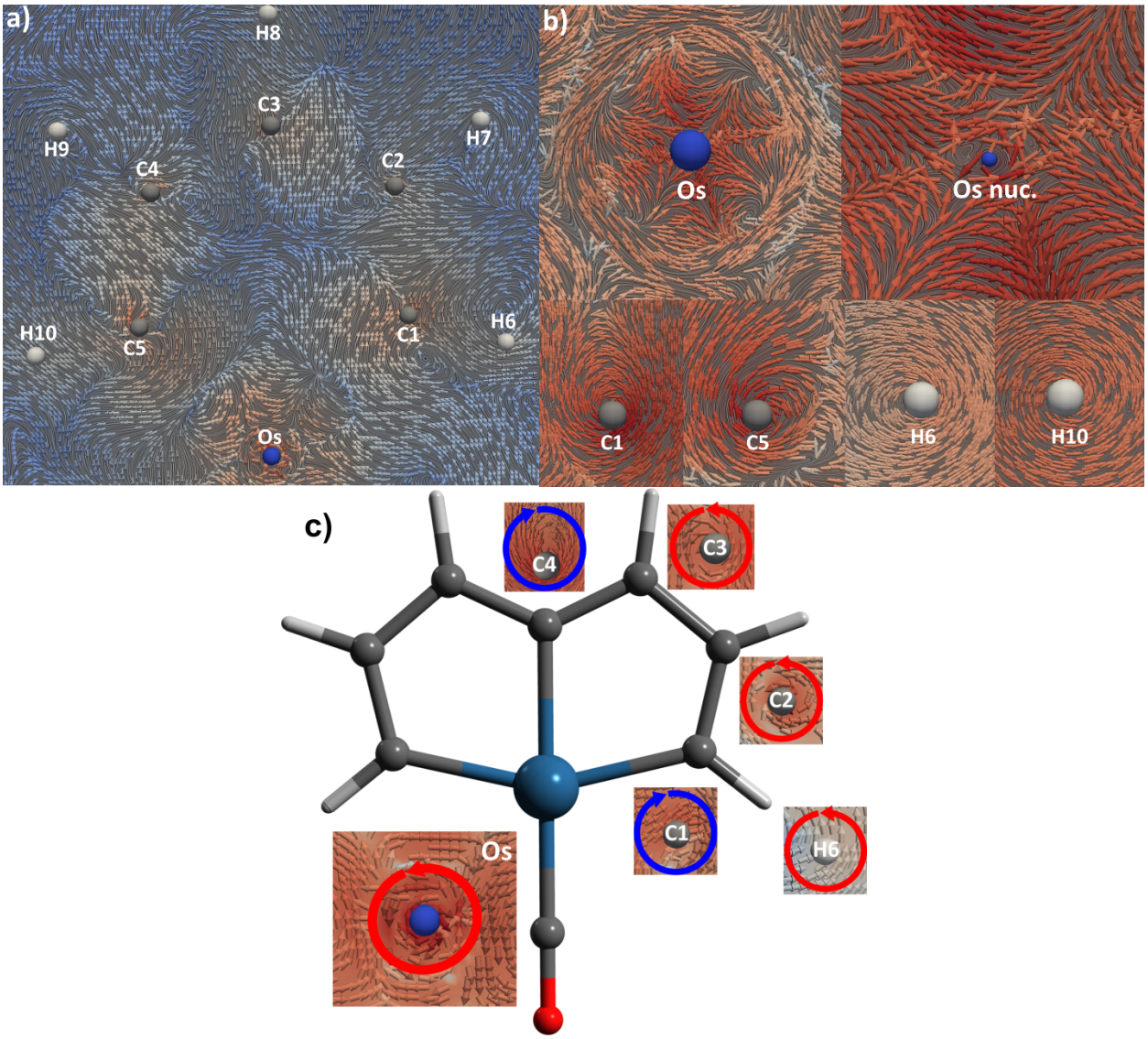

Figure S2. a) SO-MIC in **1** (mag. field perpendicular the plane of the ring) obtained as a difference between MIC calculated at 4c and 1c levels. b) Details of SO-MIC direction around Os and its nucleus (top), and C1, C5, H6 and H10 (bottom). c) SO-MIC in **2** (magnetic field is perpendicular to the orientation of largest SO shielding tensor component) obtained as a difference between MIC calculated at 4c and 1c levels.

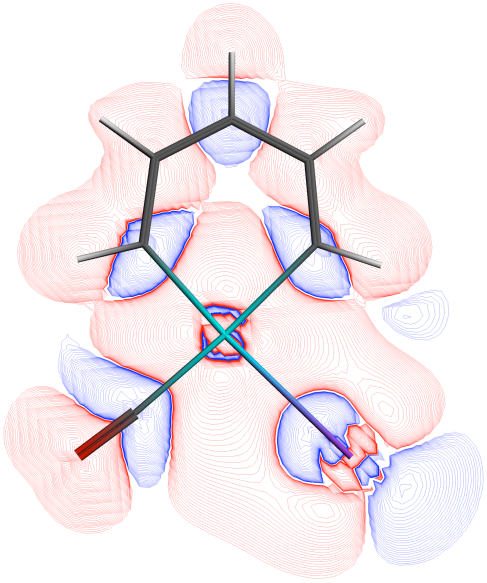

Figure S3: Spin-orbit and magnetically induced density (SOM-ISD) plot for 1. Calculated at 4c level. The red and blue color represents SO and magnetic field induced depletion/concentration of spin density.

Molecular Coordinates

1

Energy: -1.381239752544388E+03

Os	-0.019624630	0.509878392	0.000000000
I	-0.769794726	-2.225406263	0.000000000
P	-0.019624630	0.093964353	2.291341161
P	-0.019624630	0.093964353	-2.291341161
O	-2.867685925	1.645276775	0.000000000
C	1.944245728	2.868873812	0.000000000
C	3.084028486	2.093541611	0.000000000
C	0.637805241	2.369836245	0.000000000
C	3.111017325	0.685811259	0.000000000
C	1.979078307	-0.079915605	0.000000000
C	-1.824107993	1.174318125	0.000000000
H	4.039296229	2.611280741	0.000000000
H	-0.095182920	3.181097226	0.000000000
H	4.090122556	0.213479736	0.000000000
H	2.176559213	-1.156305805	0.000000000
H	2.079785278	3.946909539	0.000000000
H	0.357811193	1.113348529	3.194308078
H	-1.225472838	-0.311902934	2.888350466
H	0.836579462	-0.929757971	2.728814866
H	-1.225472838	-0.311902934	-2.888350466
H	0.357811193	1.113348529	-3.194308078
H	0.836579462	-0.929757971	-2.728814866

2

Energy: -1.160202934786927E+03

Os	0.000000000	0.000000000	0.324334005
P	-2.306184434	0.000000000	0.101807692
P	2.306184434	0.000000000	0.101807692
O	0.000000000	0.000000000	3.387053329
C	0.000000000	1.254432608	-2.385803480
C	0.000000000	2.329384734	-1.484981927
C	0.000000000	2.008619225	-0.127819959
C	0.000000000	0.000000000	-1.786308507
C	0.000000000	-2.008619225	-0.127819959
C	0.000000000	-2.329384734	-1.484981927
C	0.000000000	-1.254432608	-2.385803480
C	0.000000000	0.000000000	2.234855770
H	0.000000000	1.405845142	-3.464169197
H	0.000000000	3.355884307	-1.844168869
H	0.000000000	2.863657145	0.551023390
H	0.000000000	-2.863657145	0.551023390
H	0.000000000	-3.355884307	-1.844168869
H	0.000000000	-1.405845142	-3.464169197
H	2.884544518	1.071845295	-0.609515388
H	3.163502654	0.000000000	1.222314951
H	2.884544518	-1.071845295	-0.609515388
H	-3.163502654	0.000000000	1.222314951
H	-2.884544518	1.071845295	-0.609515388
H	-2.884544518	-1.071845295	-0.609515388

3

Energy: -1.176235933476504E+03

Os	0.000084543	0.312938987	0.000000000
P	-0.004234589	0.137689537	2.312808045
P	-0.004234589	0.137689537	-2.312808045
O	-0.056045511	3.379975308	0.000000000
N	-2.334940074	-1.502371385	0.000000000
C	-1.277031255	-2.332296506	0.000000000
C	-1.984990212	-0.209337717	0.000000000
C	-0.004234589	-1.777543395	0.000000000
C	2.013756694	-0.154539166	0.000000000
C	2.323658603	-1.514574752	0.000000000
C	1.236941157	-2.401903195	0.000000000
C	-0.029853100	2.228633456	0.000000000
H	-1.481515192	-3.402110538	0.000000000
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H	2.876283357	0.514856181	0.000000000
H	3.346237501	-1.884364364	0.000000000
H	1.371934400	-3.482088096	0.000000000
H	1.038719281	-0.606695853	-2.902316015
H	-1.097484404	-0.505130785	-2.928987522
H	0.057023457	1.284287867	-3.130974626
H	0.057023457	1.284287867	3.130974626
H	-1.097484404	-0.505130785	2.928987522
H	1.038719281	-0.606695853	2.902316015

4

Energy: -3.907792504446568E+03

Os	0.229691725	0.195338106	0.000000000
Se	-0.510530010	-2.379369299	0.000000000
Cl	2.573523135	-0.501551920	0.000000000
P	0.287408104	0.185802433	2.329107805
P	0.287408104	0.185802433	-2.329107805
C	1.057975353	2.055870747	0.000000000
C	-1.462208768	-0.855703065	0.000000000
C	-1.374128252	1.546792481	0.000000000
C	-2.748766219	-0.335779969	0.000000000
C	0.287408104	3.187137917	0.000000000
C	-1.085773680	2.895445897	0.000000000
C	-2.685907582	1.043235952	0.000000000
H	2.142992944	2.126687120	0.000000000
H	-3.650924394	-0.932049895	0.000000000
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H	-3.559848507	1.689029182	0.000000000
H	-0.198823876	1.312996776	3.023099473
H	1.548525282	0.044709125	2.938102547
H	-0.429134228	-0.832041666	2.992241036
H	-0.429134228	-0.832041666	-2.992241036
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5

Energy: -1.239680014107051E+03

Os	0.083478137	-0.287595219	0.000050012
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P	0.262767202	-0.274060971	2.302321017
C	1.548305801	1.250897111	-0.000206871
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C	3.060877177	-0.536492167	0.000079037
C	1.064394284	2.567703476	-0.000424146
C	1.917043837	-1.296211051	0.000207080
C	-3.373924759	0.603390866	-0.000135170
C	-1.051504775	1.466894257	-0.000265968
C	-2.465567753	1.622377190	-0.000312501
C	-0.305347935	2.675039884	-0.000456836
C	-1.754756388	-1.170982827	0.000209740
C	-0.860229446	-2.248911776	0.000433491
H	3.695312708	1.573162611	-0.000271028
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H	-0.734186156	-2.836168684	-0.906207990

6

Energy: -1.506403841106832E+03

Os	-0.211844932	-0.171331084	0.000000000
Cl	-0.804138938	-2.523465666	0.000000000
P	-0.087246926	-0.273825534	2.327241302
P	-0.087246926	-0.273825534	-2.327241302
C	2.122410860	1.698261716	0.000000000
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H	1.025578693	0.340649744	2.935945049
H	-1.112379907	0.281039525	3.118934108