

**Supporting Information: Comment on "Polycyclic aromatic hydrocarbons containing antiaromatic chalcogenopyrrole b]-chalcogenopyrans" by W. Chen, H. Zong, Y. Xie, J. Xu, J.-W. Cai, S.-D. Wang and G. Zhou, Org. Chem. Front., 2024, 11, 390.†**

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# 1 Computational Details

All geometries were fully optimized using the CAM-B3LYP<sup>1</sup> and B3LYP<sup>2</sup> DFAs, in combination with the 6-311G(d,p) basis set,<sup>3</sup> and Grimme’s dispersion correction with Beck-Johnson damping D3(BJ).<sup>4</sup> The frequency analysis was used to confirm that the minimum was obtained.

We evaluated the  $\text{EDDB}_H(r)$  function,<sup>5</sup> that is, by excluding hydrogen atoms, which is recommended for organic molecules.<sup>6</sup> The  $\text{EDDB}_H$  function reflects the population of delocalized electrons across all conjugated bonds in a molecule. In addition, the  $\text{EDDB}_F$  function was estimated. Run EDDB program, requires the one-electron density matrix that was calculated at the CAM-B3LYP/6-311G(d,p) level in conjunction with the natural bond orbital (NBO) version 3 code.<sup>7</sup> The geometry optimizations and the EDDB functions ( $\text{EDDB}_H(r)$  and  $\text{EDDB}_F(r)$ ) were carried out in Gaussian 16 software.<sup>8</sup>

The calculation of the electronic aromaticity indices (AV1245,<sup>9</sup> AVmin,<sup>10</sup> and BOA<sup>11</sup>) employs the quantum theory of atoms in molecules<sup>12</sup> (QTAIM) atomic partition performed by the AIMAll software.<sup>13</sup> The atomic overlap matrices resulting from this partition and the wavefunction files (obtained with Gaussian 16 package<sup>8</sup>) are the input of the in-house ESI-3D code,<sup>11,14,15</sup> which provides AV1245, AVmin, BOA, Iring and MCI values. The numerical integrations of the atoms in the QTAIM have errors below 0.0004 (in all the molecules). The ESI-3D code is available upon request (ematito@gmail.com).

To quantify the electron current density ( $J$ ) in the bonds, the perturbed wave function was calculated through the Gauge-Independent Atomic Orbital (GIAO) method,<sup>16</sup> with the Gaussian 16 computational package. Then we use the gauge-including magnetically induced current method (GIMIC) method<sup>17</sup> which calculates the current flow passing through a plane perpendicular to the molecule. The plane was created in AIMAll software with a mesh size of 0.05 a.u. The length of the plane was 5 a.u. up and down from the origin. In all cases, the origin is located at the central bond’s midpoint. Finally, the surface was integrated using Paraview 4.2.0.<sup>18</sup> The current density maps display the current flowing through the plane lying 1 a.u. above the molecular plane.

## 2 Singlet and triplet state energies

Table S1: Energies for  $S = 0$  (singlets) and  $S = 1$  (triplets). The methodologies used were CAM-B3LYP/6-311G(d,p) and B3LYP/6-311G(d,p). For systems SS1 and SeSe1 it was not possible to obtain a minimum on the potential energy surface. All values in a.u.

Molecule	CAM-B3LYP		B3LYP	
	$S = 0$	$S = 1$	$S = 0$	$S = 1$
SS	-1104.72971094	-1104.69509478	-1104.94938732	-1104.91371215
SSe	-3108.15542818	-3108.12065282	-3108.28130263	-3108.24576046
SeSe	-5111.58112866	-5111.54630768	-5111.61325463	-5111.57797051
SS1	-1334.48518877	-1334.43550758	-1334.84960067	–
SSe1	-3337.90962095	-3337.87202143	-3338.18011832	-3338.14293585
SeSe1	-5341.33400127	-5341.29691960	-5341.51064915	–
SS2	-1948.90125845	-1948.86070188	-1949.65406646	-1949.61710221
SSe2	-3952.32619463	-3952.28623344	-3952.98511958	-3952.94840715
SeSe2	-5955.75114957	-5955.71154522	-5956.31626918	-5956.27992353

### 3 EDDB function: CAM-B3LYP and B3LYP

The Figure S1 shows the names assigned to each of the rings of the molecules, allowing a better analysis of Table S2.

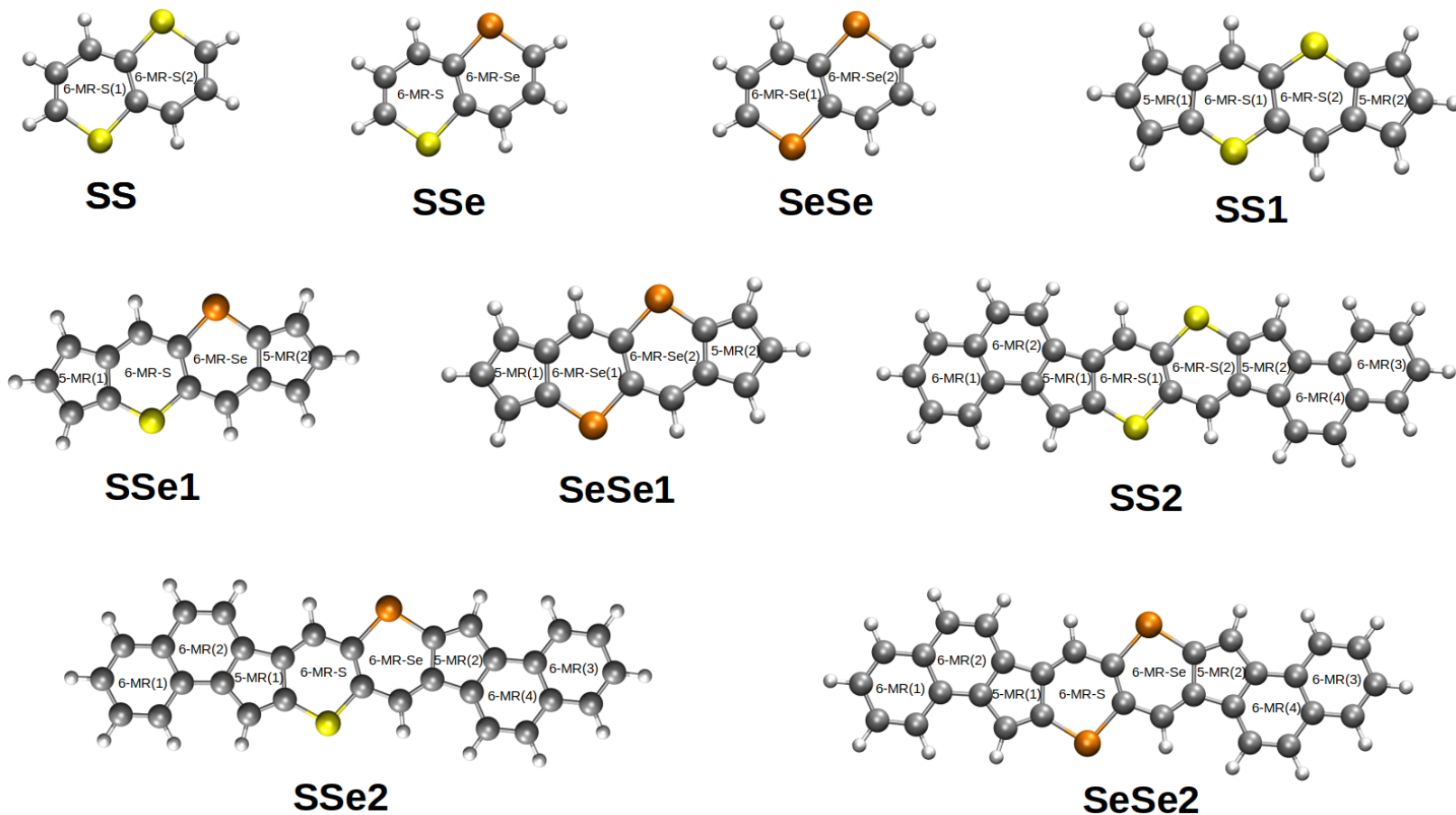


Figure S1: SS: Thiopyrano[3,2-b]thiopyran; SSe: Selenopyrano[3,2-b]thiopyran; SeSe: Selenopyrano[3,2-b]selenopyran; SS1: Cyclopenta[5,6]Thiopyrano[3,2-b]cyclopenta[e]Thiopyran; SSe1: Cyclopenta[5,6]Selenopyrano[3,2-b]cyclopenta[e]Thiopyran; SeSe1: Cyclopenta[5,6]Selenopyrano[3,2-b]cyclopenta[e]Selenopyran; polycyclic aromatic hydrocarbons containing chalcogenopyrano[3,2-b] chalcogenopyran : SS2, SSe2, SeSe2. Molecules optimized with the CAM-B3LYP/6-311G(d,p) methodology. White spheres: hydrogen atoms; gray spheres: carbon atoms; yellow spheres: sulfur atoms; orange spheres: selenium atoms.



Table S2: EDDB<sub>F</sub> values for the 5-MRs, 6-MRs, 6-MR-Se and for 6-MR-S. In parentheses the average values. The methodologies used were CAM-B3LYP/6-311G(d,p) and B3LYP/6-311G(d,p). All values in e

Molecule	Ring	CAM-B3LYP	B3LYP
SS	6-MR-S(1)	1.54 (0.26)	1.71 (0.28)
	6-MR-S(2)	1.54 (0.26)	1.71 (0.28)
SSe	6-MR-S	1.55 (0.26)	1.72 (0.29)
	6-MR-Se	1.44 (0.24)	1.63 (0.27)
SeSe	6-MR-Se(1)	1.45 (0.24)	1.64 (0.27)
	6-MR-Se(2)	1.45 (0.24)	1.64 (0.27)
SS1	5-MR(1)	1.20 (0.24)	1.42 (0.28)
	5-MR(2)	1.20 (0.24)	1.42 (0.28)
	6-MR-S(1)	1.82 (0.30)	2.18 (0.36)
	6-MR-S(2)	1.82 (0.30)	2.18 (0.36)
SSe1	5-MR(1)	1.24 (0.25)	1.48 (0.30)
	5-MR(2)	1.10 (0.22)	1.27 (0.25)
	6-MR-S	1.90 (0.32)	2.29 (0.38)
	6-MR-Se	1.64 (0.27)	2.01 (0.33)
SeSe1	5-MR(1)	1.12 (0.22)	1.31 (0.26)
	5-MR(2)	1.12 (0.22)	1.31 (0.26)
	6-MR-Se(1)	1.71 (0.29)	2.10 (0.35)
	6-MR-Se(2)	1.71 (0.29)	2.10 (0.35)
SS2	5-MR(1)	0.88 (0.18)	1.09 (0.22)
	5-MR(2)	0.88 (0.18)	1.09 (0.22)
	6-MR(1)	3.38 (0.56)	3.50 (0.58)
	6-MR(2)	2.78 (0.46)	2.95 (0.49)
	6-MR(3)	3.38 (0.56)	3.50 (0.58)
	6-MR(4)	2.78 (0.46)	2.95 (0.49)
	6-MR-S(1)	1.60 (0.27)	1.94 (0.32)
	6-MR-S(2)	1.60 (0.27)	1.94 (0.32)
SSe2	5-MR(1)	0.90 (0.18)	1.12 (0.22)
	5-MR(2)	0.81 (0.16)	1.00 (0.20)
	6-MR(1)	3.39 (0.56)	3.51 (0.58)
	6-MR(2)	2.77 (0.46)	2.94 (0.49)
	6-MR(3)	3.34 (0.56)	3.46 (0.57)
	6-MR(4)	2.86 (0.48)	3.03 (0.50)
	6-MR-S	1.66 (0.28)	2.00 (0.33)
	6-MR-Se	1.50 (0.25)	1.83 (0.31)
SeSe2	5-MR(1)	0.82 (0.16)	1.02 (0.20)
	5-MR(2)	0.82 (0.16)	1.02 (0.20)
	6-MR(1)	3.35 (0.56)	3.47 (0.58)
	6-MR(2)	2.85 (0.47)	3.02 (0.50)
	6-MR(3)	3.35 (0.56)	3.47 (0.58)
	6-MR(4)	2.85 (0.47)	3.02 (0.50)
	6-MR-Se(1)	1.56 (0.26)	1.90 (0.32)
	6-MR-Se(2)	1.56 (0.26)	1.90 (0.32)

## 4 Aromatic stabilization energies

To calculate the aromatic stabilization energy (ASE) of SS, SSe and SeSe compounds we use a scheme similar to that reported for naphthalene.<sup>19</sup> The scheme reported by Dixit, V. and Singh, Y. shows good performance in predicting ASE for naphthalene. Therefore we set up the following reaction scheme:

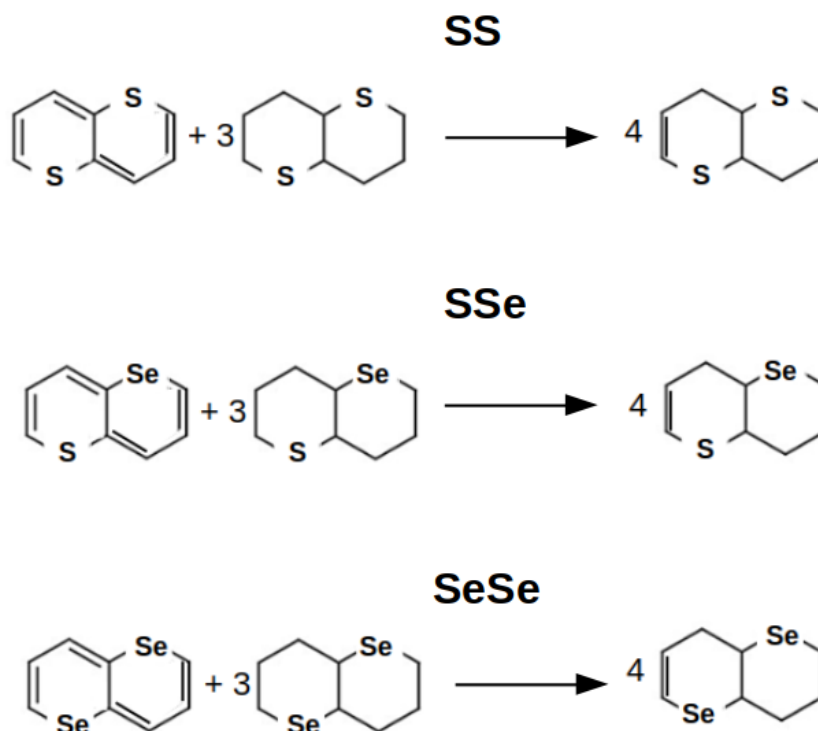


Figure S2: Chemical reactions of SS, SSe and SeSe compounds to calculate the aromatic stabilization energy.

Table S3: Aromatic stabilization energy were calculated using CAM-B3LYP/6-311G(d,p) and B3LYP/6-311G(d,p). All values in kcal/mol. The value of naphthalene is -63.96 kcal/mol taken from reference 19. Note that in the case of naphthalene the sign corresponds to an aromatic system.

Molecule	CAM-B3LYP		B3LYP	
	ASE	ASE per ring	ASE	ASE per ring
SS	15.28	7.64	25.09	12.54
SSe	14.33	7.16	24.03	12.01
SeSe	22.20	11.10	24.15	12.07

## 5 Electronic Indices

### 5.1 CAM-B3LYP

Table S4: Electronic indices (BOA, AV1245, |AVmin|) for the 5-MRs, 6-MRs, 6-MR-Se and 6-MR-S. The methodology used was CAM-B3LYP/6-311G(d,p). By definition it is not possible to obtain AV1245 and |AVmin| for rings of 5 atoms.

Molecule	Ring	BOA	MCI	MCI <sup>1/n</sup>	Iring	Iring <sup>1/n</sup>	AV1245	AVmin
SS	6-MR-S(1)	0.341	0.007	0.437	0.005	0.414	0.993	0.274
	6-MR-S(2)	0.341	0.007	0.437	0.005	0.414	0.993	0.273
SSe	6-MR-S	0.337	0.007	0.437	0.005	0.414	1.069	0.253
	6-MR-Se	0.343	0.007	0.437	0.005	0.414	0.931	0.270
SeSe	6-MR-Se(1)	0.340	0.007	0.437	0.005	0.414	1.003	0.253
	6-MR-Se(2)	0.340	0.007	0.437	0.005	0.414	1.003	0.252
SS1	5-MR(1)	1.310	0.017	0.443	0.020	0.457	–	–
	5-MR(2)	1.400	0.017	0.443	0.020	0.457	–	–
	6-MR-S(1)	0.245	0.006	0.426	0.006	0.426	0.833	-0.903
	6-MR-S(2)	0.245	0.006	0.426	0.006	0.426	0.833	-0.903
SSe1	5-MR(1)	1.300	0.017	0.443	0.020	0.457	–	–
	5-MR(2)	0.997	0.017	0.443	0.020	0.457	–	–
	6-MR-S	0.244	0.007	0.437	0.006	0.426	0.878	-0.988
	6-MR-Se	0.258	0.006	0.426	0.005	0.414	0.808	-0.646
SeSe1	5-MR(1)	1.348	0.017	0.443	0.020	0.457	–	–
	5-MR(1)	1.415	0.017	0.443	0.020	0.457	–	–
	6-MR-Se(1)	0.259	0.006	0.426	0.005	0.414	0.860	-0.707
	6-MR-Se(2)	0.259	0.006	0.426	0.005	0.414	0.860	-0.708
SS2	5-MR(1)	1.231	0.012	0.413	0.015	0.432	–	–
	5-MR(2)	1.268	0.012	0.413	0.015	0.432	–	–
	6-MR(1)	0.149	0.041	0.587	0.029	0.554	6.366	4.367
	6-MR(2)	0.132	0.027	0.548	0.020	0.521	4.252	3.007
	6-MR(3)	0.149	0.041	0.587	0.029	0.554	6.366	4.367
	6-MR(4)	0.132	0.027	0.548	0.020	0.521	4.252	3.007
	6-MR-S(1)	0.269	0.006	0.426	0.005	0.414	0.896	-0.430
	6-MR-S(2)	0.269	0.006	0.426	0.005	0.414	0.896	-0.430
SSe2	5-MR(1)	1.227	0.012	0.413	0.015	0.432	–	–
	5-MR(2)	0.860	0.012	0.413	0.015	0.432	–	–
	6-MR(1)	0.148	0.041	0.587	0.029	0.554	6.380	4.386
	6-MR(2)	0.133	0.027	0.548	0.020	0.521	4.221	2.987
	6-MR(3)	0.152	0.040	0.585	0.028	0.551	6.305	4.286
	6-MR(4)	0.129	0.028	0.551	0.021	0.525	4.392	3.097
	6-MR-S	0.270	0.007	0.437	0.006	0.426	0.939	-0.461
	6-MR-Se	0.279	0.006	0.426	0.005	0.414	0.854	-0.284
SeSe2	5-MR(1)	1.256	0.012	0.413	0.015	0.432	–	–
	5-MR(2)	0.860	0.012	0.413	0.015	0.432	–	–
	6-MR(1)	0.152	0.040	0.585	0.028	0.551	6.315	4.301
	6-MR(2)	0.129	0.028	0.551	0.021	0.525	4.366	3.079
	6-MR(3)	0.152	0.040	0.585	0.028	0.551	6.315	4.301
	6-MR(4)	0.129	0.028	0.551	0.021	0.525	4.366	3.079
	6-MR-Se(1)	0.281	0.006	0.426	0.005	0.414	0.899	-0.304
	6-MR-Se(2)	0.281	0.006	0.426	0.005	0.414	0.899	-0.304

## AVmin colored

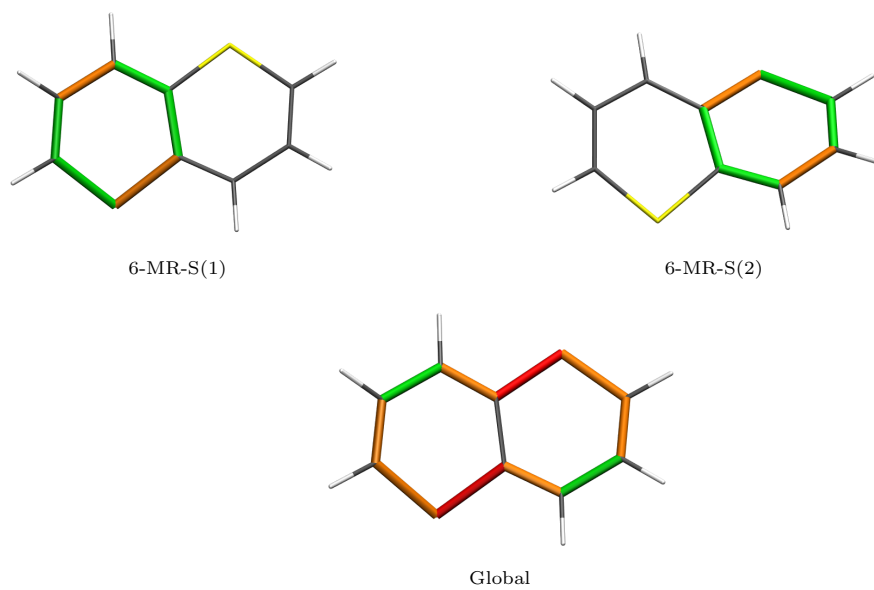


Figure S3: AVmin colored representation across of 6-MRs and global circuits in SS molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

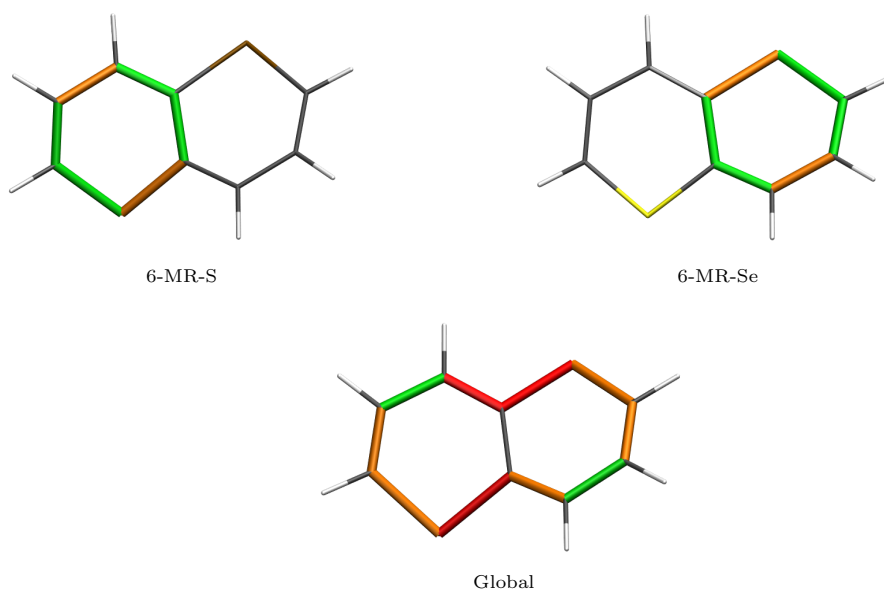


Figure S4: AVmin colored representation across of 6-MRs and global circuits in SSe molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

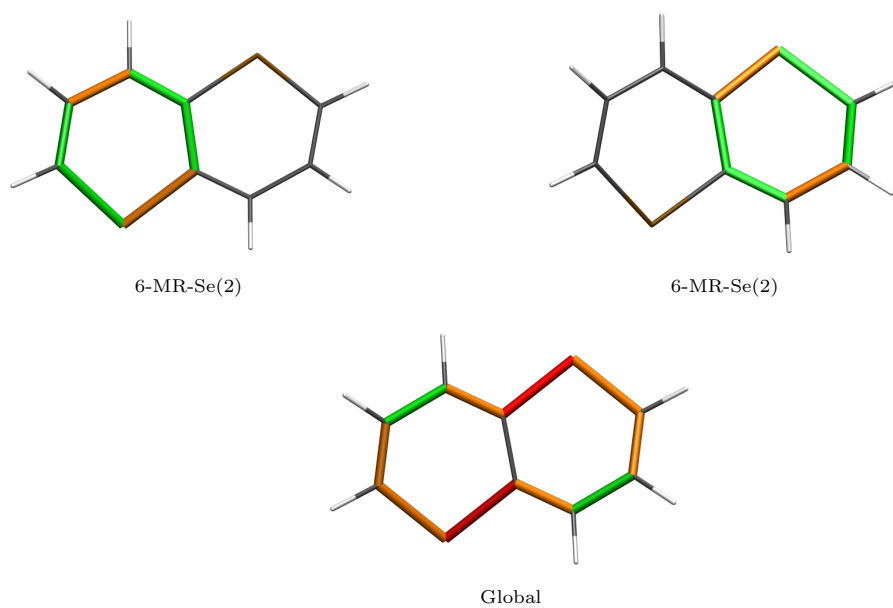


Figure S5: AVmin colored representation across of 6-MRs and global circuits in SeSe molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

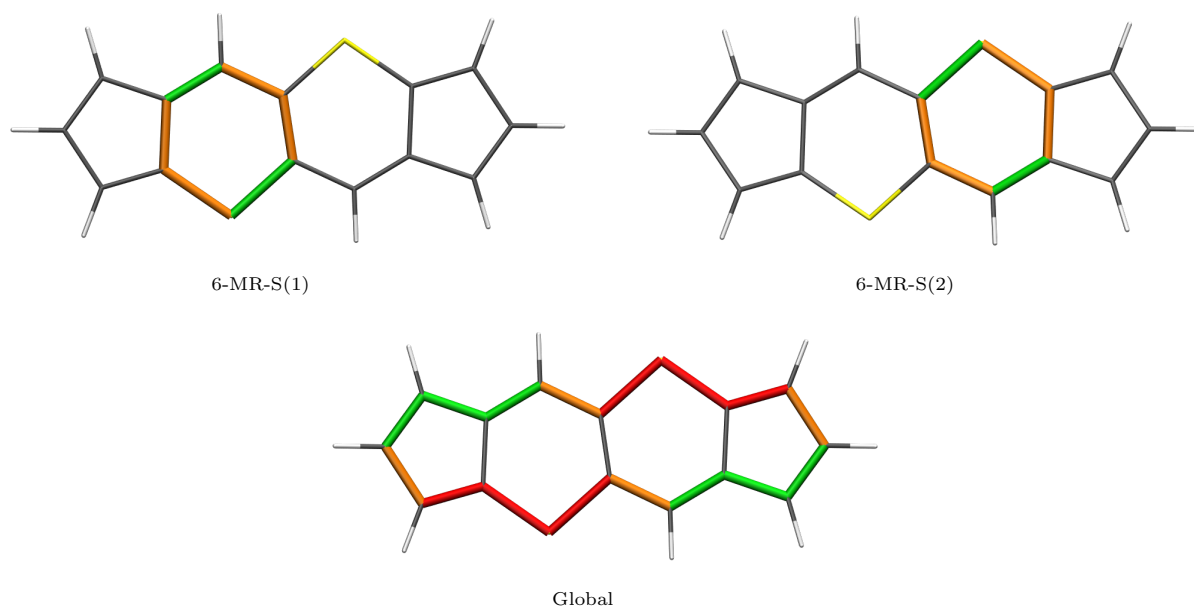


Figure S6: AVmin colored representation across of 6-MRs and global circuits in SS1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

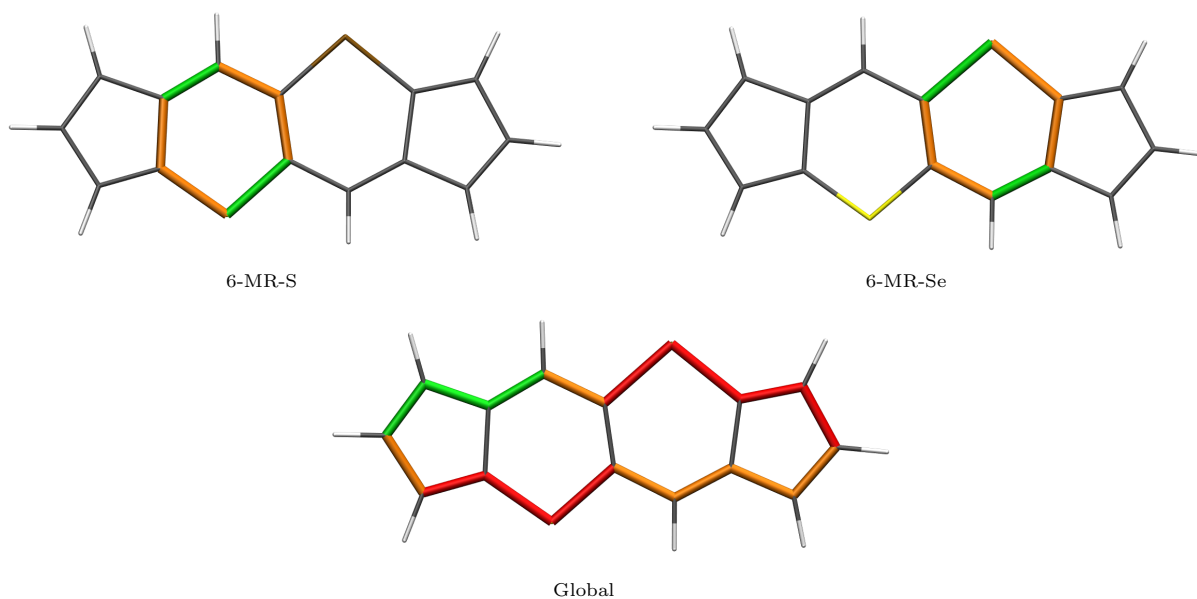


Figure S7: AVmin colored representation across a 6-MR and global circuits in SSe1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

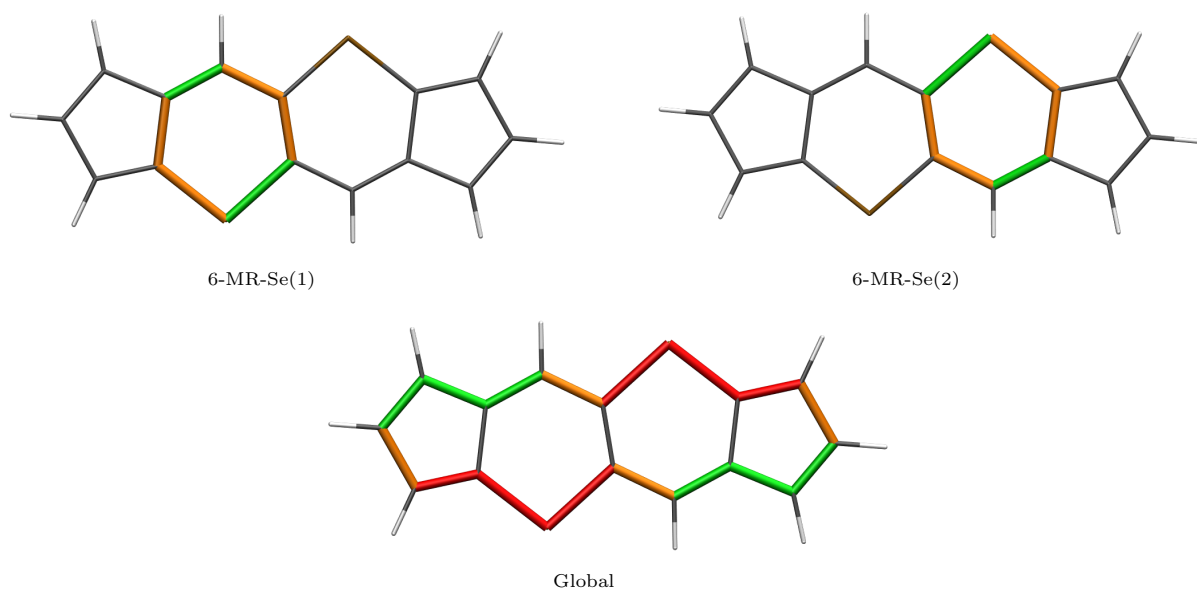


Figure S8: AVmin colored representation across a 6-MR and global circuits in SeSe1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

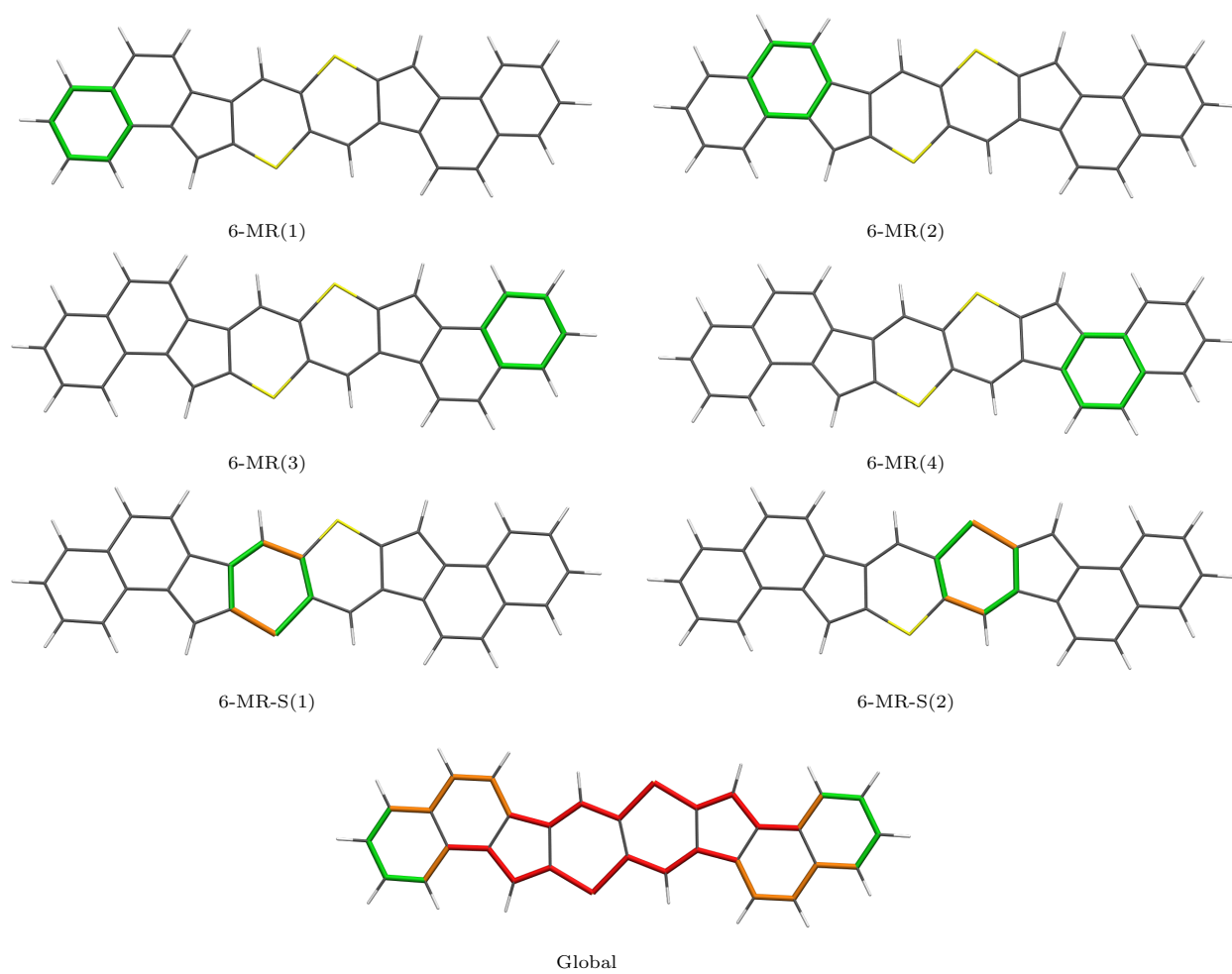


Figure S9: AVmin colored representation across a 6-MR and global circuits in SS2 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

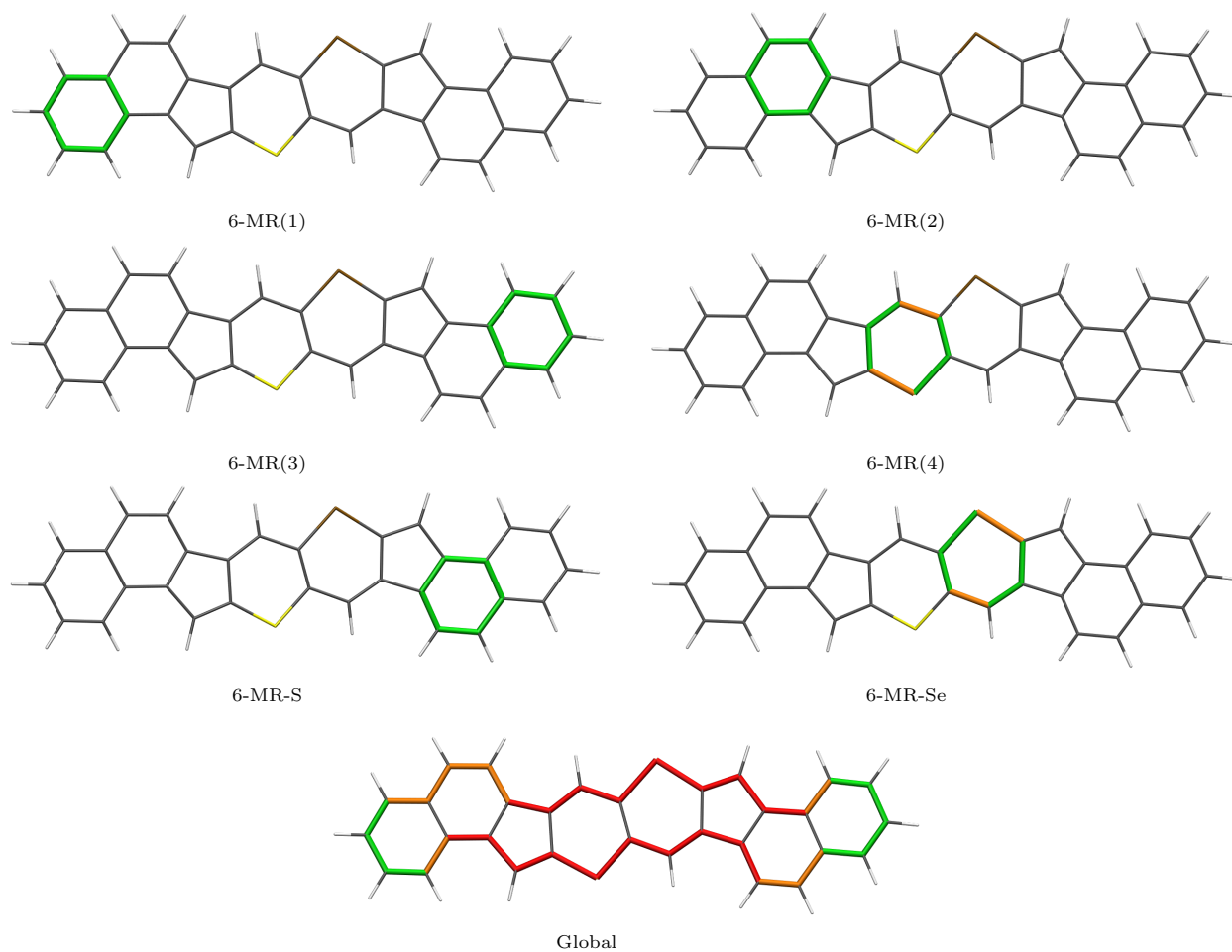


Figure S10: AVmin colored representation across a 6-MR and global circuits in SSe2 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.



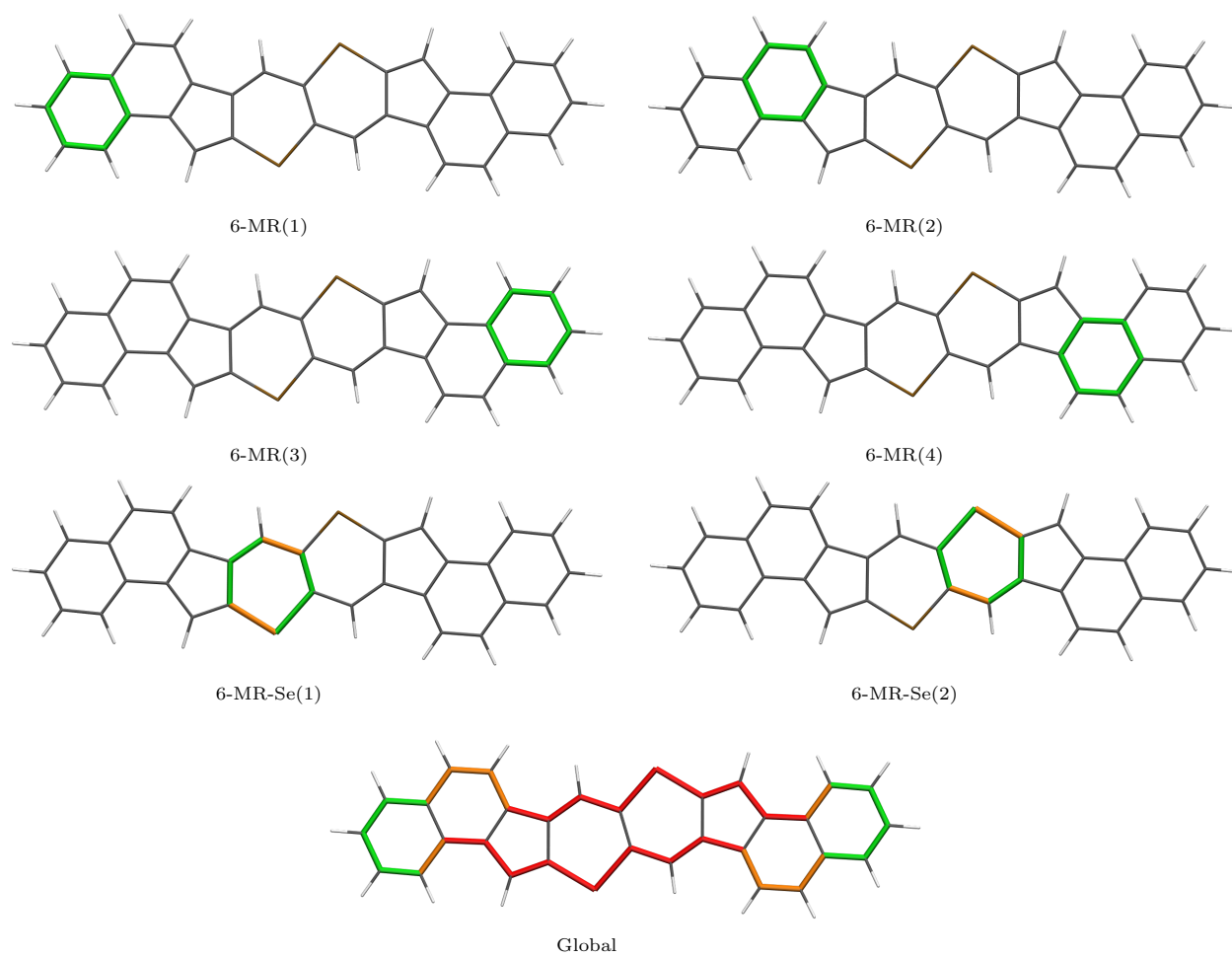


Figure S11: AVmin colored representation across a 6-MR and global circuits in SeSe<sub>2</sub> molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

## 5.2 B3LYP

Table S5: Electronic indices (BOA, AV1245, |AVmin|) for the 5-MRs, 6-MRs, 6-MR-Se and 6-MR-S. The methodology used was B3LYP/6-311G(d,p). By definition it is not possible to obtain AV1245 and |AVmin| for rings of 5 atoms.

Molecule	Ring	BOA	MCI	MCI <sup>1/n</sup>	Iring	Iring <sup>1/n</sup>	AV1245	AVmin
SS	6-MR-S(1)	0.296	0.009	0.456	0.006	0.006	1.272	0.447
	6-MR-S(2)	0.296	0.009	0.456	0.006	0.006	1.272	0.447
SSe	6-MR-S	0.290	0.009	0.456	0.007	0.007	1.362	0.433
	6-MR-Se	0.290	0.008	0.447	0.006	0.006	1.230	0.455
SeSe	6-MR-Se(1)	0.289	0.009	0.456	0.006	0.006	1.318	0.442
	6-MR-Se(2)	0.289	0.009	0.456	0.006	0.006	1.318	0.442
SS1	5-MR(1)	1.254	0.019	0.453	0.022	0.022	–	–
	5-MR(2)	1.372	0.019	0.453	0.022	0.022	–	–
	6-MR-S(1)	0.201	0.007	0.437	0.006	0.006	0.782	0.885
	6-MR-S(2)	0.201	0.007	0.437	0.006	0.006	0.782	0.885
SSe1	5-MR(1)	1.242	0.019	0.453	0.023	0.023	–	–
	5-MR(2)	0.982	0.019	0.453	0.022	0.022	–	–
	6-MR-S	0.201	0.007	0.437	0.006	0.006	0.810	0.949
	6-MR-Se	0.212	0.006	0.426	0.006	0.006	0.797	-0.714
SeSe1	5-MR(1)	1.293	0.019	0.453	0.023	0.023	–	–
	5-MR(1)	1.386	0.019	0.453	0.023	0.023	–	–
	6-MR-Se(1)	0.213	0.007	0.437	0.006	0.006	0.835	-0.789
	6-MR-Se(2)	0.213	0.007	0.437	0.006	0.006	0.835	-0.789
SS2	5-MR(1)	1.184	0.014	0.426	0.017	0.017	–	–
	5-MR(2)	1.236	0.014	0.426	0.017	0.017	–	–
	6-MR(1)	0.119	0.040	0.585	0.028	0.028	6.153	4.065
	6-MR(2)	0.095	0.026	0.544	0.019	0.019	3.860	2.655
	6-MR(3)	0.119	0.040	0.585	0.028	0.028	6.153	4.065
	6-MR(4)	0.095	0.026	0.544	0.019	0.019	3.860	2.655
	6-MR-S(1)	0.222	0.007	0.437	0.006	0.006	0.914	-0.404
	6-MR-S(2)	0.222	0.007	0.437	0.006	0.006	0.914	-0.404
SSe2	5-MR(1)	1.180	0.014	0.426	0.017	0.017	–	–
	5-MR(2)	0.856	0.014	0.426	0.017	0.017	–	–
	6-MR(1)	0.118	0.040	0.585	0.028	0.028	6.165	4.084
	6-MR(2)	0.096	0.025	0.541	0.019	0.019	3.825	2.634
	6-MR(3)	0.122	0.040	0.585	0.028	0.028	6.096	3.985
	6-MR(4)	0.091	0.026	0.544	0.020	0.020	3.998	2.735
	6-MR-S	0.223	0.007	0.437	0.006	0.006	0.948	-0.438
	6-MR-Se	0.229	0.006	0.426	0.006	0.006	0.910	-0.238
SeSe2	5-MR(1)	1.211	0.014	0.426	0.017	0.017	–	–
	5-MR(2)	0.856	0.014	0.426	0.017	0.017	–	–
	6-MR(1)	0.122	0.040	0.585	0.028	0.028	6.105	4.000
	6-MR(2)	0.092	0.026	0.544	0.020	0.020	3.969	2.716
	6-MR(3)	0.122	0.040	0.585	0.028	0.028	6.105	4.000
	6-MR(4)	0.092	0.026	0.544	0.020	0.020	3.969	2.716
	6-MR-Se(1)	0.232	0.007	0.437	0.006	0.006	0.947	-0.261
	6-MR-Se(2)	0.232	0.007	0.437	0.006	0.006	0.947	-0.261

## AVmin colored

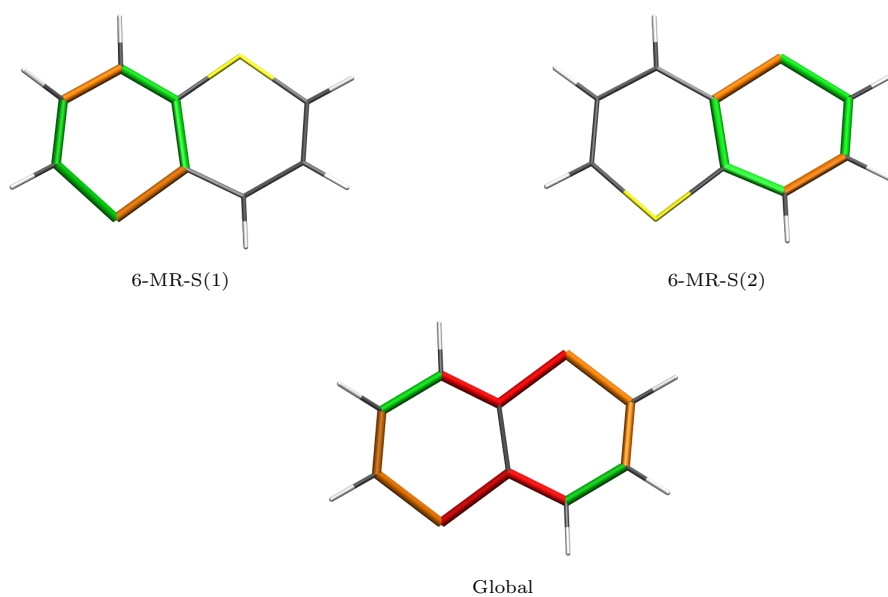


Figure S12: AVmin colored representation across of 6-MRs and global circuits in SS molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

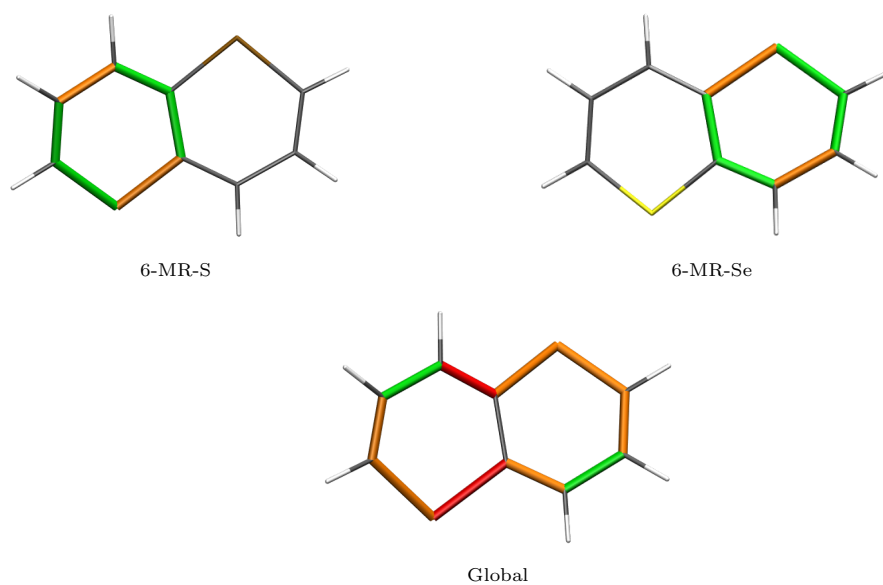


Figure S13: AVmin colored representation across of 6-MRs and global circuits in SSe molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

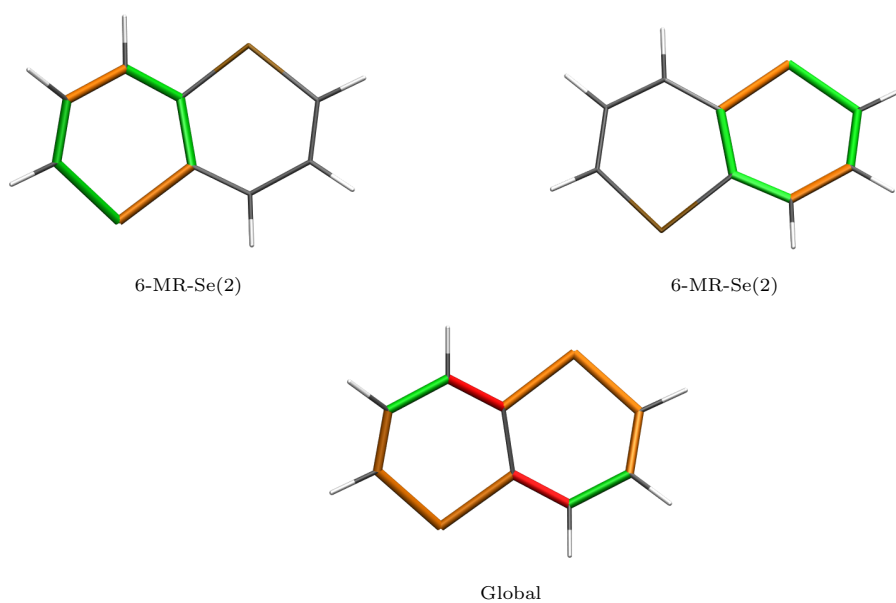


Figure S14: AVmin colored representation across of 6-MRs and global circuits in SeSe molecule. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

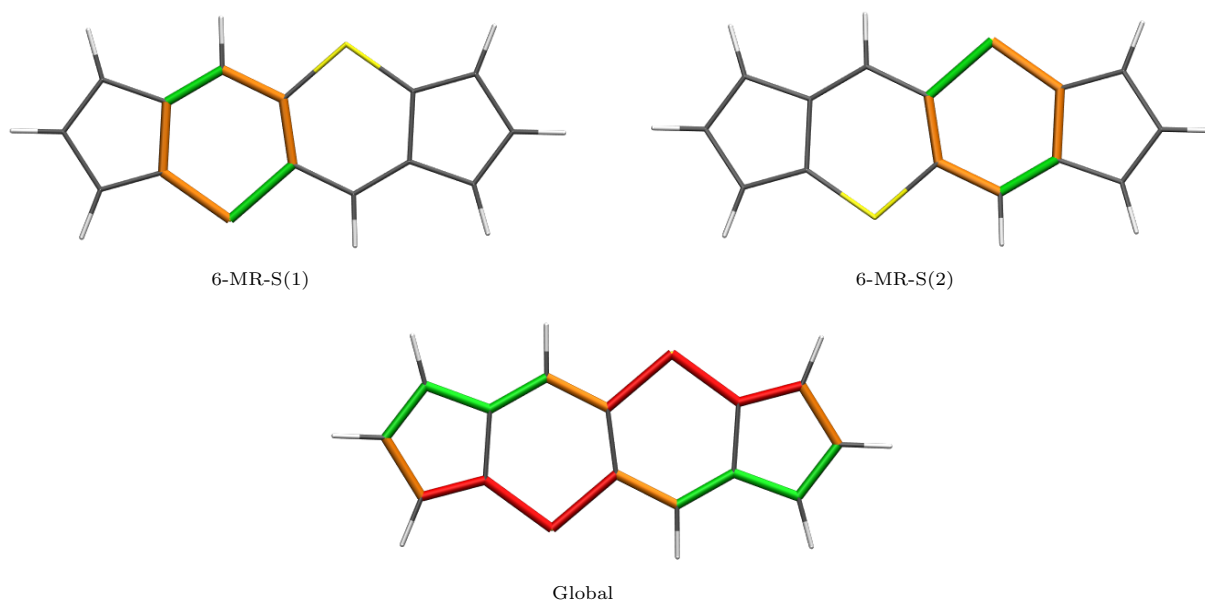


Figure S15: AVmin colored representation across of 6-MRs and global circuits in SS1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

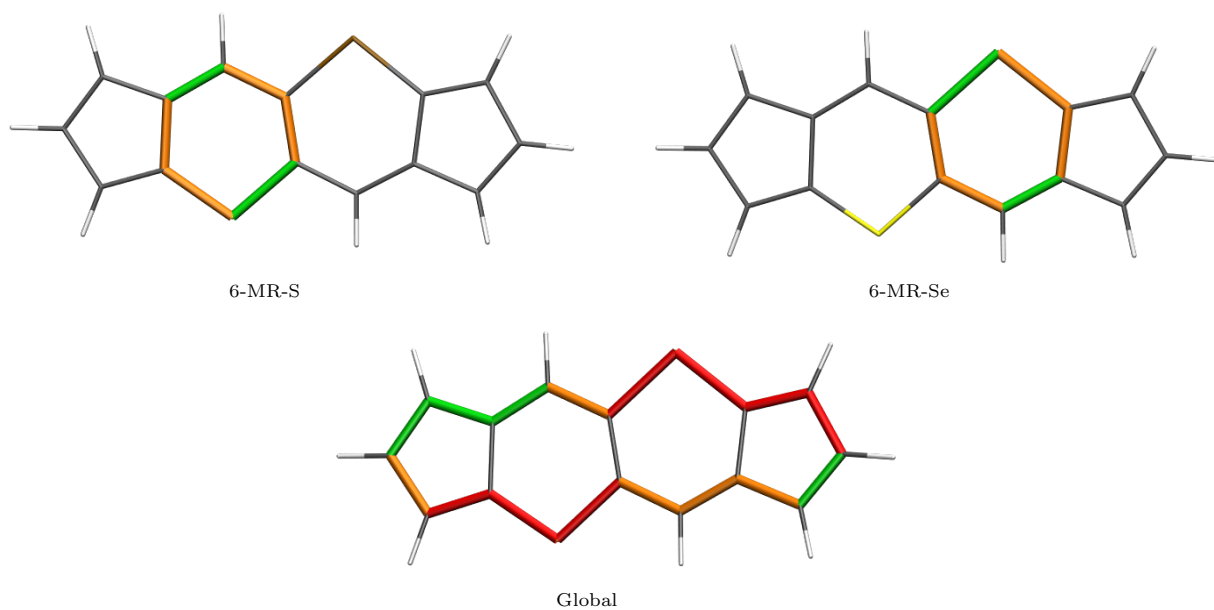


Figure S16: AVmin colored representation across a 6-MR and global circuits in SSe1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

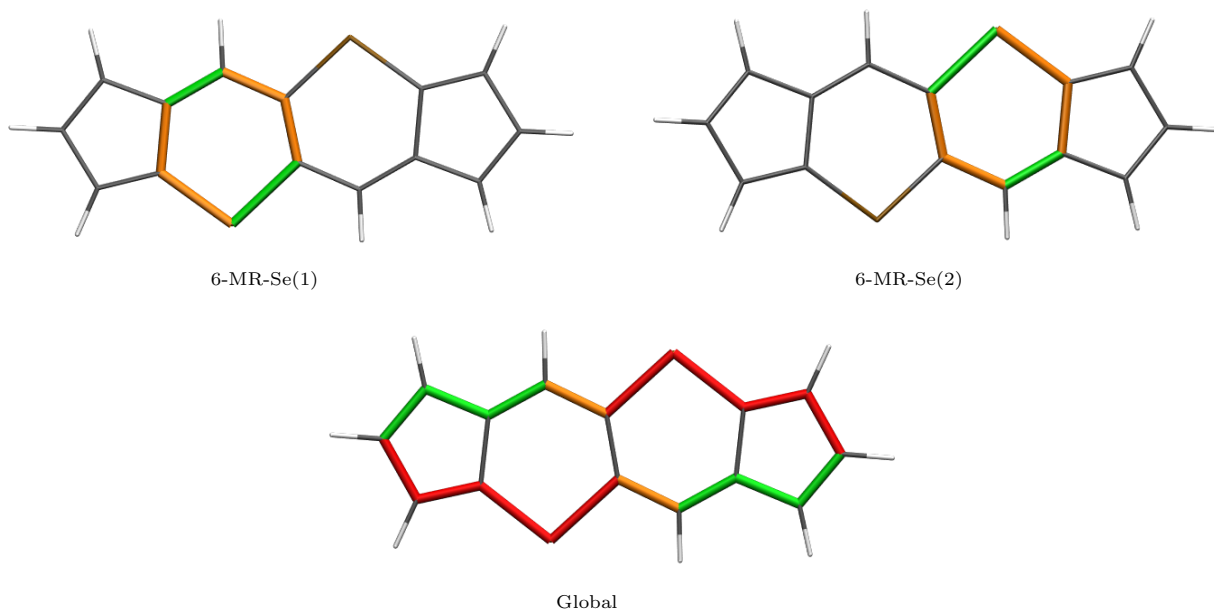


Figure S17: AVmin colored representation across a 6-MR and global circuits in SeSe1 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

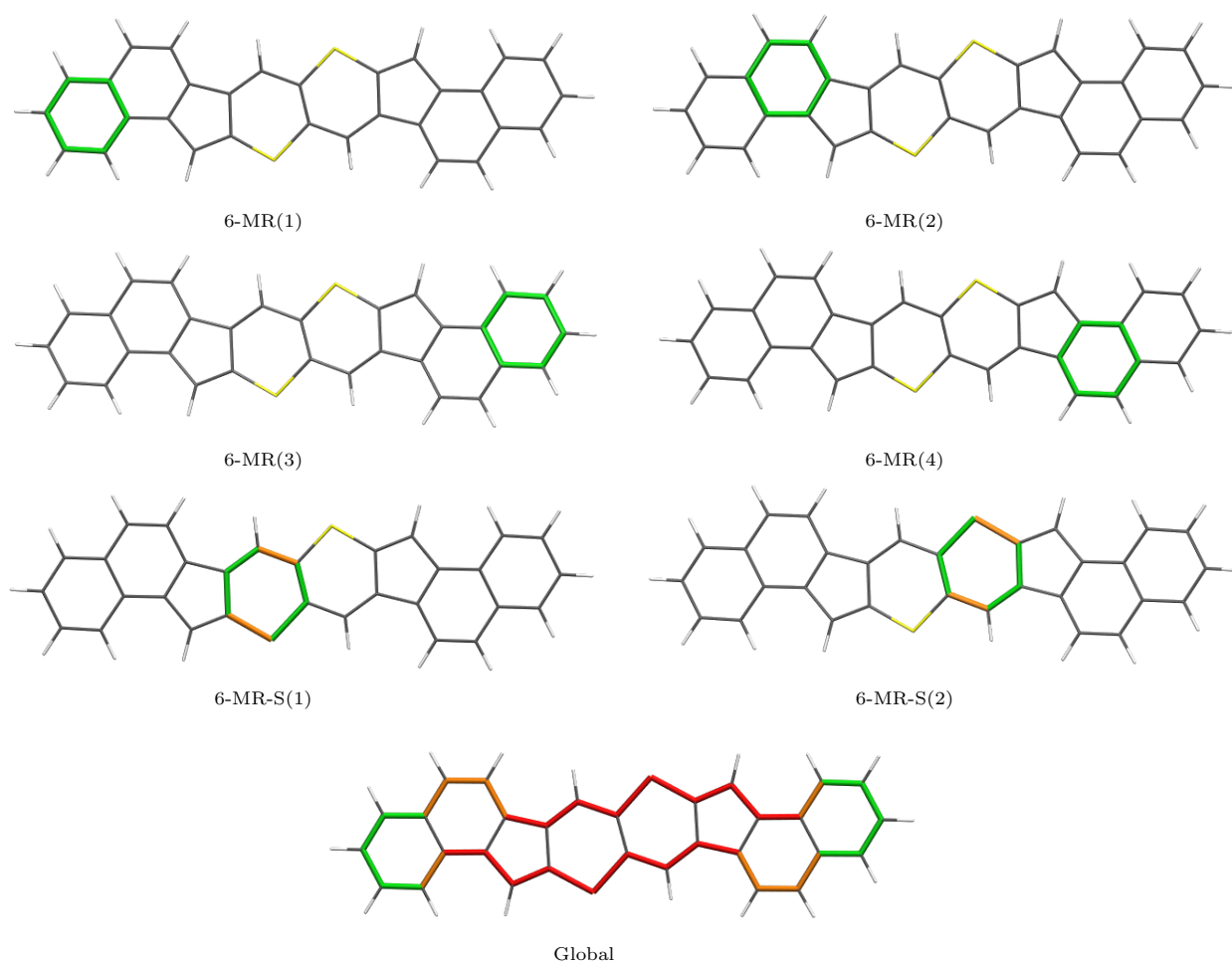


Figure S18: AVmin colored representation across a 6-MR and global circuits in SS2 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

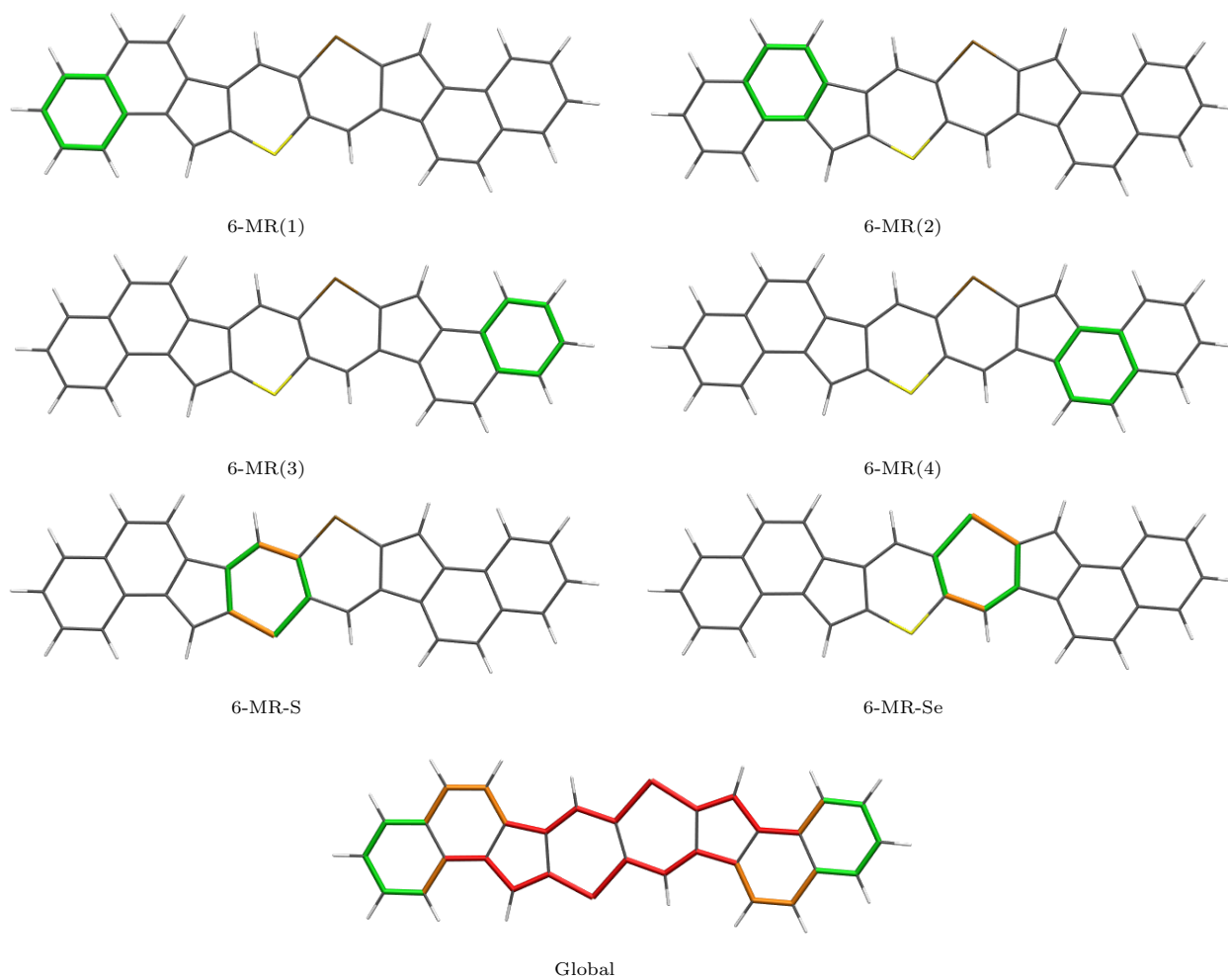


Figure S19: AVmin colored representation across a 6-MR and global circuits in SSe2 molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.

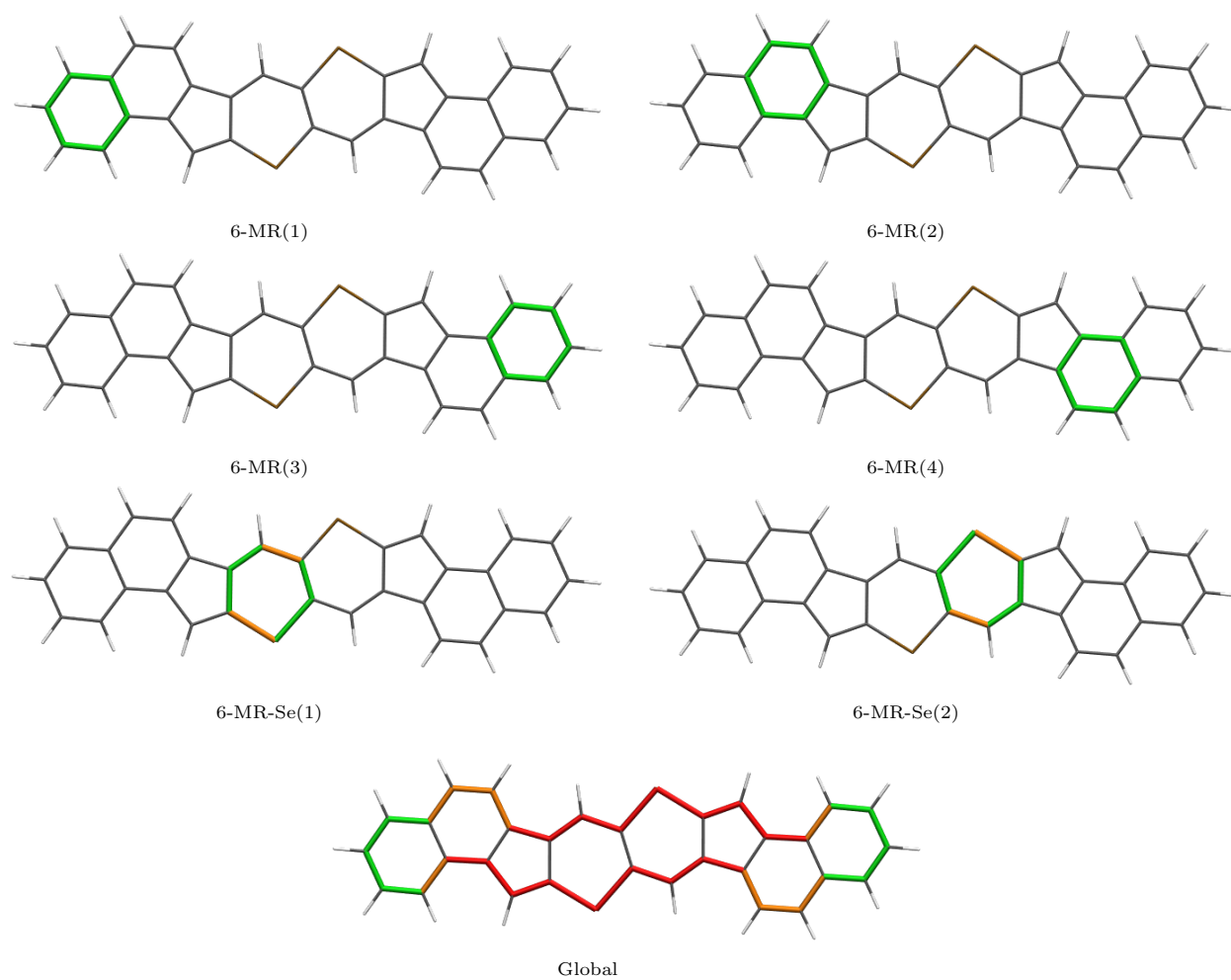


Figure S20: AVmin colored representation across a 6-MR and global circuits in SeSe<sub>2</sub> molecule. By definition it is not possible to obtain AVmin for rings of 5 atoms. Green, orange, and red colors indicate bond contributions to conjugation that are, respectively, 75-100%, 5-75%, and 0-25%.



## 6 Current density maps

CAM-B3LYP

Benzene

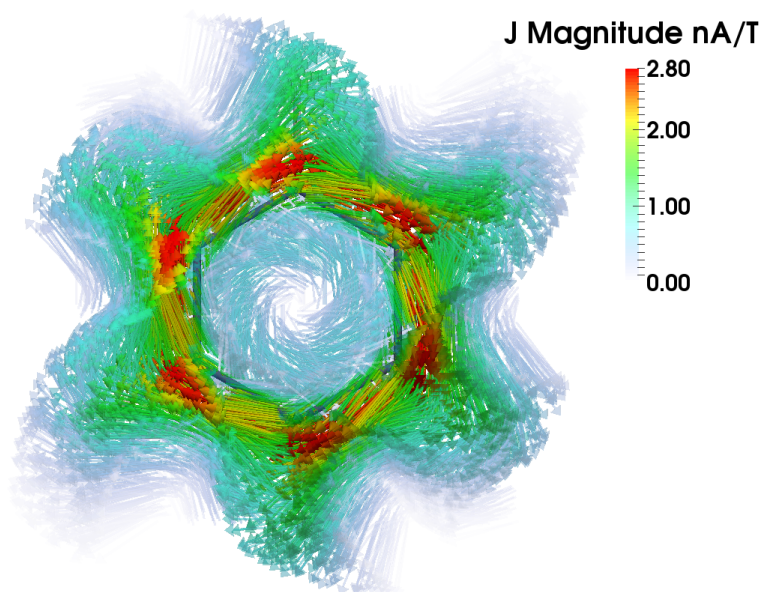


Figure S21: The map shows that  $J$  is diatropic. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms.

Cyclobutadiene

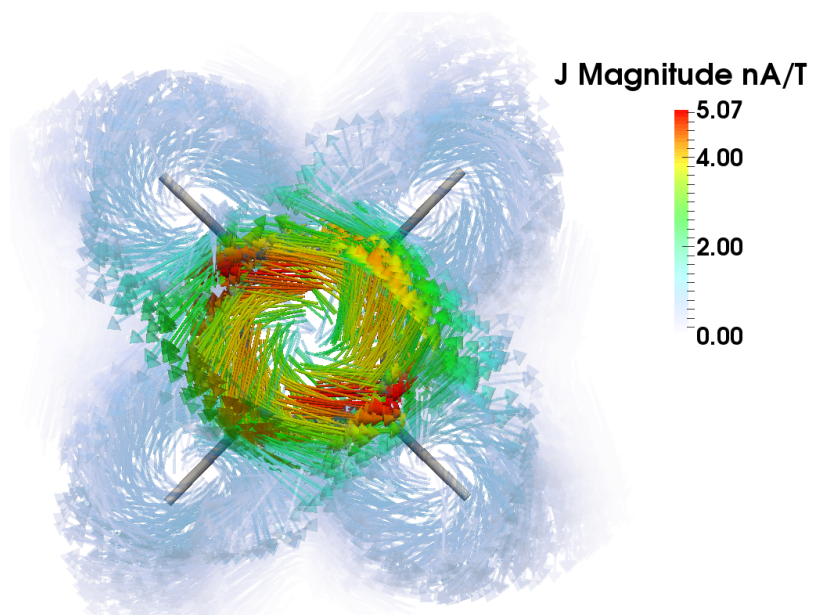


Figure S22: The map shows that  $J$  is paratropic. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms.

SS1

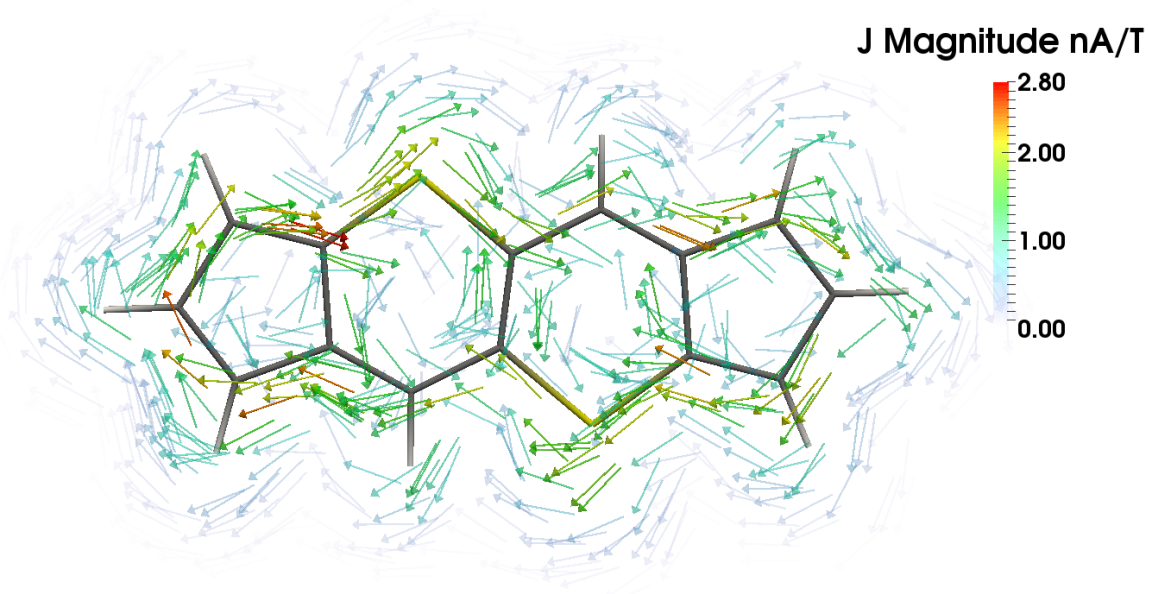


Figure S23: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms.

SSe1

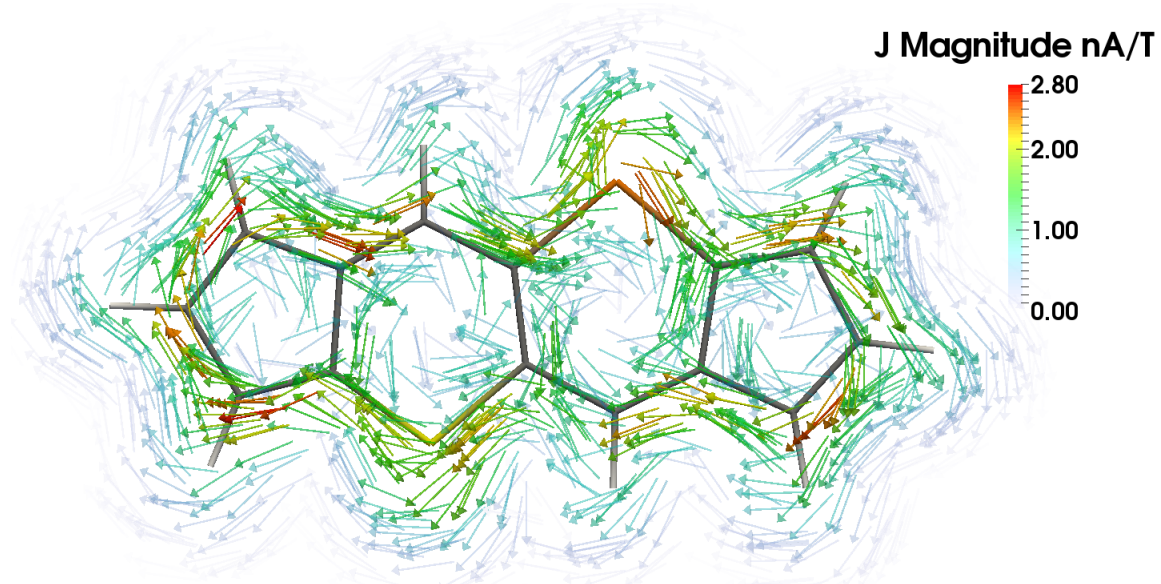


Figure S24: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms; orange bonds: selenium atoms.

### SeSe1

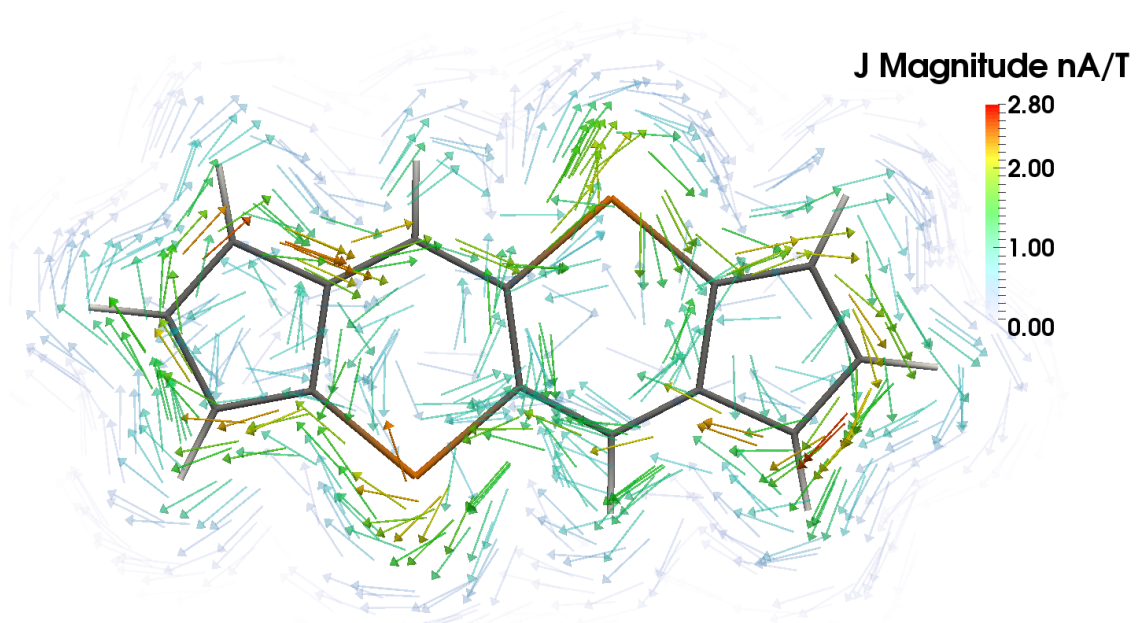


Figure S25: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; orange bonds: selenium atoms.

### SS

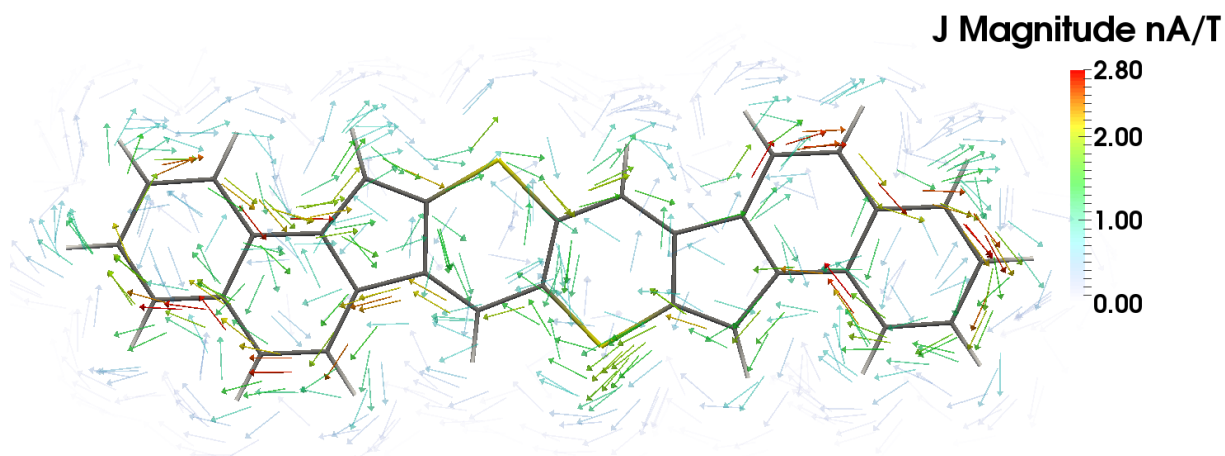


Figure S26: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms.

SSe

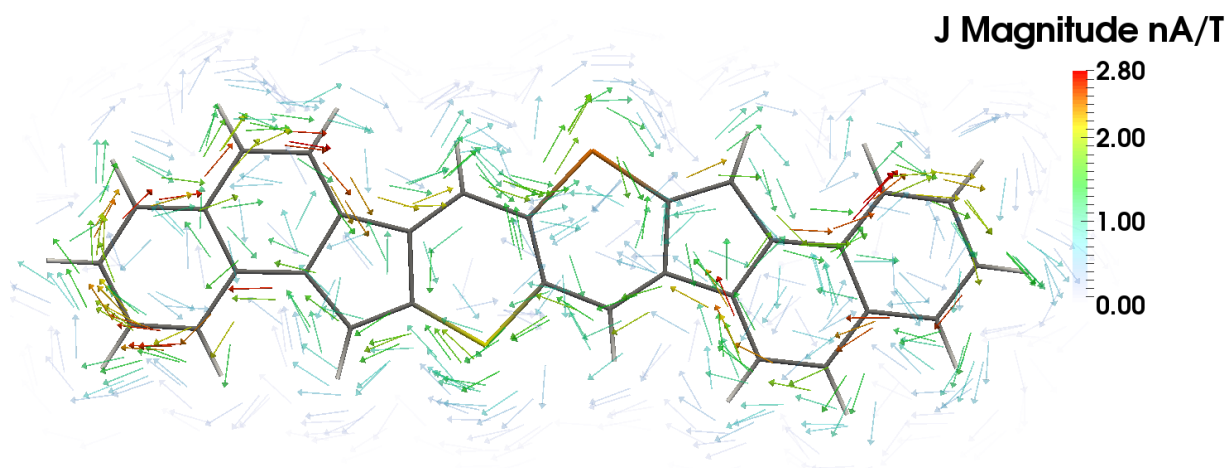


Figure S27: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms; orange bonds: selenium atoms.

SeSe

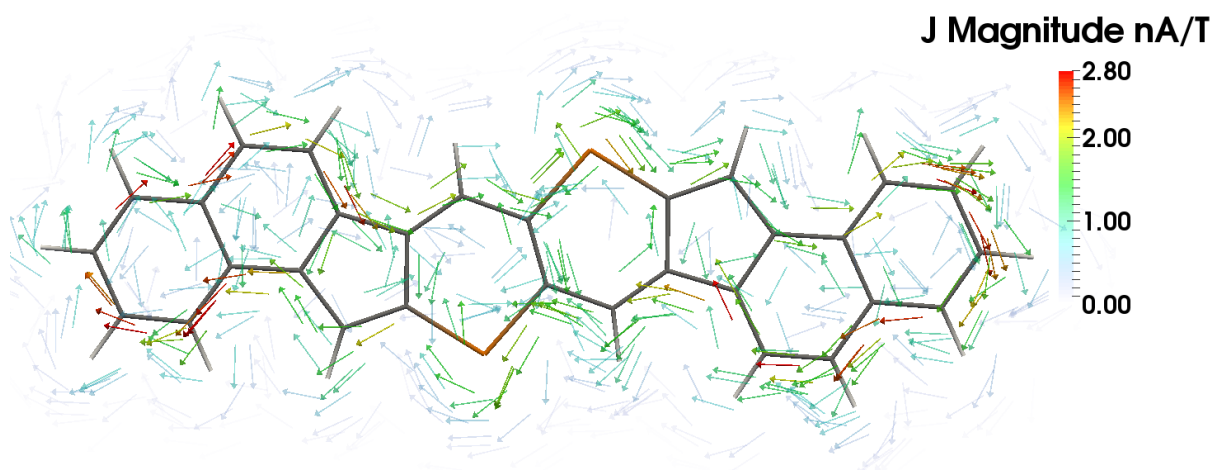


Figure S28: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was CAM-B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; orange bonds: selenium atoms.



B3LYP

Benzene

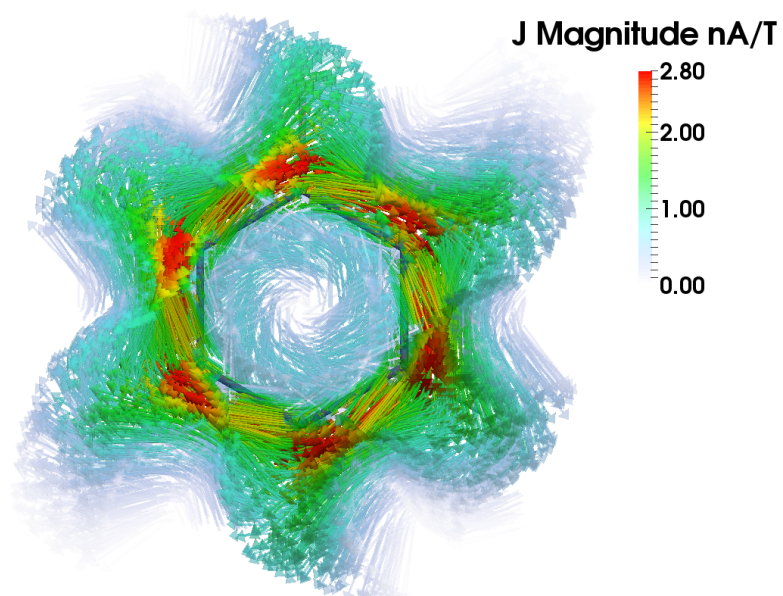


Figure S29: The map shows that J is diatropic. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms.

Cyclobutadiene

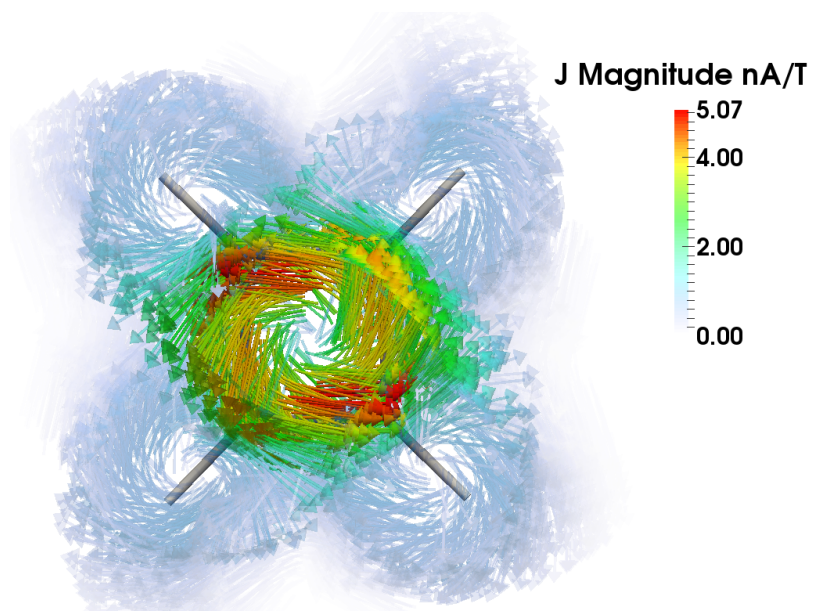


Figure S30: The map shows that J is paratropic. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms.

SS1

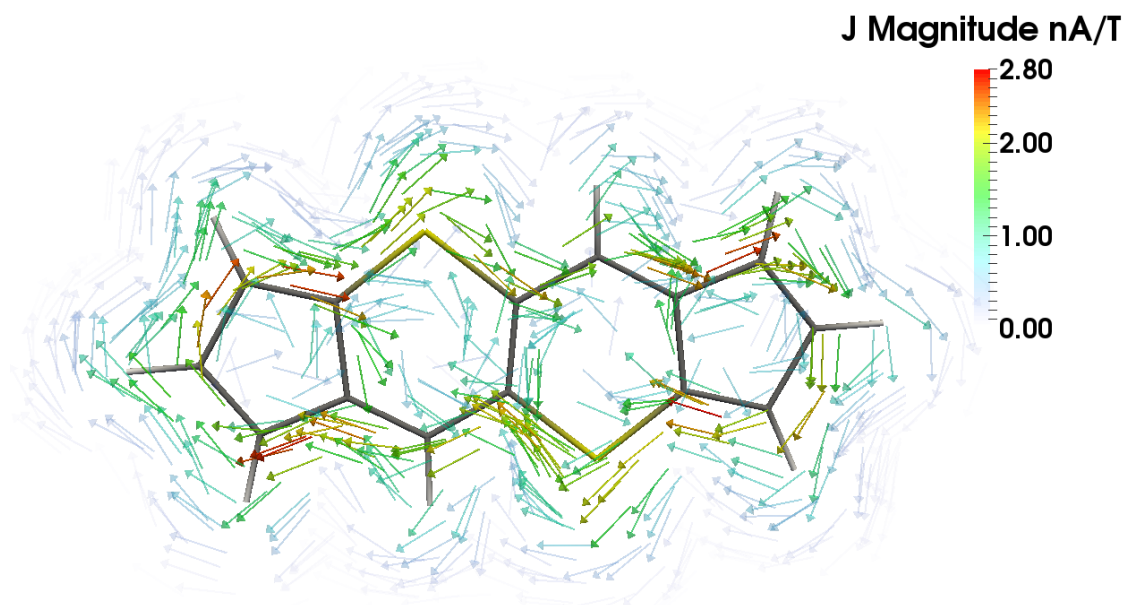


Figure S31: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms.

SSe1

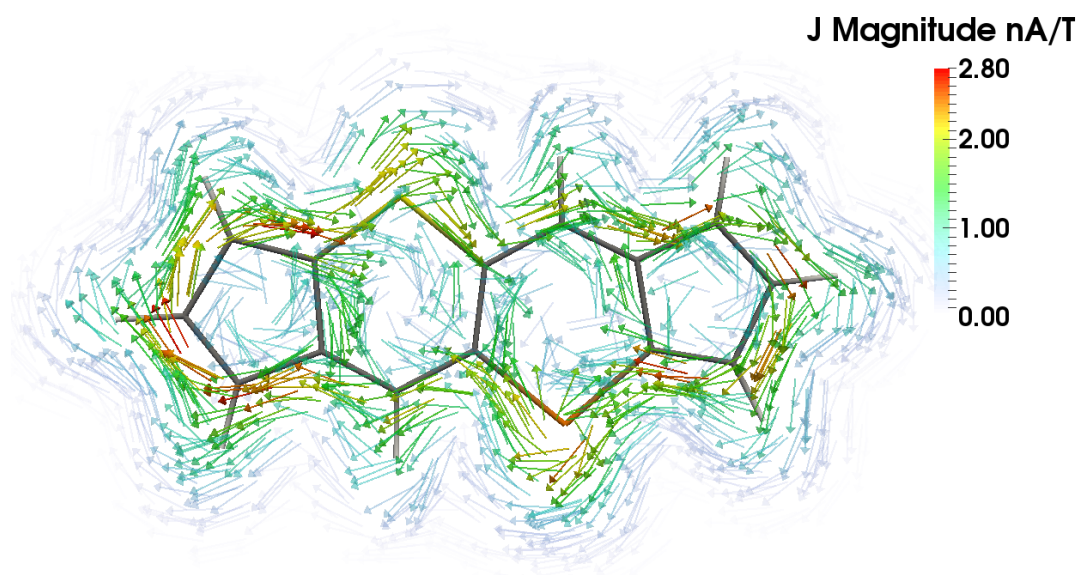


Figure S32: The map shows that  $J$  is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms; orange bonds: selenium atoms.

SeSe1

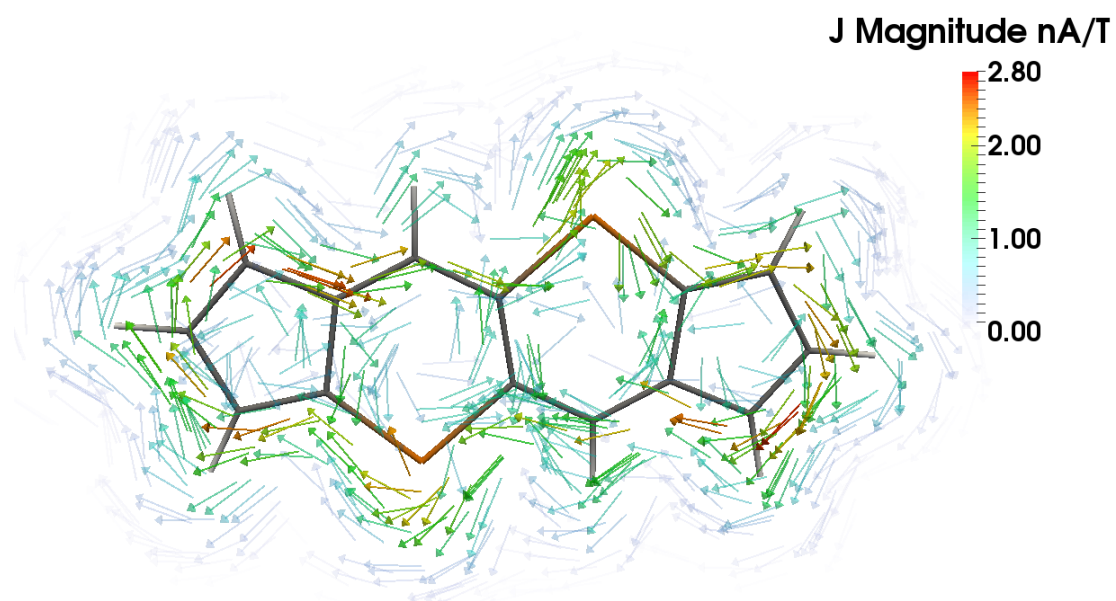


Figure S33: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; orange bonds: selenium atoms.

SS

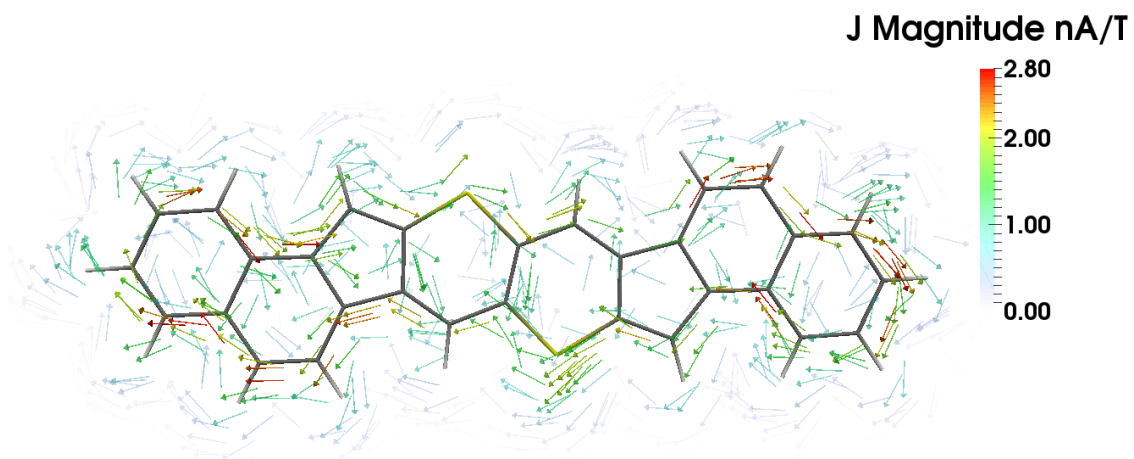


Figure S34: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms.

SSe

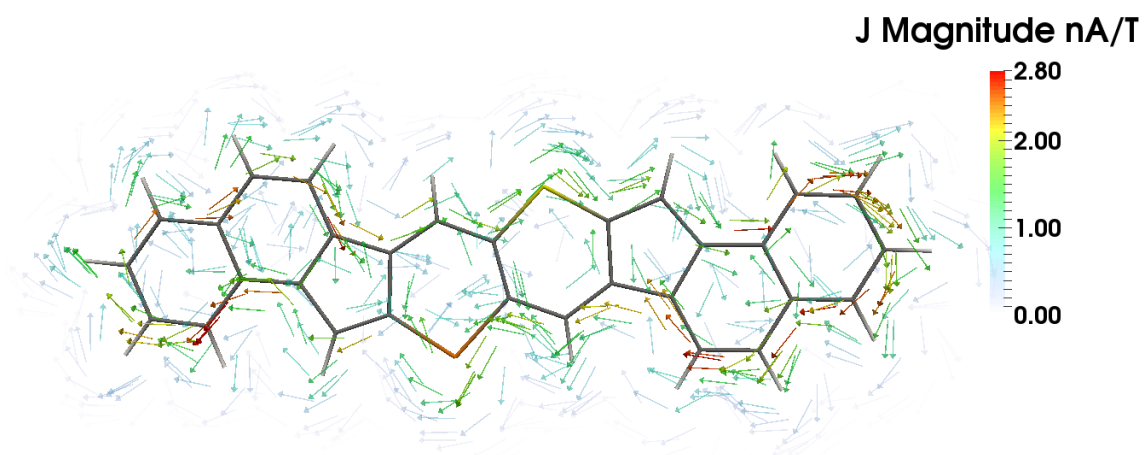


Figure S35: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; yellow bonds: sulfur atoms; orange bonds: selenium atoms.

SeSe

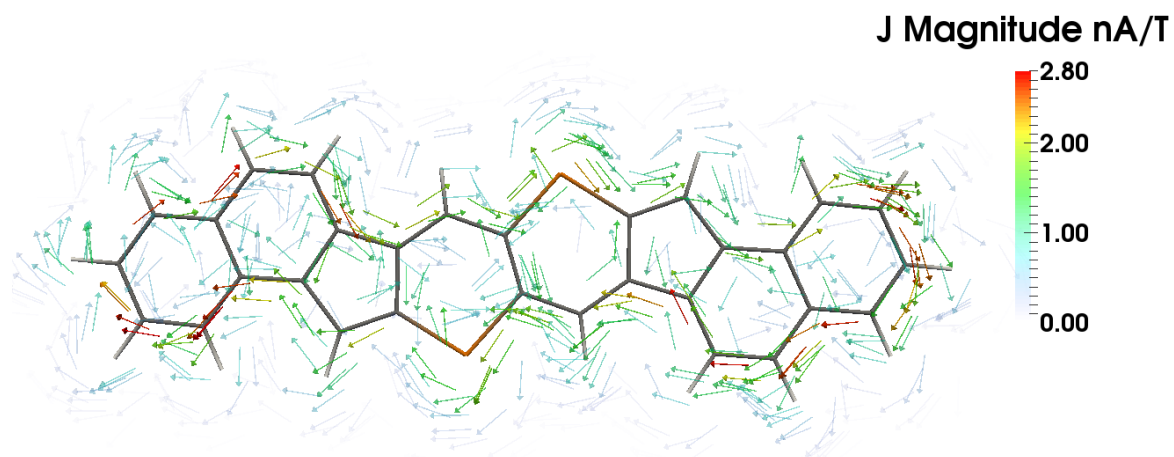


Figure S36: The map shows that J is diatropic. We use the benzene scale as a reference. The methodology used was B3LYP/6-311G(d,p). White bonds: hydrogen atoms; gray bonds: carbon atoms; orange bonds: selenium atoms.



## 7 Cartesian coordinates of the optimized structures with CAM-B3LYP

**SS** E=-1104.72971094 a.u.  $\nu=73.3866$  cm<sup>-1</sup>

H 3.493818 -0.751571 0.521956  
H -3.415528 -1.634314 0.023985  
H -3.493818 0.751571 0.521956  
C 0.174536 -0.709647 -0.217253  
C -2.538281 -1.006413 -0.057291  
C 1.415556 -1.167613 0.030224  
C -1.415556 1.167613 0.030224  
H 3.415528 1.634314 0.023985  
C -2.562259 0.303205 0.198871  
S -1.112422 -1.867646 -0.603786  
H -1.573564 2.236933 0.098795  
C 2.538281 1.006413 -0.057291  
C 2.562259 -0.303205 0.198871  
S 1.112422 1.867646 -0.603786  
C -0.174536 0.709647 -0.217253  
H 1.573564 -2.236933 0.098795

**SSe** E=-3108.15542818 a.u.  $\nu=62.0898$  cm<sup>-1</sup>

H 3.487693 -0.809723 0.520205  
H -3.412659 -1.670844 0.015379  
H -3.534536 0.711389 0.531200  
C 0.165104 -0.676755 -0.221434  
C -2.546742 -1.026479 -0.059873  
C 1.407195 -1.138815 0.017841  
C -1.464121 1.164993 0.034737  
H 3.547272 1.573047 0.061710  
C -2.595615 0.280926 0.205224  
S -1.106676 -1.855871 -0.610206  
H -1.646652 2.230471 0.107440  
C 2.636650 0.999211 -0.044807  
C 2.581114 -0.311542 0.194645  
Se 1.148532 2.008825 -0.625820  
C -0.215075 0.732395 -0.215584  
H 1.548517 -2.211227 0.080343

**SeSe** E=-5111.58112866 a.u.  $\nu=51.8660$  cm<sup>-1</sup>

H 3.529669 -0.770812 0.529566  
H -3.547071 -1.611448 0.054910  
H -3.529669 0.770812 0.529566  
C 0.205499 -0.699062 -0.219942  
C -2.646620 -1.020747 -0.046857  
C 1.455459 -1.136497 0.021736  
C -1.455459 1.136497 0.021736  
H 3.547071 1.611448 0.054910  
C -2.615257 0.289466 0.200770  
Se -1.141585 -1.997501 -0.632751  
H -1.621298 2.205506 0.088068  
C 2.646620 1.020747 -0.046857  
C 2.615257 -0.289466 0.200770  
Se 1.141585 1.997501 -0.632751  
C -0.205499 0.699062 -0.219942  
H 1.621298 -2.205506 0.088068

**SS1** E=-1334.48518877 a.u.  $\nu=49.0205$  cm<sup>-1</sup>

H 4.127005 -2.581048 -0.000232  
H -1.613331 -2.258733 -0.000244  
H -4.127005 2.581048 -0.000232  
H 5.782993 -0.474057 -0.000256  
H 1.613331 2.258733 -0.000244  
H 4.371324 1.764617 -0.000230  
C -4.704102 0.401604 -0.000251  
C -3.988827 -0.755634 -0.000235  
H -5.782993 0.474057 -0.000256  
C 3.818334 -1.546891 -0.000236  
C -3.818334 1.546891 -0.000236  
C -2.546447 1.072587 -0.000241  
C -2.594410 -0.400637 -0.000245  
S -1.054487 1.935242 -0.000241  
C 0.155284 0.671081 -0.000244  
C -0.155284 -0.671081 -0.000244  
C -1.492145 -1.180190 -0.000245  
C 1.492145 1.180190 -0.000245  
C 2.594410 0.400637 -0.000245

C 2.546447 -1.072587 -0.000241  
S 1.054487 -1.935242 -0.000241  
C 3.988827 0.755634 -0.000235  
C 4.704102 -0.401604 -0.000251  
H -4.371324 -1.764617 -0.000230

**SSe1** E=-3337.90962095 a.u.  $\nu=45.0063$  cm<sup>-1</sup>

H 4.178961 2.716240 -0.000213  
H -4.227186 1.927102 -0.000113  
C 3.893979 1.675327 -0.000206  
H -4.227568 -2.422795 -0.000092  
H 1.776453 -2.177528 -0.000172  
H 4.520187 -1.622936 -0.000194  
C -4.685293 -0.212926 -0.000104  
C -3.905575 0.896832 -0.000118  
H -5.766422 -0.226281 -0.000087  
H -1.517173 2.293258 -0.000179  
C -3.858355 -1.408285 -0.000105  
C -2.564308 -1.009024 -0.000124  
C -2.526455 0.462697 -0.000152  
Se -0.998398 -2.016399 -0.000150  
C 0.281244 -0.622553 -0.000168  
C -0.062189 0.708524 -0.000175  
C -1.405857 1.213327 -0.000172  
C 1.626163 -1.102348 -0.000177  
C 2.713988 -0.299994 -0.000190  
C 2.632452 1.171740 -0.000195  
S 1.121926 1.997935 -0.000189  
C 4.114246 -0.623123 -0.000197  
C 4.803848 0.551071 -0.000209  
H 5.880933 0.647137 -0.000217

**SeSe1** E=-5341.33400127 a.u.  $\nu=40.9642$  cm<sup>-1</sup>

H 1.680168 -2.211905 -0.000302  
H -4.378059 1.787806 -0.000327  
H 4.283856 2.561053 -0.000285  
H -5.869630 -0.398786 -0.000305

H -4.283856 -2.561053 -0.000277  
C -3.937296 -1.538619 -0.000291  
C 4.788977 0.362392 -0.000262  
C 4.033227 -0.765086 -0.000292  
H 5.869630 0.398786 -0.000243  
H -1.680168 2.211905 -0.000328  
C 3.937296 1.538619 -0.000287  
C 2.651754 1.110437 -0.000294  
C 2.646543 -0.361625 -0.000297  
Se 1.063789 2.079990 -0.000315  
C -0.188152 0.659174 -0.000313  
C 0.188152 -0.659174 -0.000309  
C 1.539700 -1.135063 -0.000303  
C -1.539700 1.135063 -0.000319  
C -2.646543 0.361625 -0.000317  
C -2.651754 -1.110437 -0.000303  
Se -1.063789 -2.079990 -0.000307  
C -4.033227 0.765086 -0.000319  
C -4.788977 -0.362392 -0.000308  
H 4.378059 -1.787806 -0.000296

**SS2** E=-1948.90125845 a.u.  $\nu=15.0474$  cm<sup>-1</sup>

C -8.321698 1.434529 0.000297  
C -6.957867 1.529043 0.000235  
C -6.151267 0.368423 0.000154  
C -6.776610 -0.908874 0.000137  
C -8.189124 -0.969364 0.000201  
C -8.944247 0.170426 0.000279  
C -4.732750 0.408713 0.000088  
C -3.994428 -0.773427 0.000011  
C -4.623118 -2.032572 -0.000002  
C -5.985877 -2.092330 0.000058  
C -3.823309 1.544009 0.000092  
C -2.558400 1.060022 0.000031  
C -2.589441 -0.410330 -0.000030  
S -1.065007 1.934253 -0.000045  
C 0.151341 0.668114 -0.000045  
C -0.151341 -0.668113 -0.000041

C -1.489554 -1.185817 -0.000053  
C 1.489554 1.185817 -0.000066  
C 2.589441 0.410330 -0.000039  
C 2.558400 -1.060021 0.000036  
S 1.065007 -1.934253 -0.000047  
C 3.994428 0.773427 -0.000000  
C 4.732750 -0.408713 0.000090  
C 3.823310 -1.544009 0.000103  
C 4.623118 2.032572 -0.000021  
C 5.985877 2.092330 0.000043  
C 6.776610 0.908874 0.000135  
C 6.151267 -0.368423 0.000161  
C 8.189124 0.969364 0.000203  
C 8.944247 -0.170425 0.000294  
C 8.321698 -1.434528 0.000321  
C 6.957867 -1.529043 0.000256  
H -8.928524 2.331748 0.000358  
H -6.482445 2.502159 0.000248  
H -8.667155 -1.942459 0.000188  
H -10.025573 0.105329 0.000328  
H -4.035064 -2.943125 -0.000064  
H -6.492610 -3.050047 0.000045  
H -4.110020 2.584283 0.000144  
H -1.604361 -2.264703 -0.000076  
H 1.604361 2.264703 -0.000098  
H 4.110021 -2.584283 0.000165  
H 4.035064 2.943125 -0.000094  
H 6.492611 3.050048 0.000023  
H 8.667155 1.942459 0.000183  
H 10.025573 -0.105328 0.000346  
H 8.928524 -2.331748 0.000393  
H 6.482445 -2.502159 0.000276

**SSe2** E=-3952.32619463 a.u.  $\nu=14.3482$  cm<sup>-1</sup>

C -8.352475 -1.048049 0.000266  
C -6.996289 -1.217551 0.000223  
C -6.126922 -0.102516 0.000133  
C -6.681818 1.207301 0.000088

C -8.089338 1.345159 0.000134  
C -8.905328 0.248614 0.000221  
C -4.713830 -0.218589 0.000084  
C -3.911104 0.918270 -0.000003  
C -4.468906 2.209422 -0.000045  
C -5.827195 2.344125 -0.000001  
C -3.863497 -1.402493 0.000113  
C -2.575488 -0.991140 0.000049  
C -2.522867 0.477627 -0.000025  
Se -1.009592 -2.009915 0.000006  
C 0.277372 -0.616945 -0.000028  
C -0.058693 0.708565 -0.000049  
C -1.402255 1.222245 -0.000063  
C 1.624545 -1.105518 -0.000041  
C 2.709342 -0.307394 -0.000034  
C 2.645708 1.161603 0.000004  
S 1.133239 2.000859 -0.000087  
C 4.121188 -0.639352 0.000001  
C 4.833472 0.559162 0.000060  
C 3.899840 1.673909 0.000058  
C 4.777899 -1.884403 0.000001  
C 6.141467 -1.914187 0.000057  
C 6.906055 -0.713392 0.000119  
C 6.252808 0.549767 0.000122  
C 8.319453 -0.742830 0.000178  
C 9.049474 0.413319 0.000239  
C 8.399352 1.663334 0.000242  
C 7.033669 1.727737 0.000185  
H -9.007718 -1.910557 0.000335  
H -6.575194 -2.215391 0.000257  
H -8.513266 2.343008 0.000100  
H -9.981493 0.372418 0.000255  
H -3.832502 3.086814 -0.000114  
H -6.279796 3.328624 -0.000035  
H -4.209558 -2.424912 0.000177  
H -1.505285 2.302648 -0.000101  
H 1.768200 -2.181242 -0.000055  
H 4.163415 2.720268 0.000096

H 4.210152 -2.807795 -0.000046  
H 6.669270 -2.860466 0.000055  
H 8.818764 -1.705191 0.000175  
H 10.131975 0.371919 0.000284  
H 8.986249 2.573721 0.000290  
H 6.536889 2.690125 0.000188

**SeSe2** E=-5955.75114957  $\nu=13.3622$  cm<sup>-1</sup>

C 8.438421 1.276676 0.000676  
C 7.078811 1.416828 0.000556  
C 6.233676 0.283404 0.000373  
C 6.816659 -1.014086 0.000316  
C 8.226741 -1.121584 0.000442  
C 9.019032 -0.007695 0.000618  
C 4.818208 0.369311 0.000241  
C 4.040009 -0.784929 0.000068  
C 4.625935 -2.063795 0.000018  
C 5.986665 -2.169244 0.000137  
C 3.943008 1.534394 0.000268  
C 2.664010 1.094831 0.000124  
C 2.643282 -0.374436 -0.000002  
Se 1.075876 2.077340 -0.000043  
C -0.184752 0.656721 -0.000041  
C 0.184752 -0.656721 -0.000038  
C 1.536946 -1.141840 -0.000061  
C -1.536946 1.141840 -0.000070  
C -2.643281 0.374436 -0.000006  
C -2.664010 -1.094831 0.000129  
Se -1.075876 -2.077340 -0.000041  
C -4.040009 0.784929 0.000061  
C -4.818208 -0.369311 0.000244  
C -3.943008 -1.534394 0.000277  
C -4.625935 2.063796 0.000006  
C -5.986665 2.169244 0.000127  
C -6.816659 1.014086 0.000315  
C -6.233676 -0.283404 0.000379  
C -8.226741 1.121584 0.000444  
C -9.019032 0.007695 0.000628

C -8.438421 -1.276676 0.000693  
C -7.078811 -1.416828 0.000570  
H 9.074881 2.153143 0.000815  
H 6.636250 2.405334 0.000600  
H 8.672089 -2.110071 0.000398  
H 10.097616 -0.108361 0.000713  
H 4.008747 -2.954846 -0.000120  
H 6.460467 -3.143723 0.000094  
H 4.266767 2.564075 0.000388  
H 1.668733 -2.219414 -0.000120  
H -1.668733 2.219414 -0.000137  
H -4.266767 -2.564075 0.000404  
H -4.008747 2.954846 -0.000139  
H -6.460467 3.143723 0.000080  
H -8.672089 2.110071 0.000395  
H -10.097616 0.108361 0.000726  
H -9.074881 -2.153143 0.000839  
H -6.636250 -2.405334 0.000620



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