#### *Supporting Information for*

#### **A Spin-Flip Study of the Diradical Isomers of Pyrrole, Furan and Thiophene**

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#### ***Warning:*** *Never print this document...it is long!*

1. **Geometric Parameters for all S1 & T1 Structures of Diradical Isomers.**

**Table S-I.1.** (a) Molecular symmetry and optimized structure for the *X* 1*A*1 state of thefuran parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference; (b-d) Molecular symmetries and optimized structures for the lowest singlet (S1) and triplet (T1) states of each diradical isomer of furan.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **(a) Furan (*X* 1*A*1)** | | | | |
| A molecule model with a red ball  Description automatically generated  **1**  **5**  **2**  **3**  **4** | | | | |
| *C2v* | | | | |
|  | **(b) 23F** | **(c) 24F** | **(d) 25F** | **(e) 34F** |
| **S1** | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated |
| *Cs* | *Cs* | *C2v* | *C2v* |
| **T1** | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated | A molecule model with a red ball  Description automatically generated |
| *Cs* | *C1* | *C2v* | *C2v* |

**Table S-I.2.** Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thefuran parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference, and (b-e) lowest singlet (S1) and triplet (T1) states of each diradical isomer, optimized at the ωB97X-D/cc-pVDZ level of theory with a BS-UKS reference.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Furan** | **(b) 23F** | | **(c) 34F** | | | | **(d) 24F** | | **(e) 25F** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.35 | 1.32 | 1.39 | | 1.37 | 1.37 | 1.35 | | 1.41 | | 1.36 | 1.34 | | ***R*23 (Å)** | 1.36 | 1.27 | 1.45 | | 1.36 | 1.40 | 1.35 | | 1.46 | | 1.37 | 1.36 | | ***R*34 (Å)** | 1.44 | 1.50 | 1.39 | | 1.28 | 1.35 | 1.40 | | 1.36 | | 1.46 | 1.45 | | ***R*45 (Å)** | 1.36 | 1.37 | 1.39 | | 1.36 | 1.40 | 1.36 | | 1.41 | | 1.37 | 1.36 | | ***R*51 (Å)** | 1.35 | 1.41 | 1.36 | | 1.37 | 1.37 | 1.36 | | 1.33 | | 1.36 | 1.34 | | ***R*24 (Å)** | 2.23 | 1.96 | 2.38 | | 2.16 | 2.20 | 1.93 | | 2.27 | | 2.23 | 2.22 | | ***R*25 (Å)** | 2.18 | 2.01 | 2.26 | | 2.20 | 2.14 | 2.06 | | 2.22 | | 2.12 | 2.14 | | **∠123 (°)** | 110.7 | 131.3 | 100.9 | | 106.9 | 112.5 | 126.6 | | 106.1 | | 114.7 | 112.8 | | **∠234 (°)** | 115.8 | 89.7 | 114.1 | | 109.8 | 106.4 | 89.3 | | 107.0 | | 104.1 | 104.4 | | **∠345 (°)** | 115.8 | 110.7 | 101.9 | | 109.8 | 106.4 | 119.7 | | 107.8 | | 104.1 | 104.4 | | **∠451 (°)** | 110.7 | 108.7 | 112.1 | | 106.9 | 112.5 | 105.5 | | 110.6 | | 114.7 | 112.7 | | **∠512 (°)** | 107.0 | 104.9 | 111.1 | | 106.5 | 102.2 | 98.9 | | 108.5 | | 102.4 | 105.2 | |

**Table S-I.3.** (a) Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thefuran parent molecule, provided for reference; (b-e) differences in bond lengths (Å) and angles (°) for the lowest singlet (S1) and triplet (T1) states of each diradical isomer, computed as diradical minus parent value.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Furan** | **(b) 23F** | | **(c) 34F** | | | | **(d) 24F** | | **(e) 25F** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.35 | -0.04 | 0.03 | | 0.02 | 0.02 | 0.00 | | 0.05 | | 0.01 | -0.01 | | ***R*23 (Å)** | 1.36 | -0.09 | 0.09 | | 0.00 | 0.04 | -0.01 | | 0.10 | | 0.01 | 0.00 | | ***R*34 (Å)** | 1.44 | 0.06 | -0.05 | | -0.16 | -0.09 | -0.04 | | -0.07 | | 0.02 | 0.02 | | ***R*45 (Å)** | 1.36 | 0.01 | 0.03 | | 0.00 | 0.04 | 0.00 | | 0.05 | | 0.01 | 0.00 | | ***R*51 (Å)** | 1.35 | 0.05 | 0.01 | | 0.02 | 0.02 | 0.00 | | -0.03 | | 0.01 | -0.01 | | ***R*24 (Å)** | 2.23 | -0.27 | 0.15 | | -0.07 | -0.03 | -0.30 | | 0.04 | | 0.00 | -0.01 | | ***R*25 (Å)** | 2.18 | -0.17 | 0.09 | | 0.03 | -0.04 | -0.12 | | 0.04 | | -0.06 | -0.04 | | **∠123 (°)** | 110.7 | 20.6 | -9.8 | | -3.8 | 1.8 | 15.9 | | -4.6 | | 4.0 | 2.1 | | **∠234 (°)** | 115.8 | -26.1 | -1.8 | | -6.0 | -9.4 | -26.5 | | -8.9 | | -11.8 | -11.4 | | **∠345 (°)** | 115.8 | -5.1 | -13.9 | | -6.0 | -9.4 | 3.9 | | -8.0 | | -11.8 | -11.4 | | **∠451 (°)** | 110.7 | -2.0 | 1.4 | | -3.8 | 1.8 | -5.2 | | -0.1 | | 4.0 | 2.0 | | **∠512 (°)** | 107.0 | -2.1 | 4.1 | | -0.4 | -4.7 | -8.1 | | 1.5 | | -4.5 | -1.7 | |

**Table S-I.4.** (a) Molecular symmetry and optimized structure for the *X* 1*A*1 state of thethiophene parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference; (b-d) Molecular symmetries and optimized structures for the lowest singlet (S1) and triplet (T1) states of each diradical isomer of thiophene.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **(a) Thiophene (*X* 1*A*1)** | | | | |
| A molecule model with a yellow ball  Description automatically generated  **1**  **5**  **2**  **3**  **4** | | | | |
| *C2v* | | | | |
|  | **(b) 23T** | **(c) 24T** | **(d) 25T** | **(e) 34T** |
| **S1** | A molecule model with a yellow ball  Description automatically generated | A molecule model with a yellow ball  Description automatically generated | A molecule model with balls and a yellow ball  Description automatically generated | A molecule model with a yellow ball  Description automatically generated |
| *Cs* | *Cs* | *C2v* | *C2v* |
| **T1** | A molecule model with a yellow ball  Description automatically generated | A molecule model with a yellow ball  Description automatically generated | A molecule model with a yellow ball  Description automatically generated with medium confidence | A molecule model with a yellow ball  Description automatically generated |
| *Cs* | *C1* | *C2v* | *C2v* |

**Table S-I.5.** Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thethiophene parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference, and (b-e) lowest singlet (S1) and triplet (T1) states of each diradical isomer, optimized at the ωB97X-D/cc-pVDZ level of theory with a BS-UKS reference.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Thiophene** | **(b) 23T** | | **(c) 34T** | | | | **(d) 24T** | | **(e) 25T** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.73 | 1.76 | 1.71 | | 1.76 | 1.75 | 1.74 | | 1.79 | | 1.68 | 1.72 | | ***R*23 (Å)** | 1.37 | 1.26 | 1.41 | | 1.36 | 1.33 | 1.35 | | 1.45 | | 1.38 | 1.44 | | ***R*34 (Å)** | 1.43 | 1.41 | 1.40 | | 1.27 | 1.43 | 1.42 | | 1.37 | | 1.42 | 1.37 | | ***R*45 (Å)** | 1.37 | 1.37 | 1.38 | | 1.36 | 1.33 | 1.35 | | 1.41 | | 1.38 | 1.44 | | ***R*51 (Å)** | 1.73 | 1.77 | 1.78 | | 1.76 | 1.75 | 1.74 | | 1.72 | | 1.68 | 1.72 | | ***R*24 (Å)** | 2.33 | 2.50 | 2.44 | | 2.26 | 2.33 | 2.17 | | 2.35 | | 2.23 | 2.34 | | ***R*25 (Å)** | 2.48 | 2.65 | 2.58 | | 2.55 | 2.54 | 2.44 | | 2.57 | | 2.16 | 2.48 | | **∠123 (°)** | 111.6 | 94.0 | 105.0 | | 105.8 | 109.4 | 118.6 | | 107.0 | | 124.3 | 111.2 | | **∠234 (°)** | 112.6 | 138.6 | 120.9 | | 118.0 | 114.2 | 102.6 | | 113.1 | | 105.7 | 112.6 | | **∠345 (°)** | 112.6 | 100.5 | 109.0 | | 118.0 | 114.2 | 122.1 | | 116.8 | | 105.7 | 112.6 | | **∠451 (°)** | 111.6 | 109.4 | 110.2 | | 105.8 | 109.4 | 107.3 | | 108.7 | | 124.3 | 111.2 | | **∠512 (°)** | 91.7 | 97.5 | 94.9 | | 92.5 | 92.9 | 89.4 | | 95.5 | | 80.0 | 92.3 | |

**Table S-I.6.** (a) Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thethiophene parent molecule, provided for reference; (b-e) differences in bond lengths (Å) and angles (°) for the lowest singlet (S1) and triplet (T1) states of each diradical isomer, computed as diradical minus parent value.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Thiophene** | **(b) 23T** | | **(c) 34T** | | | | **(d) 24T** | | **(e) 25T** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.73 | 0.03 | -0.01 | | 0.04 | 0.02 | 0.01 | | 0.06 | | -0.05 | -0.01 | | ***R*23 (Å)** | 1.37 | -0.10 | 0.04 | | -0.01 | -0.04 | -0.01 | | 0.09 | | 0.01 | 0.07 | | ***R*34 (Å)** | 1.43 | -0.02 | -0.03 | | -0.16 | 0.00 | -0.01 | | -0.06 | | -0.01 | -0.06 | | ***R*45 (Å)** | 1.37 | 0.00 | 0.02 | | -0.01 | -0.04 | -0.01 | | 0.05 | | 0.01 | 0.07 | | ***R*51 (Å)** | 1.73 | 0.05 | 0.06 | | 0.04 | 0.02 | 0.01 | | -0.01 | | -0.05 | -0.01 | | ***R*24 (Å)** | 2.33 | 0.18 | 0.12 | | -0.07 | 0.01 | -0.16 | | 0.03 | | -0.10 | 0.01 | | ***R*25 (Å)** | 2.48 | 0.18 | 0.10 | | 0.07 | 0.06 | -0.03 | | 0.10 | | -0.32 | 0.00 | | **∠123 (°)** | 111.6 | -17.6 | -6.6 | | -5.8 | -2.2 | 7.0 | | -4.6 | | 12.7 | -0.4 | | **∠234 (°)** | 112.6 | 26.0 | 8.3 | | 5.4 | 1.6 | -9.9 | | 0.5 | | -6.9 | 0.1 | | **∠345 (°)** | 112.6 | -12.1 | -3.6 | | 5.4 | 1.6 | 9.5 | | 4.2 | | -6.9 | 0.1 | | **∠451 (°)** | 111.6 | -2.1 | -1.4 | | -5.8 | -2.2 | -4.3 | | -2.9 | | 12.7 | -0.4 | | **∠512 (°)** | 91.7 | 5.9 | 3.2 | | 0.8 | 1.2 | -2.3 | | 3.8 | | -11.7 | 0.6 | |

**Table S-I.7.** (a) Molecular symmetry and optimized structure for the *X* 1*A*1 state of thepyrrole parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference; (b-d) Molecular symmetries and optimized structures for the lowest singlet (S1) and triplet (T1) states of each diradical isomer of pyrrole (reproduction of Table 1 of the main text for completeness).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **(a) Pyrrole (*X* 1*A*1)** | | | | |
| **1**  **5**  **4**  **2**  **3** | | | | |
| *C2v* | | | | |
|  | **(b) 23P** | **(c) 24P** | **(d) 25P** | **(e) 34P** |
| **S1** | A molecule model with a blue ball  Description automatically generated | A blue and grey molecule  Description automatically generated | A blue and grey molecule  Description automatically generated | A molecule model with a blue ball  Description automatically generated |
| *Cs* | *Cs* | *C2v* | *C2v* |
| **T1** | A molecule model with a blue ball  Description automatically generated | A molecule model with a blue ball  Description automatically generated | A blue and grey molecule  Description automatically generated | A molecule model with a blue ball  Description automatically generated |
| *Cs* | *C1* | *C2v* | *C2v* |

**Table S-I.8.** Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thepyrrole parent molecule, optimized at the ωB97X-D/cc-pVDZ level of theory with a RKS reference, and (b-e) lowest singlet (S1) and triplet (T1) states of each diradical isomer, optimized at the ωB97X-D/cc-pVDZ level of theory with a BS-UKS reference.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Pyrrole** | **(b) 23P** | | **(c) 34P** | | | | **(d) 24P** | | **(e) 25P** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.37 | 1.37 | 1.37 | | 1.39 | 1.38 | 1.36 | | 1.36 | | 1.37 | 1.37 | | ***R*23 (Å)** | 1.38 | 1.33 | 1.40 | | 1.38 | 1.42 | 1.37 | | 1.39 | | 1.38 | 1.42 | | ***R*34 (Å)** | 1.42 | 1.44 | 1.40 | | 1.27 | 1.34 | 1.38 | | 1.41 | | 1.44 | 1.39 | | ***R*45 (Å)** | 1.38 | 1.39 | 1.39 | | 1.38 | 1.42 | 1.38 | | 1.37 | | 1.38 | 1.41 | | ***R*51 (Å)** | 1.37 | 1.39 | 1.38 | | 1.39 | 1.38 | 1.36 | | 1.39 | | 1.37 | 1.37 | | ***R*24 (Å)** | 2.26 | 2.26 | 2.29 | | 2.19 | 2.23 | 1.94 | | 2.20 | | 2.25 | 2.25 | | ***R*25 (Å)** | 2.24 | 2.23 | 2.24 | | 2.28 | 2.20 | 2.16 | | 2.23 | | 2.18 | 2.22 | | **∠123 (°)** | 107.7 | 109.9 | 105.7 | | 103.6 | 109.4 | 121.9 | | 110.4 | | 112.2 | 108.3 | | **∠234 (°)** | 107.3 | 108.8 | 110.2 | | 111.3 | 107.7 | 89.7 | | 103.8 | | 105.4 | 106.7 | | **∠345 (°)** | 107.3 | 104.9 | 104.8 | | 111.3 | 107.7 | 124.1 | | 110.7 | | 105.4 | 106.7 | | **∠451 (°)** | 107.7 | 108.9 | 109.1 | | 103.6 | 109.4 | 99.8 | | 106.0 | | 112.2 | 108.4 | | **∠512 (°)** | 109.9 | 107.5 | 109.4 | | 110.1 | 105.8 | 104.4 | | 108.3 | | 104.8 | 108.8 | |

**Table S-I.9.** (a) Bond lengths (Å) and angles (°) for optimized structures of (a) the *X* 1*A*1 state of thepyrrole parent molecule, provided for reference; (b-e) differences in bond lengths (Å) and angles (°) for the lowest singlet (S1) and triplet (T1) states of each diradical isomer, computed as diradical minus parent value.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | |  | **(a) Pyrrole** | **(b) 23P** | | **(c) 34P** | | | | **(d) 24P** | | **(e) 25P** | | | | **Parameter** | ***X* 1*A*1** | **S1** | **T1** | | **S1** | **T1** | **S1** | | **T1** | | **S1** | **T1** | | ***R*12 (Å)** | 1.37 | 0.01 | 0.00 | | 0.02 | 0.01 | 0.00 | | -0.01 | | 0.00 | 0.00 | | ***R*23 (Å)** | 1.38 | -0.05 | 0.02 | | 0.00 | 0.05 | -0.01 | | 0.01 | | 0.01 | 0.04 | | ***R*34 (Å)** | 1.42 | 0.02 | -0.02 | | -0.15 | -0.09 | -0.05 | | -0.01 | | 0.02 | -0.03 | | ***R*45 (Å)** | 1.38 | 0.01 | 0.01 | | 0.00 | 0.05 | 0.00 | | -0.01 | | 0.01 | 0.04 | | ***R*51 (Å)** | 1.37 | 0.02 | 0.01 | | 0.02 | 0.01 | -0.01 | | 0.02 | | 0.00 | 0.00 | | ***R*24 (Å)** | 2.26 | 0.00 | 0.04 | | -0.07 | -0.03 | -0.32 | | -0.05 | | -0.01 | 0.00 | | ***R*25 (Å)** | 2.24 | -0.01 | 0.00 | | 0.03 | -0.04 | -0.09 | | -0.01 | | -0.06 | -0.02 | | **∠123 (°)** | 107.7 | 2.1 | -2.0 | | -4.1 | 1.7 | 14.1 | | 2.6 | | 4.4 | 0.5 | | **∠234 (°)** | 107.3 | 1.5 | 2.9 | | 4.0 | 0.4 | -17.6 | | -3.5 | | -1.9 | -0.6 | | **∠345 (°)** | 107.3 | -2.4 | -2.5 | | 4.0 | 0.4 | 16.8 | | 3.4 | | -1.9 | -0.6 | | **∠451 (°)** | 107.7 | 1.2 | 1.4 | | -4.1 | 1.7 | -7.9 | | -1.7 | | 4.4 | 0.6 | | **∠512 (°)** | 109.9 | -2.4 | -0.5 | | 0.1 | -4.2 | -5.5 | | -1.6 | | -5.1 | -1.1 | |

**Table S-I.10.** First vibrational frequencies (cm-1) of optimized S1 and T1 structures for all diradical isomers, computed at the same levels of theory as their respective geometry optimizations.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  | **Furan** | **Thiophene** | **Pyrrole** |
| **23** | **S1** | 83.52 | 334.32 | 325.75 |
| **T1** | 516.29 | 437.70 | 463.72 |
| **24** | **S1** | 234.29 | 336.28 | 246.31 |
| **T1** | 509.01 | 472.34 | 371.59 |
| **25** | **S1** | 541.40 | 163.79 | 587.06 |
| **T1** | 237.53 | 393.09 | 373.36 |
| **34** | **S1** | 351.18 | 248.94 | 398.75 |
| **T1** | 457.52 | 424.11 | 400.35 |

1. **Reference State Preparation for EOM-SF-CC Computations.**

To apply EOM-SF-CC computations to access the low-spin (*Ms* = 0) states of our diradical isomers, it is first necessary to prepare a high-spin (*Ms* = +1) triplet reference determinant which singly occupies the radical σ and σ\* molecular orbitals by α electrons, i.e., | (σ)α (σ\*)α 〉. While Q-Chem often prepares this reference determinant automatically, occasions do exist where the MOs are initially occupied incorrectly, whereby the user must manually specify the correct orbital occupations to ensure that the proper reference is prepared for future utilization by EOM-SF-CC. Visualized in the tables presented below in Sections S-II.A-C are the relevant frontier molecular orbitals prepared at the UHF/cc-pVDZ which are *correctly* occupied, either by default or by manual intervention, and which are then utilized for EOM-SF-CCSD/cc-pVDZ computations on each diradical isomer.

* 1. **Diradical Isomers of Furan.**

**Table S-II.A.1.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **23F** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+3** | 17 *a*' | 5 *a*" | **LUMO+5** |
| **A red and blue human organs  Description automatically generated** | A group of colorful spheres  Description automatically generated |
|  | π5\* |
| **LUMO+2** | 5 *a*" | 17 *a*' | **LUMO+4** |
| **A group of colorful spheres  Description automatically generated** | A red and blue spheres  Description automatically generated |
| π5\* |  |
| **LUMO+1** | 16 *a*' | 16 *a*' | **LUMO+3** |
| **A red and blue object with blue and red objects  Description automatically generated with medium confidence** | A blue and red object with a black background  Description automatically generated |
|  |  |
| **LUMO** | 4 *a*" | 4 *a*" | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π4\* | π4\* |
| **HOMO** | 3 *a*" | 15 *a*' | **LUMO+1** |
| **A blue and red molecule  Description automatically generated** | A red and blue colored structure  Description automatically generated with medium confidence |
| π3 | σ\* |
| **HOMO-1** | 2 *a*" | 14 *a*' | **LUMO** |
| **A blue and red molecule  Description automatically generated** | A red and blue molecule  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 15 *a*' | 3 *a*" | **HOMO** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres with a molecule  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 14 *a*' | 2 *a*" | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red object with a black background  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 13 *a*' | 13 *a*' | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 12 *a*' | 12 *a*' | **HOMO-3** |
| **A blue and red spheres  Description automatically generated** | A red and blue spheres  Description automatically generated |
|  |  |
| **HOMO-6** | 1 *a*" | 1 *a*" | **HOMO-4** |
| **A blue and red spheres with spheres on it  Description automatically generated** | A red and blue sphere with a molecule  Description automatically generated with medium confidence |
| π1 | π1 |

**Table S-II.A.2.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **24F** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+3** | 5 *a*" | 5 *a*" | **LUMO+5** |
| **A group of colorful spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π5\* | π5\* |
| **LUMO+2** | 17 *a*' | 17 *a*' | **LUMO+4** |
| **A blue and red human organs  Description automatically generated** | A blue and red human organs  Description automatically generated |
|  |  |
| **LUMO+1** | 16 *a*' | 4 *a*" | **LUMO+3** |
| **A blue object with red dots  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  | π4\* |
| **LUMO** | 4 *a*" | 16 *a*' | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A red object with blue and red spheres  Description automatically generated |
| π4\* |  |
| **HOMO** | 3 *a*" | 15 *a*' | **LUMO+1** |
| **A red and blue spheres  Description automatically generated** | A red and blue spleen  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 15 *a*' | 14 *a*' | **LUMO** |
| **A red and blue model of a human body  Description automatically generated** | A red and blue molecule  Description automatically generated |
| σ\* | σ |
| **HOMO-2** | 2 *a*" | 3 *a*" | **HOMO** |
| **A blue and red object with silver balls  Description automatically generated** | A blue and red spheres with molecules  Description automatically generated |
| π2 | π3 |
| **HOMO-3** | 14 *a*' | 2 *a*" | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red object with white dots  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 13 *a*' | 13 *a*' | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 12 *a*' | 12 *a*' | **HOMO-3** |
| **A red and blue spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-6** | 1 *a*" | 1 *a*" | **HOMO-4** |
| **A red and blue molecule  Description automatically generated** | A blue and red object with a black background  Description automatically generated |
| π1 | π1 |

**Table S-II.A.3.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **25F** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+3** | 7 *b*2 | 7 *b*2 | **LUMO+5** |
| **A red and blue lungs  Description automatically generated** | A red and blue kidneys  Description automatically generated |
|  |  |
| **LUMO+2** | 2 *a*2 | 2 *a*2 | **LUMO+4** |
| **A group of blue and red spheres  Description automatically generated** | A group of spheres with molecules  Description automatically generated |
| π5\* | π5\* |
| **LUMO+1** | 10 *a*1 | 10 *a*1 | **LUMO+3** |
| **A blue and red blob  Description automatically generated** | A blue and red blob  Description automatically generated |
|  |  |
| **LUMO** | 3 *b*1 | 3 *b*1 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π4\* | π4\* |
| **HOMO** | 1 *a*2 | 6 *b*2 | **LUMO+1** |
| **A blue and red spheres  Description automatically generated** | A red and blue lungs  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 2 *b*1 | 9 *a*1 | **LUMO** |
| **A blue and red object with a black background  Description automatically generated** | A blue and red object with a black background  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 6 *b*2 | 1 *a*2 | **HOMO** |
| **A red and blue structure  Description automatically generated** | A blue and red spheres with black dots  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 9 *a*1 | 2 *b*1 | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red molecule  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 8 *a*1 | 8 *a*1 | **HOMO-2** |
| **A blue and red shapes  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 5 *b*2 | 5 *b*2 | **HOMO-3** |
| **A group of balloons in a circle  Description automatically generated** | A group of colorful balls  Description automatically generated |
|  |  |
| **HOMO-6** | 1 *b*1 | 7 *a*1 | **HOMO-4** |
| **A blue and red sphere with white balls  Description automatically generated** | A human organs with a blue object  Description automatically generated |
| π1 |  |
| **HOMO-7** | 7 *a*1 | 1 *b*1 | **HOMO-5** |
| **A blue and red object with a red object in the middle  Description automatically generated** | A red and blue sphere with a black background  Description automatically generated |
|  | π1 |

**Table S-II.A.4.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **34F** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+3** | 2 *a*2 | 2 *a*2 | **LUMO+5** |
| **A group of blue and red spheres  Description automatically generated** | A group of colorful spheres  Description automatically generated |
| π5\* | π5\* |
| **LUMO+2** | 7 *b*2 | 7 *b*2 | **LUMO+4** |
| **A red and blue lungs  Description automatically generated** | A red and blue kidneys  Description automatically generated |
|  |  |
| **LUMO+1** | 10 *a*1 | 10 *a*1 | **LUMO+3** |
| **A blue and red structure  Description automatically generated** | A blue and red object with holes  Description automatically generated |
|  |  |
| **LUMO** | 3 *b*1 | 6 *b*2 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue and red model of human organs  Description automatically generated |
| π4\* | σ\* |
| **HOMO** | 1 *a*2 | 3 *b*1 | **LUMO+1** |
| **A blue and red spheres with molecules  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π3 | π4\* |
| **HOMO-1** | 6 *b*1 | 9 *a*1 | **LUMO** |
| **A blue and red spheres  Description automatically generated** | A red and blue structure  Description automatically generated |
| σ\* | σ |
| **HOMO-2** | 2 *b*1 | 1 *a*2 | **HOMO** |
| **A red and blue spheres with spheres in the center  Description automatically generated** | A blue and red spheres with molecules  Description automatically generated |
| π2 | π3 |
| **HOMO-3** | 9 *a*1 | 2 *b*1 | **HOMO-1** |
| **A blue and red object  Description automatically generated** | A blue and red molecule  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 8 *a*1 | 8 *a*1 | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 5 *b*2 | 5 *b*2 | **HOMO-3** |
| **A red and blue molecule  Description automatically generated** | A red and blue spheres  Description automatically generated |
|  |  |
| **HOMO-6** | 1 *b*1 | 1 *b*1 | **HOMO-4** |
| **A blue and red molecule  Description automatically generated** | A red and blue circle with a black background  Description automatically generated |
| π1 | π1 |

* 1. **Diradical Isomers of Thiophene.**

**Table S-II.B.1.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **23T** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 21 *a*' | 6 *a*" | **LUMO+6** |
| **A blue and red blobs  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  | π5\* |
| **LUMO+3** | 6 *a*" | 21 *a*' | **LUMO+5** |
| **A blue and red spheres  Description automatically generated** | A blue and red paint  Description automatically generated with medium confidence |
| π5\* |  |
| **LUMO+2** | 20 *a*' | 20 *a*' | **LUMO+4** |
| **A red and blue liquid  Description automatically generated** | A blue and red cell  Description automatically generated |
|  |  |
| **LUMO+1** | 19 *a*' | 19 *a*' | **LUMO+3** |
| **A red and blue object  Description automatically generated** | A blue and red object  Description automatically generated |
|  |  |
| **LUMO** | 5 *a*" | 18 *a*' | **LUMO+2** |
| **A group of colorful spheres  Description automatically generated** | A red and blue kidneys  Description automatically generated |
| π4\* | σ\* |
| **HOMO** | 18 *a*' | 5 *a*" | **LUMO+1** |
| **A blue and red spheres  Description automatically generated** | A group of colorful spheres  Description automatically generated |
| σ\* | π4\* |
| **HOMO-1** | 4 *a*" | 17 *a*' | **LUMO** |
| **A blue and red spheres  Description automatically generated** | A red and blue object with spheres  Description automatically generated with medium confidence |
| π3 | σ |
| **HOMO-2** | 3 *a*" | 4 *a*" | **HOMO** |
| **A colorful spheres with dots and lines  Description automatically generated with medium confidence** | A blue and red spheres with white spheres  Description automatically generated |
| π2 | π3 |
| **HOMO-3** | 17 *a*' | 3 *a*" | **HOMO-1** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres with molecules  Description automatically generated |
|  | π2 |
| **HOMO-4** | 16 *a*' | 16 *a*' | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| σ |  |
| **HOMO-5** | 2 *a*" | 2 *a*" | **HOMO-3** |
| **A blue and red object with a black background  Description automatically generated** | A red and blue circle with a black background  Description automatically generated |
| π1 | π1 |
| **HOMO-6** | 15 *a*' | 15 *a*' | **HOMO-6** |
| A blue and red molecule  Description automatically generated | A blue and red spheres  Description automatically generated |
|  |  |

**Table S-II.B.2.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **24T** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 21 *a*' | 6 *a*" | **LUMO+6** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  | π5\* |
| **LUMO+3** | 6 *a*" | 21 *a*' | **LUMO+5** |
| **A group of colorful spheres  Description automatically generated** | A blue and red liquid  Description automatically generated |
| π5\* |  |
| **LUMO+2** | 20 *a*' | 20 *a*' | **LUMO+4** |
| **A red and blue object with blue and yellow objects  Description automatically generated** | A red and blue human organs  Description automatically generated |
|  |  |
| **LUMO+1** | 19 *a*' | 19 *a*' | **LUMO+3** |
| **A blue and red spheres  Description automatically generated** | A red and blue human organs  Description automatically generated |
|  |  |
| **LUMO** | 5 *a*" | 5 *a*" | **LUMO+2** |
| **A group of colorful spheres  Description automatically generated** | A close up of a molecule  Description automatically generated |
| π4\* | π4\* |
| **HOMO** | 4 *a*" | 18 *a*' | **LUMO+1** |
| **A close up of a computer  Description automatically generated** | A red and blue kidneys  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 3 *a*" | 17 *a*' | **LUMO** |
| **A blue and red spheres  Description automatically generated** | A red and blue molecule  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 18 *a*' | 4 *a*" | **HOMO** |
| **A red and blue kidneys  Description automatically generated** | A blue and red spheres with spheres connected together  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 17 *a*' | 3 *a*" | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red spheres with molecules  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 16 *a*' | 16 *a*' | **HOMO-2** |
| **A blue and red molecule  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 2 *a*" | 2 *a*" | **HOMO-3** |
| **A red and blue molecule  Description automatically generated with medium confidence** | A red and blue object with a black background  Description automatically generated |
| π1 | π1 |

**Table S-II.B.3.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **25T** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 9 *b*2 | 9 *b*2 | **LUMO+6** |
| **A red and blue lungs  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **LUMO+3** | 2 *a*2 | 2 *a*2 | **LUMO+5** |
| **A blue and red spheres  Description automatically generated** | A colorful spheres with molecules  Description automatically generated with medium confidence |
| π5\* | π5\* |
| **LUMO+2** | 12 *a*1 | 12 *a*1 | **LUMO+4** |
| **A blue and red object  Description automatically generated** | A blue and red blob  Description automatically generated |
|  |  |
| **LUMO+1** | 8 *b*2 | 8 *b*2 | **LUMO+3** |
| **A colorful shapes on a black background  Description automatically generated** | A colorful balloons in a black background  Description automatically generated with medium confidence |
|  |  |
| **LUMO** | 4 *b*1 | 7 *b*2 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A red and blue kidneys  Description automatically generated |
| π4\* | σ\* |
| **HOMO** | 1 *a*2 | 4 *b*1 | **LUMO+1** |
| **A blue and red spheres with spheres in the middle  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π3 | π4\* |
| **HOMO-1** | 3 *b*1 | 11 *a*1 | **LUMO** |
| **A blue and red spheres with a black background  Description automatically generated** | A blue and red molecule  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 7 *b*2 | 1 *a*2 | **HOMO** |
| **A model of a human body  Description automatically generated** | A blue and red spheres  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 11 *a*1 | 3 *b*1 | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red spheres with spheres on it  Description automatically generated with medium confidence |
| σ | π2 |
| **HOMO-4** | 10 *a*1 | 10 *a*1 | **HOMO-2** |
| **A stack of colorful objects  Description automatically generated** | A stack of colorful objects  Description automatically generated |
|  |  |
| **HOMO-5** | 2 *b*1 | 2 *b*1 | **HOMO-3** |
| **A blue and red object with a molecule  Description automatically generated** | A blue egg with a molecule design  Description automatically generated |
| π1 | π1 |

**Table S-II.B.4.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **34T** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+5** | 13 *a*1 | 2 *a*2 | **LUMO+7** |
| **A blue and red object with red dots  Description automatically generated** | A group of colorful spheres  Description automatically generated |
|  | π5\* |
| **LUMO+4** | 9 *b*2 | 13 *a*1 | **LUMO+6** |
| **A red and blue kidneys  Description automatically generated** | A red and blue object with holes  Description automatically generated |
|  |  |
| **LUMO+3** | 2 *a*2 | 9 *b*2 | **LUMO+5** |
| **A group of colorful spheres  Description automatically generated** | A blue and red paint  Description automatically generated with medium confidence |
| π5\* |  |
| **LUMO+2** | 12 *a*1 | 8 *b*2 | **LUMO+4** |
| **A blue and red model of human organs  Description automatically generated** | A red and blue lungs  Description automatically generated |
|  |  |
| **LUMO+1** | 8 *b*2 | 12 *a*1 | **LUMO+3** |
| **A red blue and yellow lungs  Description automatically generated** | A blue and red model of human organs  Description automatically generated |
|  |  |
| **LUMO** | 4 *b*1 | 7 *b*2 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue red and yellow colored structure  Description automatically generated with medium confidence |
| π4\* | σ\* |
| **HOMO** | 1 *a*2 | 4 *b*1 | **LUMO+1** |
| **A blue and red spheres with molecules  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π3 | π4\* |
| **HOMO-1** | 3 *b*1 | 11 *a*1 | **LUMO** |
| **A blue and red spheres with white spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 7 *b*2 | 1 *a*2 | **HOMO** |
| **A blue red and yellow balloons  Description automatically generated** | A blue and red spheres  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 11 *a*1 | 3 *b*1 | **HOMO-1** |
| **A red and blue spheres  Description automatically generated** | A blue and red spheres with silver balls  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 2 *b*1 | 10 *a*1 | **HOMO-2** |
| **A red and blue circle with a black background  Description automatically generated** | A blue and red molecule  Description automatically generated |
| π1 |  |
| **HOMO-5** | 10 *a*1 | 2 *b*1 | **HOMO-3** |
| **A blue and red logo  Description automatically generated** | A colorful circle with a molecule  Description automatically generated with medium confidence |
|  | π1 |

**C. Diradical Isomers of Pyrrole.**

**Table S-II.C.1.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **23P** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 18 *a*' | 5 *a*" | **LUMO+6** |
| **A blue and red colored object  Description automatically generated with medium confidence** | A blue and red spheres  Description automatically generated |
|  | π5\* |
| **LUMO+3** | 5 *a*" | 18 *a*' | **LUMO+5** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π5\* |  |
| **LUMO+2** | 17 *a*' | 17 *a*' | **LUMO+4** |
| **A red and blue object  Description automatically generated** | A blue and red human organs  Description automatically generated |
|  |  |
| **LUMO+1** | 16 *a*' | 16 *a*' | **LUMO+3** |
| **A blue and red object  Description automatically generated** | A blue and red object with a black background  Description automatically generated |
|  |  |
| **LUMO** | 4 *a*" | 4 *a*" | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π4\* | π4\* |
| **HOMO** | 3 *a*" | 15 *a*' | **LUMO+1** |
| **A blue and red spheres with a black background  Description automatically generated** | A blue and red object with red dots  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 2 *a*" | 14 *a*' | **LUMO** |
| **A blue and red spheres with a silver stick  Description automatically generated** | A red and blue molecule  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 15 *a*' | 3 *a*" | **HOMO** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres with a black background  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 14 *a*' | 2 *a*" | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red spheres with spheres on it  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 13 *a*' | 13 *a*' | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 1 *a*" | 1 *a*" | **HOMO-3** |
| **A red and blue sphere with a black background  Description automatically generated** | A red and blue sphere with a black background  Description automatically generated |
| π1 | π1 |

**Table S-II.C.2.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*A*’ reference determinant prepared for the S1 structure of **24P** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 5 *a*" | 5 *a*" | **LUMO+6** |
| **A group of colorful spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π5\* | π5\* |
| **LUMO+3** | 18 *a*' | 18 *a*' | **LUMO+5** |
| **A red and blue object with silver rods  Description automatically generated with medium confidence** | A red and blue colored structure  Description automatically generated with medium confidence |
|  |  |
| **LUMO+2** | 17 *a*' | 4 *a*" | **LUMO+4** |
| **A blue and red object  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  | π4\* |
| **LUMO+1** | 4 *a*" | 17 *a*' | **LUMO+3** |
| **A blue and red spheres  Description automatically generated** | A red and blue human organs  Description automatically generated |
| π4\* |  |
| **LUMO** | 16 *a*' | 16 *a*' | **LUMO+2** |
| **A red and blue object with blue spheres  Description automatically generated** | A red and blue object  Description automatically generated |
|  |  |
| **HOMO** | 3 *a*" | 15 *a*' | **LUMO+1** |
| **A blue and red spheres  Description automatically generated** | A red and blue object  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 15 *a*' | 14 *a*' | **LUMO** |
| **A red and blue spheres  Description automatically generated** | A blue and red molecule  Description automatically generated |
| σ\* | σ |
| **HOMO-2** | 2 *a*" | 3 *a*" | **HOMO** |
| **A blue and red spheres with dots  Description automatically generated with medium confidence** | A blue and red spheres  Description automatically generated |
| π2 | π3 |
| **HOMO-3** | 14 *a*' | 2 *a*" | **HOMO-1** |
| **A red and blue molecule  Description automatically generated** | A blue and red spheres with white balls  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 13 *a*' | 13 *a*' | **HOMO-2** |
| **A blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 1 *a*" | 1 *a*" | **HOMO-3** |
| **A red and blue circle with a molecule  Description automatically generated with medium confidence** | A blue and red object with a black background  Description automatically generated |
| π1 | π1 |

**Table S-II.C.3.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **25P** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 7 *b*2 | 7 *b*2 | **LUMO+6** |
| **A close-up of a human lungs  Description automatically generated** | A red and blue organs  Description automatically generated with medium confidence |
|  |  |
| **LUMO+3** | 2 *a*2 | 2 *a*2 | **LUMO+5** |
| **A group of blue and red spheres  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π5\* | π5\* |
| **LUMO+2** | 11 *a*1 | 11 *a*1 | **LUMO+4** |
| **A blue and red model of a human body  Description automatically generated** | A red and blue object  Description automatically generated |
|  |  |
| **LUMO+1** | 10 *a*1 | 3 *b*1 | **LUMO+3** |
| **A model of human body  Description automatically generated** | A blue and red spheres  Description automatically generated |
|  | π4\* |
| **LUMO** | 3 *b*1 | 10 *a*1 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A blue and red object with a black background  Description automatically generated |
| π4\* |  |
| **HOMO** | 1 *a*2 | 6 *b*2 | **LUMO+1** |
| **A blue and red spheres  Description automatically generated** | A red and blue lungs  Description automatically generated |
| π3 | σ\* |
| **HOMO-1** | 2 *b*1 | 9 *a*1 | **LUMO** |
| **A blue and red spheres with spheres on it  Description automatically generated with medium confidence** | A blue and red spheres  Description automatically generated |
| π2 | σ |
| **HOMO-2** | 6 *b*2 | 1 *a*2 | **HOMO** |
| **A red and blue model of human organs  Description automatically generated** | A blue and red spheres with spheres in the middle  Description automatically generated |
| σ\* | π3 |
| **HOMO-3** | 9 *a*1 | 2 *b*1 | **HOMO-1** |
| **A blue and red molecule  Description automatically generated** | A blue and red spheres  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 5 *b*2 | 5 *b*2 | **HOMO-2** |
| **A group of colorful balls  Description automatically generated with medium confidence** | A group of colorful spheres  Description automatically generated |
|  |  |
| **HOMO-5** | 1 *b*1 | 1 *b*1 | **HOMO-3** |
| **A blue and red sphere with a black background  Description automatically generated** | A close up of a molecule  Description automatically generated |
| π1 | π1 |

**Table S-II.C.4.** Relevant frontier molecular orbitals for the high-spin (*Ms* = +1) 1 3*B*2 reference determinant prepared for the S1 structure of **34P** at the UHF/cc-pVDZ level of theory, to be utilized by further EOM-SF-UCCSD/cc-pVDZ computations to construct the singlet g.s. wavefunction. Also provided are orbital symmetry labels, location relative to the HOMO and LUMO in both α and β orbital manifolds, and chemical designations (viz. radical σ/σ\*, π1-5) where appropriate.

|  |  |  |  |
| --- | --- | --- | --- |
| **α Frontier MOs** | | **β Frontier MOs** | |
| **LUMO+4** | 2 *a*2 | 2 *a*2 | **LUMO+6** |
| **A blue and red spheres  Description automatically generated** | A group of spheres with molecules  Description automatically generated |
| π5\* | π5\* |
| **LUMO+3** | 11 *a*1 | 7 *b*2 | **LUMO+5** |
| **A red and blue structure  Description automatically generated** | A red and blue kidneys  Description automatically generated |
|  |  |
| **LUMO+2** | 7 *b*2 | 11 *a*1 | **LUMO+4** |
| **A red and blue lungs  Description automatically generated** | A red and blue structure  Description automatically generated |
|  |  |
| **LUMO+1** | 10 *a*1 | 10 *a*1 | **LUMO+3** |
| **A blue and red object  Description automatically generated** | A red and blue structure  Description automatically generated |
|  |  |
| **LUMO** | 3 *b*1 | 6 *b*2 | **LUMO+2** |
| **A blue and red spheres  Description automatically generated** | A red and blue human organs  Description automatically generated |
| π4\* | σ\* |
| **HOMO** | 1 *a*2 | 3 *b*1 | **LUMO+1** |
| **A blue and red spheres with spheres connected together  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π3 | π4\* |
| **HOMO-1** | 6 *b*2 | 9 *a*1 | **LUMO** |
| **A blue and red spheres  Description automatically generated** | A blue and red object with spheres  Description automatically generated with medium confidence |
| σ\* | σ |
| **HOMO-2** | 2 *b*1 | 1 *a*2 | **HOMO** |
| **A blue and red spheres with spheres and spheres on a black background  Description automatically generated** | A blue and red spheres with spheres connected together  Description automatically generated |
| π2 | π3 |
| **HOMO-3** | 9 *a*1 | 2 *b*1 | **HOMO-1** |
| **A blue and red molecule  Description automatically generated** | A blue and red spheres with spheres and spheres on a black background  Description automatically generated |
| σ | π2 |
| **HOMO-4** | 1 *b*1 | 8 *a*1 | **HOMO-2** |
| **A blue and red circle with a molecule  Description automatically generated** | A blue and red spheres  Description automatically generated |
| π1 |  |
| **HOMO-5** | 5 *b*2 | 1 *b*1 | **HOMO-3** |
| **A red and blue molecule  Description automatically generated** | A blue and red circle with a molecule  Description automatically generated |
|  | π1 |

**S-III. Natural Orbital Analysis of EOM-SF-CC Wavefunctions.**

**A. Diradical Isomers of Furan.**

**Table S-III.A.1.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **23F** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.214 | A model of a molecule  Description automatically generated  0.186 | 0.400 |
| **σ** | A model of a molecule  Description automatically generated  0.805 | A model of a molecule  Description automatically generated  0.778 | 1.583 |

**Table S-III.A.2.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **24F** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A diagram of a molecule  Description automatically generated  0.159 | A model of a molecule  Description automatically generated  0.139 | 0.298 |
| **σ** | A molecule model with red and blue balls  Description automatically generated  0.853 | A molecule model with red and blue balls  Description automatically generated  0.830 | 1.683 |

**Table S-III.A.3.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **25F** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.294 | A model of a molecule  Description automatically generated  0.267 | 0.560 |
| **σ** | A model of a molecule  Description automatically generated  0.727 | A model of a molecule  Description automatically generated  0.691 | 1.419 |

**Table S-III.A.4.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **34F** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.148 | A model of a molecule  Description automatically generated  0.127 | 0.274 |
| **σ** | A model of a molecule  Description automatically generated  0.866 | A model of a molecule  Description automatically generated  0.846 | 1.711 |

**B. Diradical Isomers of Thiophene.**

**Table S-III.B.1.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **23T** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A molecule model of a molecule  Description automatically generated  0.059 | A model of a molecule  Description automatically generated  0.039 | 0.097 |
| **σ** | A model of a molecule  Description automatically generated  0.953 | A model of a molecule  Description automatically generated  0.935 | 1.888 |

**Table S-III.B.2.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **24T** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.202 | A model of a molecule  Description automatically generated  0.180 | 0.383 |
| **σ** | A molecule model of a molecule  Description automatically generated  0.811 | A molecule model of a molecule  Description automatically generated  0.781 | 1.592 |

**Table S-III.B.3.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **25T** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.163 | A model of a molecule  Description automatically generated  0.141 | 0.304 |
| **σ** | A model of a molecule  Description automatically generated  0.852 | A model of a molecule  Description automatically generated  0.825 | 1.676 |

**Table S-III.B.4.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **34T** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.131 | A model of a molecule  Description automatically generated  0.108 | 0.239 |
| **σ** | A model of a molecule  Description automatically generated  0.883 | A model of a molecule  Description automatically generated  0.859 | 1.742 |

**C. Diradical Isomers of Pyrrole.**

**Table S-III.C.1.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **23P** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A molecule model with a grid and a red and blue mesh  Description automatically generated with medium confidence  0.212 | A model of a molecule  Description automatically generated  0.185 | 0.397 |
| **σ** | A model of a molecule  Description automatically generated  0.805 | A model of a molecule  Description automatically generated  0.783 | 1.588 |

**Table S-III.C.2.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **24P** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.133 | A model of a molecule  Description automatically generated  0.115 | 0.248 |
| **σ** | A molecule model with red and blue balls  Description automatically generated  0.877 | A model of a molecule  Description automatically generated  0.856 | 1.734 |

**Table S-III.C.3.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **25P** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.261 | A model of a molecule  Description automatically generated  0.237 | 0.497 |
| **σ** | A model of a molecule  Description automatically generated  0.757 | A model of a molecule  Description automatically generated  0.726 | 1.483 |

**Table S-III.C.4.** Radical σ and σ\* natural orbitals and their occupation numbers in α and β manifolds [*nϕ*(α) and *nϕ*(β) for the generic orbital label *ϕ*, respectively], computed for the g.s. wavefunction of **34P** at the EOM-SF-UCCSD/cc-pVDZ level of theory with its S1 structure. Also provided for convenience are effective total occupations *nϕ* = *nϕ*(α) + *nϕ*(β).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital** | **α** | **β** | ***nϕ*** |
| **σ\*** | A model of a molecule  Description automatically generated  0.136 | A model of a molecule  Description automatically generated  0.116 | 0.252 |
| **σ** | A model of a molecule  Description automatically generated  0.876 | A model of a molecule  Description automatically generated  0.859 | 1.735 |