# Supplementary data

## Electron transfer within a reaction path model calibrated by constrained DFT calculations : Application to mixed-valence organic compounds.

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### 1. Geometries

The root mean square of the distances (RMSD) is calculated with all bonds denoted on Fig. 1 (for which experimental data are available) for both donor and acceptor cycles. Geometries of each $DMP_n$ are provided in separate *.xyz files.

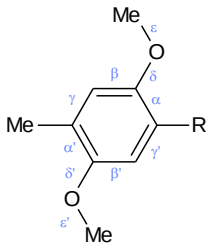


**Fig. 1** Numbering of the bond lengths

### 2. Influence of exchange-correlation functional

On the following table, we summarize the RMSD of the equilibrium geometries obtained by different exchange-correlation functionals as indicated.

**Table 1**. Choice of exchange-correlation functional - RMSD (Root mean square of bond distances) in DMP cycles between experimental and cDFT or DFT results for DMP_n (n = 0,1,2)

| RMSD | cDFT OPTX-PBE | cDFT PBE98-LYP | DFT OPTX-PBE | DFT B3LYP | DFT M06HF | DFT ωB97XD |
|---|---|---|---|---|---|---|
| $DMP_0$ | 0.022 | 0.027 | 0.013 | 0.010 | 0.027 | 0.015 |
| $DMP_1$ | 0.011 | 0.022 | 0.012 | 0.011 | 0.016 | 0.014 |
| $DMP_2$ | 0.009 | 0.019 | 0.019 | 0.018 | 0.013 | 0.013 |

### 3. Effect of including diffuse functions

Several calculations have been performed to assess the influence of including diffuse functions. This can been seen on Tab. 2. We found a negligible effect.

**Table 2**. Influence of diffuse functions - RMSD (Root mean square of bond distances) in DMP cycles between 6-311g** basis set and 6-311++g** DFT results for DMP_n (n = 0,1,2) (XC functional : ωB97XD)

| RMSD | 6-311g** vs 6-311++g** |
|---|---|
| $DMP_0$ | 0.0005 |
| $DMP_1$ | 0.003 |
| $DMP_2$ | 0.001 |

**4. Effect of dispersion correction**

In the case of cDFT calculations, we present here the effect of dispersion correction for a selected exchange-correlation functional (PBE98-LYP). As above, we found a negligible contribution.

**Table 3**. Influence of dispersion corrections - RMSD (Root mean square of bond distances) in DMP cycles between cDFT calculations with or without dispersion corrections for DMP_n (n = 0,1,2) (XC functional : PBE98-LYP)

| RMSD | Dispersion correction |
|---|---|
| $DMP_0$ | 0.0007 |
| $DMP_1$ | 0.0007 |
| $DMP_2$ | 0.0009 |