

SUPPORTING INFORMATION

Intermolecular Interactions in Eumelanins: a Computational
Bottom-Up Approach. I. Small Building Blocks.

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February 16, 2015

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1. Computational Details on CCSD(T)@cbs calculations

The reference data for dimer interaction energies (ΔE^{inter}) are obtained using the gold standard¹ of quantum chemistry, *i.e.* the coupled cluster level of theory, considering single, double and (perturbatively) triple excitations, estimated at the complete basis set limit (CCSD(T)@cbs). Within this framework, based on the empirical observation that the molecular properties obtained by CCSD(T) and Möller-Plesset second order perturbation theory (MP2) methods exhibit approximately the same basis set dependence, the CCSD(T)@cbs value can be obtained from the MP2@cbs limit (ΔE_{CBS}^{MP2}), corrected with the difference $\Delta^{CCSD(T)-MP2}$ between the MP2 and CCSD(T) interaction energy, computed with a reliable, medium-size basis set:

$$\Delta^{CCSD(T)-MP2} = \left[\Delta E^{CCSD(T)} - \Delta E^{MP2} \right]_{medium-size\ basis\ set}$$

In other words, the CCSD(T) complete basis set limit is obtained as

$$\Delta E_{CBS}^{CCSD(T)} = \Delta E_{CBS}^{MP2} + \Delta^{CCSD(T)-MP2}$$

Although this procedure has been extensively used by several groups (see references [2-6], just to cite a few) the best route to correctly estimate both ΔE_{CBS}^{MP2} and $\Delta^{CCSD(T)-MP2}$ values has not yet been uniquely assessed. Considering the similarity of the moieties investigated in this work with the quinhydrone complex, whose interaction energy was recently⁷ studied by us also with the CCSD(T)@cbs technique, herein this the same route has been followed: the $\Delta^{CCSD(T)-MP2}$ correction term is computed estimating the CCSD(T)-MP2 difference at the aug-cc-pvDZ level, whereas the MP2@cbs is estimated through the procedure proposed by Halkier *et al.*⁸ Similarly to quinhydrone, the latter extrapolation was performed using the augmented Dunning's correlation consistent basis sets, aug-cc-pvDZ and aug-cc-pvTz basis sets for *o*-quinones and pyrrole dimers, whereas the c-pvDZ and cc-pvTz were employed in the MP2 calculations of the larger DHI related pairs, for computational feasibility. The basis set superposition error was handled in all CCSD(T), MP2 and MP2mod calculations by means of the Counterpoise (CP) correction.⁹

2. MP2mod validation on *o*-benzoquinone/*o*-hydroquinone hetero-dimers

The polarization exponents of aromatic Carbon ($\alpha_C=0.25$) and Oxygen ($\alpha_O=0.44$) atoms, previously⁷ tuned for the quinhydrone complex, were transferred on the atoms of *o*-benzoquinone/*o*-hydroquinone pairs, and the resulting modified 6-31G*(0.25,0.44) basis set was used with the MP2 method to compute ΔE^{inter} curves for the three arrangements shown in Figure A.

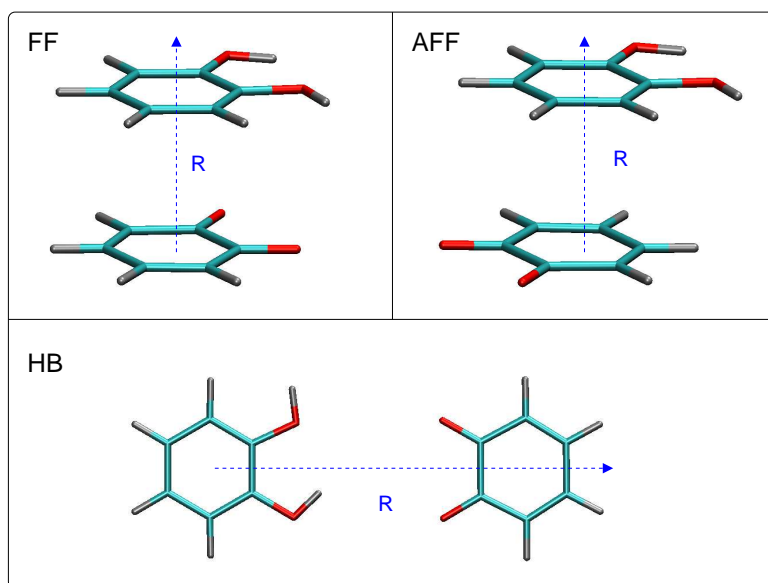


Figure A: Selected arrangements for *o*-benzoquinone/*o*-hydroquinone hetero-dimers: face-to-face (FF), antiparallel face-to-face (AFF) and hydrogen bonded (HB). The translation vector \mathbf{R} is displayed with a blue dashed arrow.

The resulting MP2mod interaction energy curves are reported in Figure B with their Hartree-Fock (HF) contributions. From the difference between the total MP2mod interaction energy and the HF term, it is evident that the role of electron correlation and, hence, of dispersion forces is determinant to the relative stability of the considered pairs, and should for this reason be accurately estimated. To assess this accuracy, an MP2 full geometry optimization was performed on the considered dimers, starting from the three minima found for FF, AFF and HB arrangements. The interaction energy of the three final structures was eventually computed at both MP2mod and CCSD(T)@cbs level, and the results compared and commented in the main text.

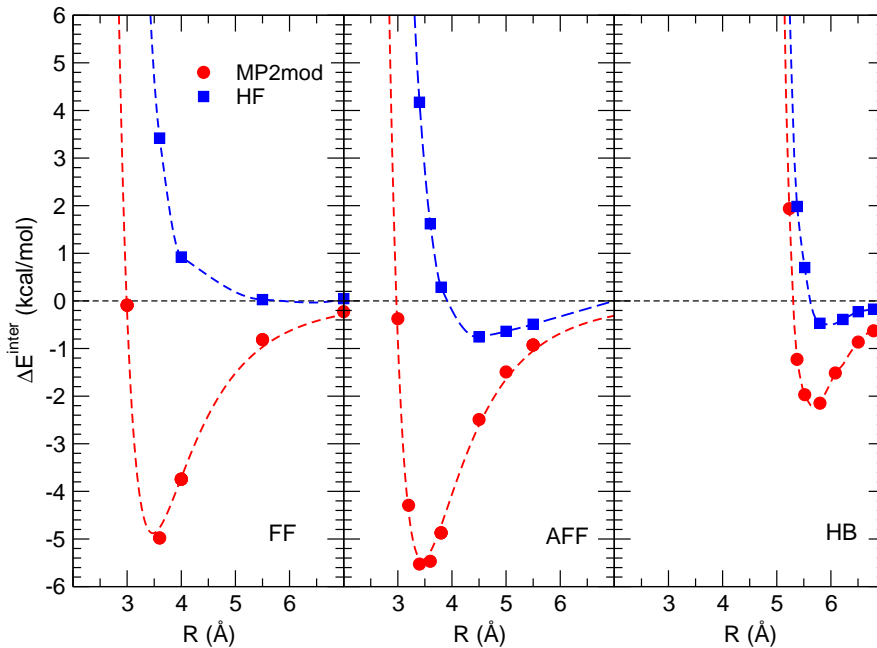


Figure B: MP2mod (red circles) and HF (blue squares) interaction energies (ΔE^{inter}) computed for *o*-benzoquinone/*o*-hydroquinone pair as a function of the translation vector \mathbf{R} , in the arrangements displayed in Fig. A.

2. MP2mod tuning on pyrrole

To tune the α_N polarization exponent of the 6-31G*(0.25, α_N) modified basis set, to be used in the MP2mod calculations on pyrrole dimers, the protocol previously employed in Ref. [7] was again adopted, *i.e.*

- i) the geometry of a pyrrole monomer is optimized at the B3LYP/aug-cc-pvDZ level
- ii) Four different arrangements for a pyrrole dimer are built by assembling the previously optimized units, varying their intermolecular distance and the relative orientation. Examples of each class are reported in Figure C. Specifically, pyrrole pairs were prepared in face-to-face (FF), antiparallel displaced (APD), T-shaped (TS) and displaced T-shaped (DTS) configurations.
- iii) For each class, different geometries were obtained by shifting stepwise one monomer along one direction (\mathbf{R} , see Figure C), in the 2.8 Å- 7.0 Å range. The interaction energy ΔE^{inter} for all the resulting conformations was initially computed at MP2/6-

31G*(0.25, 0.25), 0.25 being the value of the polarization exponent for Carbon atoms indicated originally by Hobza and coworkers¹⁰ (α_N is also initially set at 0.25). It may be worth mentioning that no geometry optimization of the whole complex was yet performed at this point.

- iv) CCSD(T)@cbs calculations were performed for 12 pyrrole pairs, three for each class. Conformations were chosen in the low repulsive region, in the minimum and at medium range attractive distance, with respect to the MP2/6-31G*(0.25,0.25) curves. From visual inspection of the resulting curves three geometries (at low repulsive, minimum and slightly attractive energies) were selected for each arrangement, and used to compute ΔE^{inter} at CCSD(T)@cbs level.
- v) The polarization exponent for the Nitrogen atom was then tuned through the EXOPT program, to minimize the energy difference between CCSD(T)@cbs values and those obtained at MP2 level with the tuned basis set.

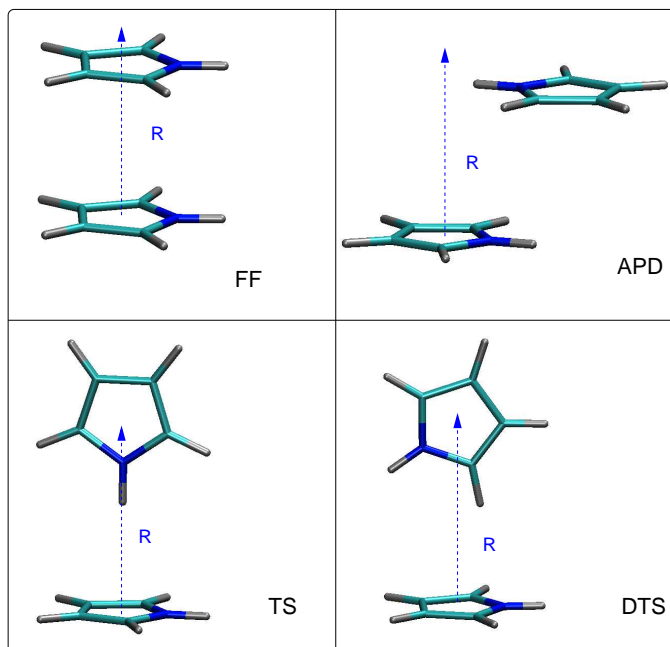


Figure C: Selected arrangements for pyrrole dimer: face-to-face (FF) antiparallel displaced (APD), T-shaped (TS) and displaced T-shaped (DTS). The translation vector \mathbf{R} is displayed with a blue dashed arrow.

The best exponent for Nitrogen atoms α_N resulted to be 0.37. It may be worth noticing that, as previously found for Carbon (0.25) and Oxygen (0.44) atoms, the optimized polarization exponent for Nitrogen is about half of its value (0.80 for all C, O and N atoms) in the standard 6-31G* basis set.

Dimer	R (Å)	$\Delta E_{CCSD(T)@cbs}^{inter}$ (kcal/mol)	$\Delta E_{MP2mod}^{inter}$ (kcal/mol)
FF	3.9	-0.20	0.44
FF	4.5	0.00	0.26
FF	6.0	0.25	0.32
APD	2.5	-1.64	-0.77
APD	3.0	-4.89	-4.47
APD	5.0	-1.03	-1.09
TS	3.8	4.41	6.54
TS	4.5	-5.21	-5.17
TS	6.0	-1.59	-1.66
DTS	4.2	-1.14	-0.16
DTS	4.7	-3.46	-3.10
DTS	6.0	-1.24	-1.20

Table 1: Interaction (ΔE^{inter}) computed with CCSD(T)@cbs and fitted MP2mod energies for the considered pyrrole dimer geometries.

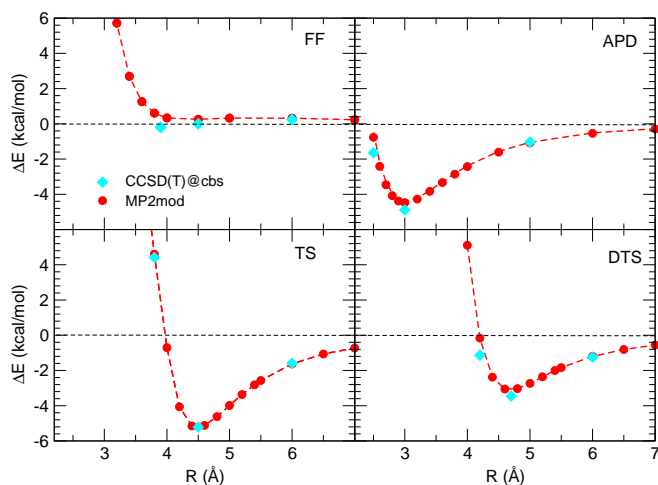


Figure D: MP2mod (red circles) and reference CCSD(T)@cbs (cyan diamonds) interaction energies (ΔE^{inter}) computed for the pyrrole dimer as a function of the translation vector R, in the arrangements displayed in Fig. C.

All the interaction curves were re-computed with at MP2mod level with the optimized 6-31G*(0.25,0.37) basis set and are displayed in Figure D with the CCSD(T) reference values. The latter are also reported in Table 1 and compared with the MP2mod value obtained for the same geometry.

Absorption spectra

Despite in a previous work performed on quinhydrone, the M06-2X functional was employed for the calculation of the absorption spectrum, in this work the popular B3LYP was preferred, based on the empirical observation of its better performances in reproducing the experimental absorption of the DHI monomer, as shown in Figure D.

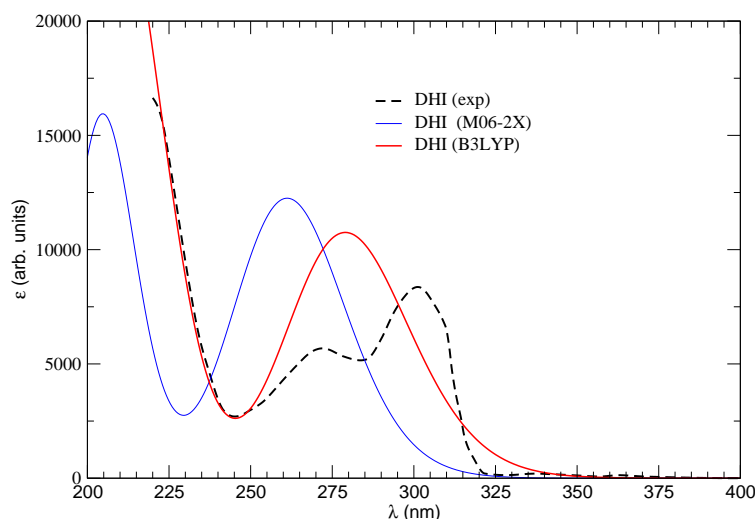


Figure E: Experimental¹¹ (dashed black lines) and TD-DFT computed (blue and red lined for M06-2X and B3LYP, respectively) absorption spectra for the DHI monomer. interaction energies (DE^{inter}) computed for the pyrrole dimer as a function of the translation vector R , in the arrangements displayed in Fig. C.

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