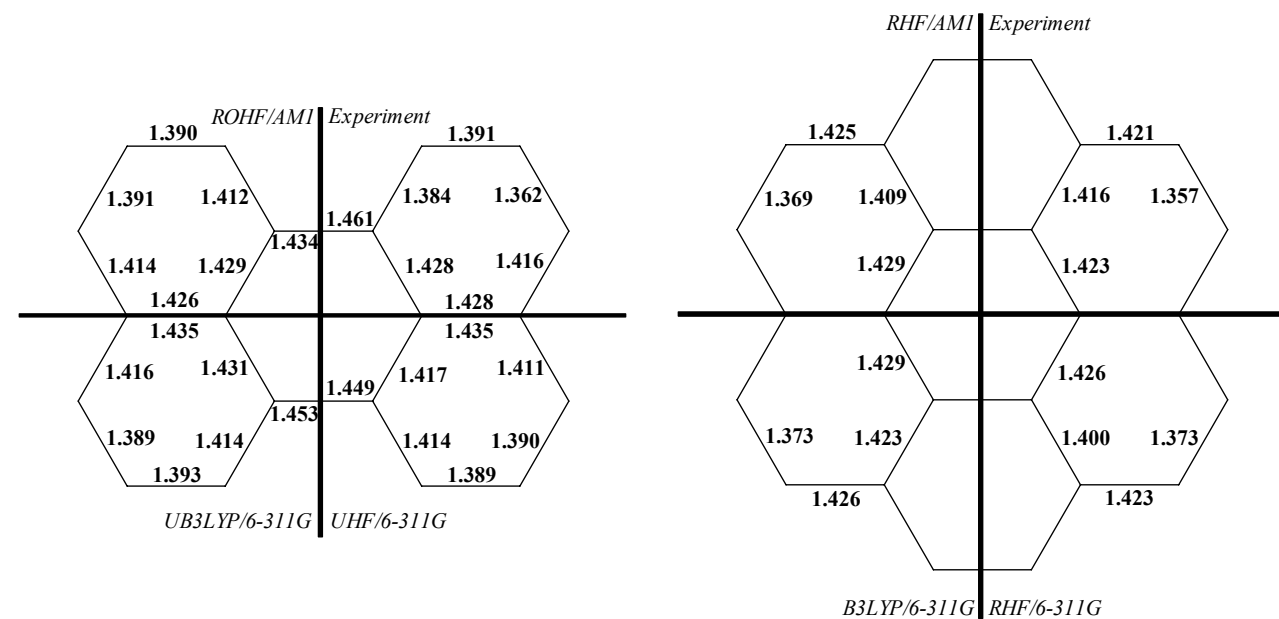
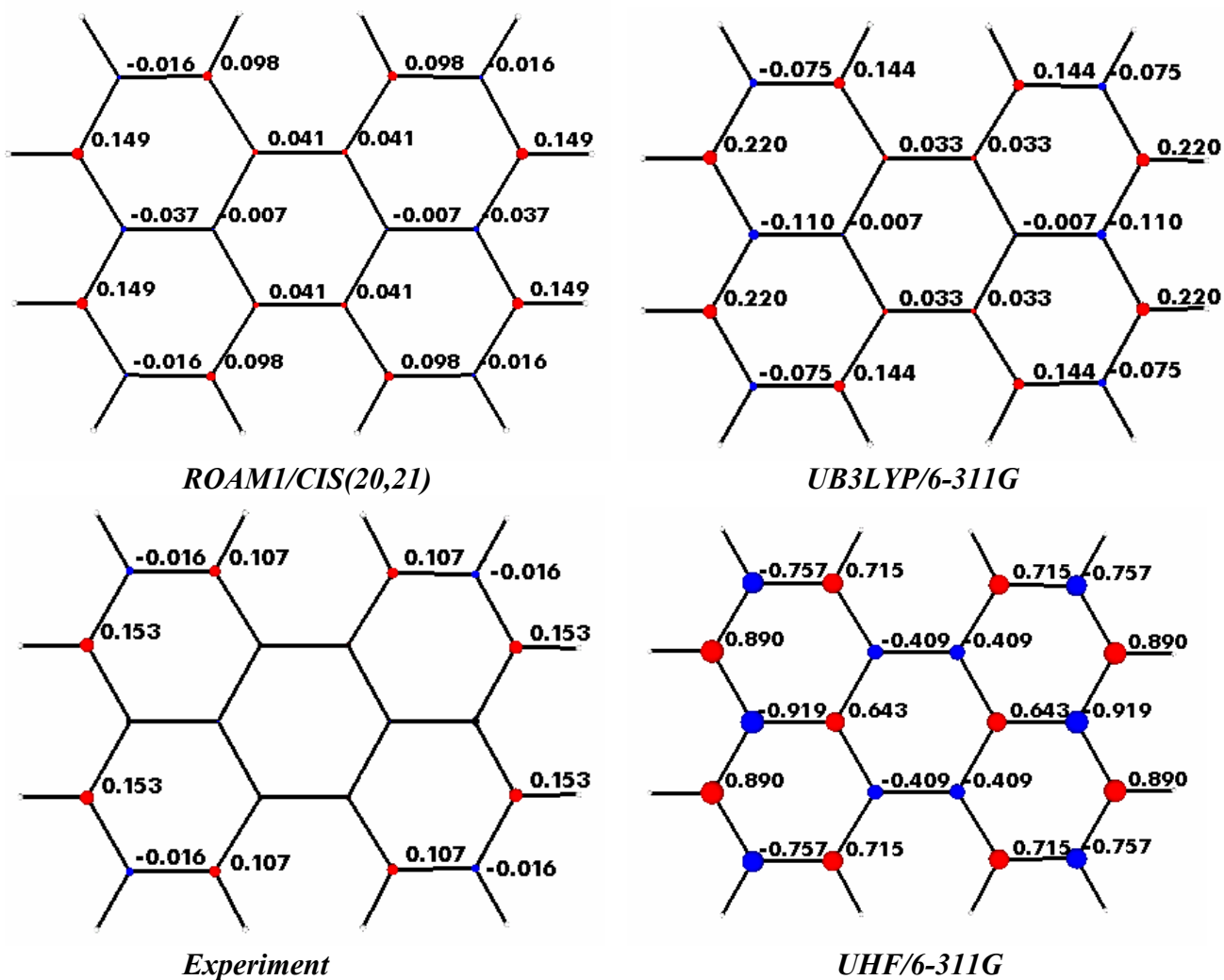


Electronic Supplementary Information



A



B

Fig. S1: Optimised geometry (A) of neutral coronene and perylene cation-radical and calculated spin densities (B) of the radical. Comparison of different levels of theory

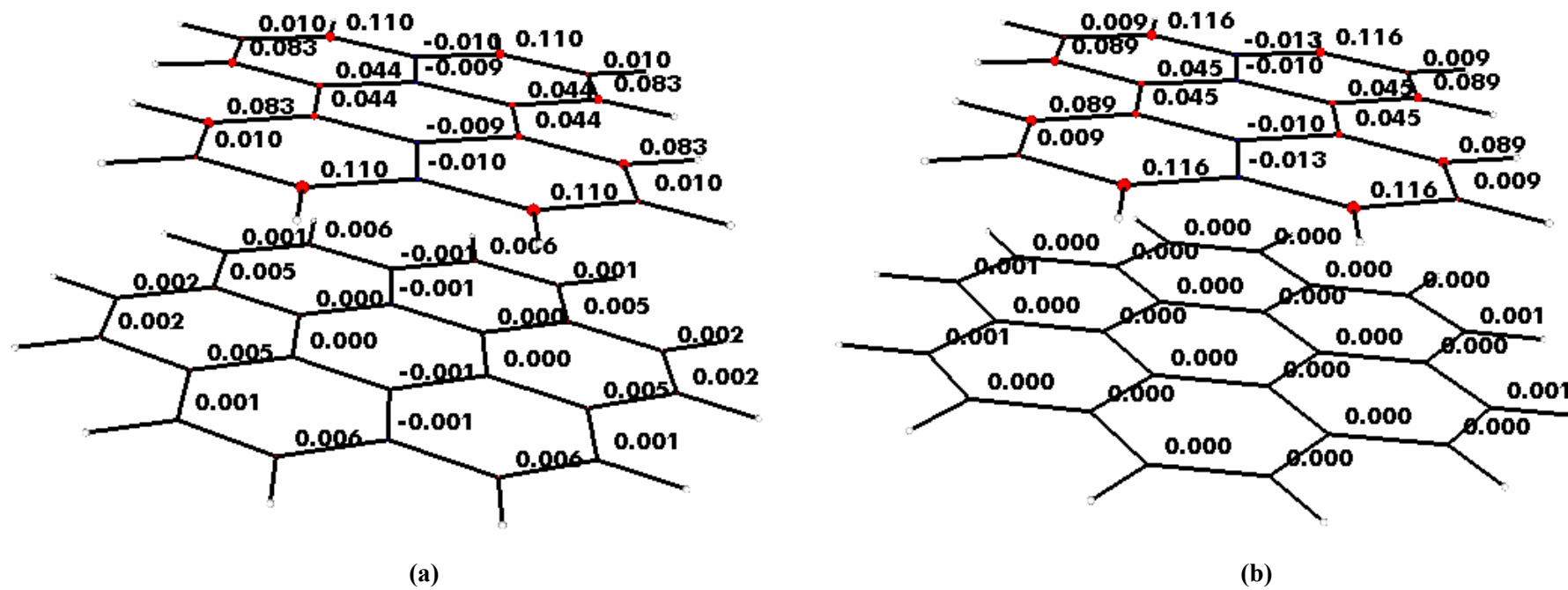


Fig. S2: ROAM1/CIS(19,19) calculated spin densities of coronene/perylene⁺ dimers - (a) strict on-top stacking; (b) 90° rotated coronene

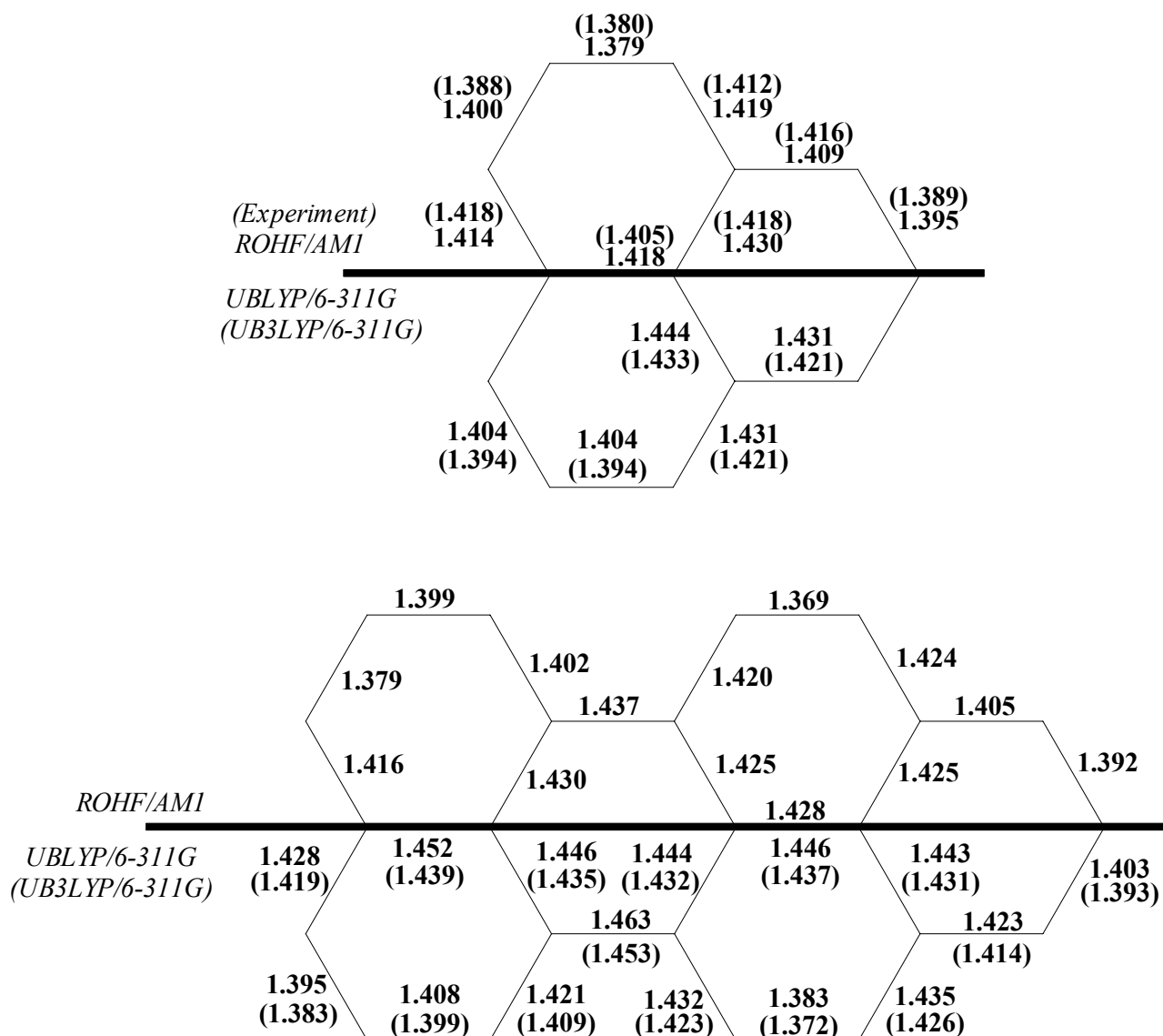


Fig. S3: Optimised bond lengths of **2** and **3**. The experimental values (averaged from the X-ray structure) for the tri-*tert*-butyl derivative of **2** are shown for comparison [27]. The symmetry breaking in the experimental bond lengths is probably due to the antisymmetric dimeric crystallisation pattern [27].

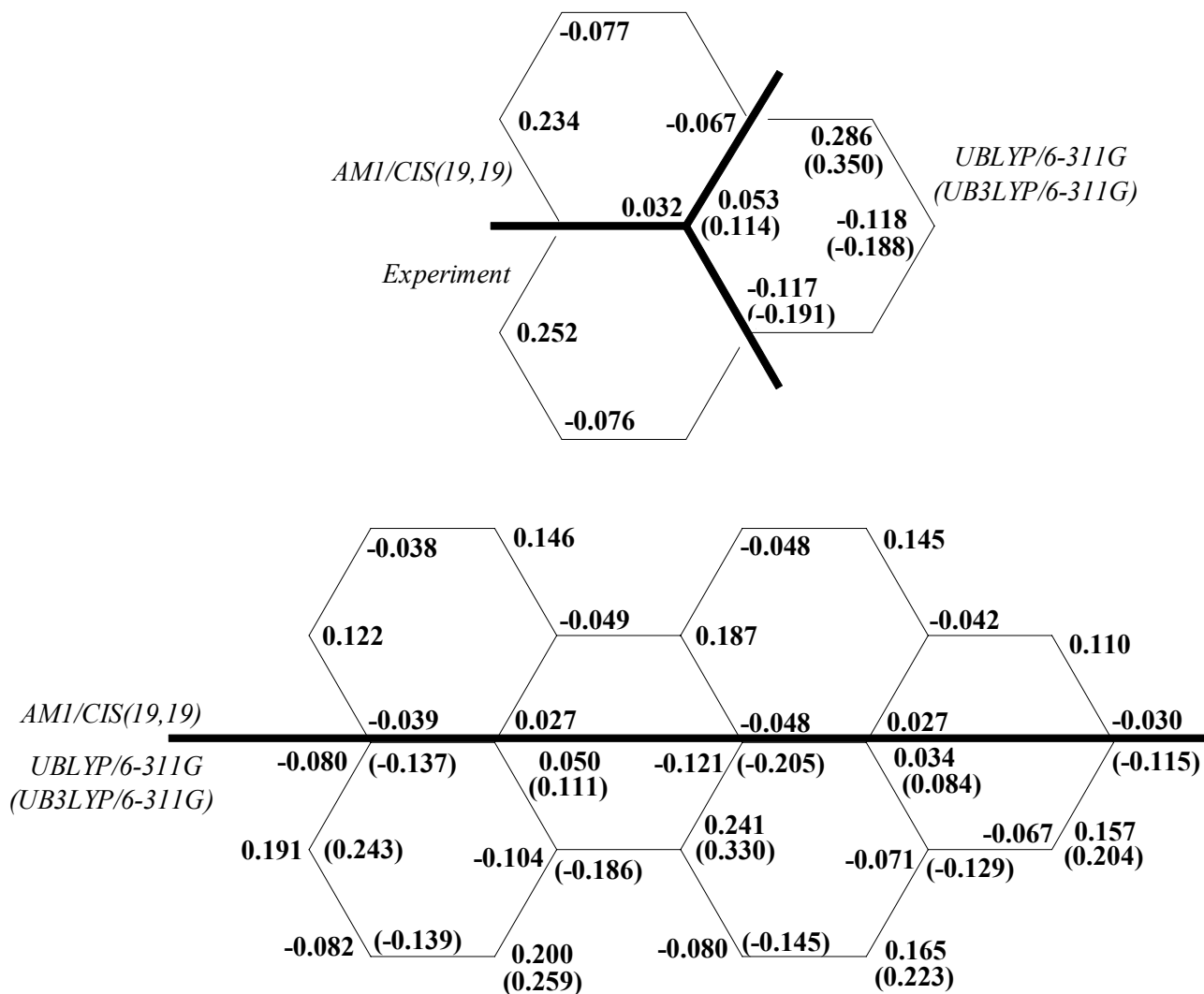


Fig. S4: Calculated AM1/CIS (19,19), UBLYP and UB3LYP spin densities of **2** and **3**. The experimental values for **2** calculated from the hyperfine coupling constants [26] according to the McConnell equation: $a_H = -Q \cdot \rho$, with $Q = 70 \text{ MHz}^{-1}$ are shown for comparison

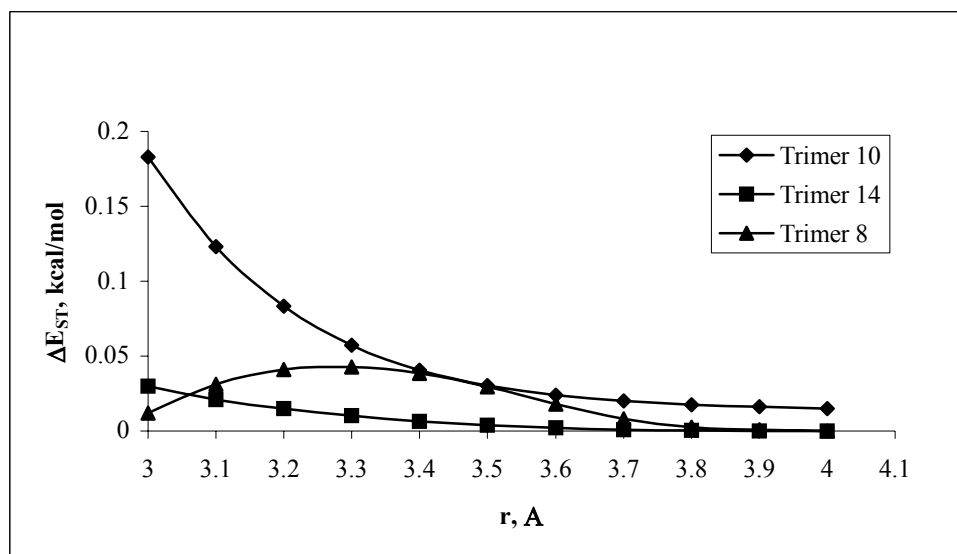


Fig. S5: ΔE_{ST} of **8** (90° -rotated), **10** and **14** as a function of the interplanar distance. The values were calculated with ROAM1 / CAS (8,10)