

SUPPORTING INFORMATION PARAGRAPH

The density matrices obtained from the CASSI procedure were used to calculate the electronic components of the electrostatic potentials that describe the electronic transitions (and the permanent states) on each of the aromatic chromophores using a modified version of the PROPERTY program in the MOLPRO 2002 suite of software [1]. Upon addition of the appropriate nuclear component (the transition nuclear components are scaled by the overlap of the two states involved), the total electrostatic potential is obtained. The potential was evaluated at intervals of 1 bohr (1 bohr = 0.529 Å) on cubic grids of dimension ± 8 , ± 9 and ± 10 bohr for benzene, phenol and indole, respectively. Grid points within the van der Waals radii of an atom were excluded from the calculations. These points were removed to prevent biasing towards the nuclear potential and, additionally, because of their relative unimportance: atoms in proteins do not become this close. Van der Waals radii of 3.21, 2.93 and 2.27 bohr were used for carbon, nitrogen and hydrogen, respectively [2]. A value of 2.65 bohr was assumed for oxygen following the suggestion of Tuñón et al. [3].

The ab initio dipole moments were obtained after the input wave functions were transformed to a non-interacting and orthonormal basis (in the CASSI procedure), whereas the charges were derived, for technical reasons, using density matrices from non-orthogonalised wave functions. Therefore, there are differences between the ab initio electric dipole moments and those described by the fitted charges. This difference is manifested in the direction of the dipole moments. To rectify this, the electrostatic potentials evaluated for each system were rotated in the symmetry plane to match the orientation of the ab initio dipole moments [4].

References

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