*ACS Omega* Supporting Information

# The relative position and relative rotation in supramolecular systems through the analysis of the principal axes of inertia: ferrocene/cucurbit[7]uril and ferrocenyl azide/β-Cyclodextrin case studies

Cleber P. A. Anconi*

*Laboratório de Química Fundamental (LQF). Departamento de Química. Universidade Federal de Lavras, 37200-900, Brazil*

*E-mail: cleberanconi@ufla.br

**Tables of contents:**

**Figure S1**. QTAIM molecular graph at B3LYP/6-31G(d) level of theory for the 7' $FcN_3$ @βCD compound. Lines represent different stabilizing interactions. Points represent (3,-1) critical points.

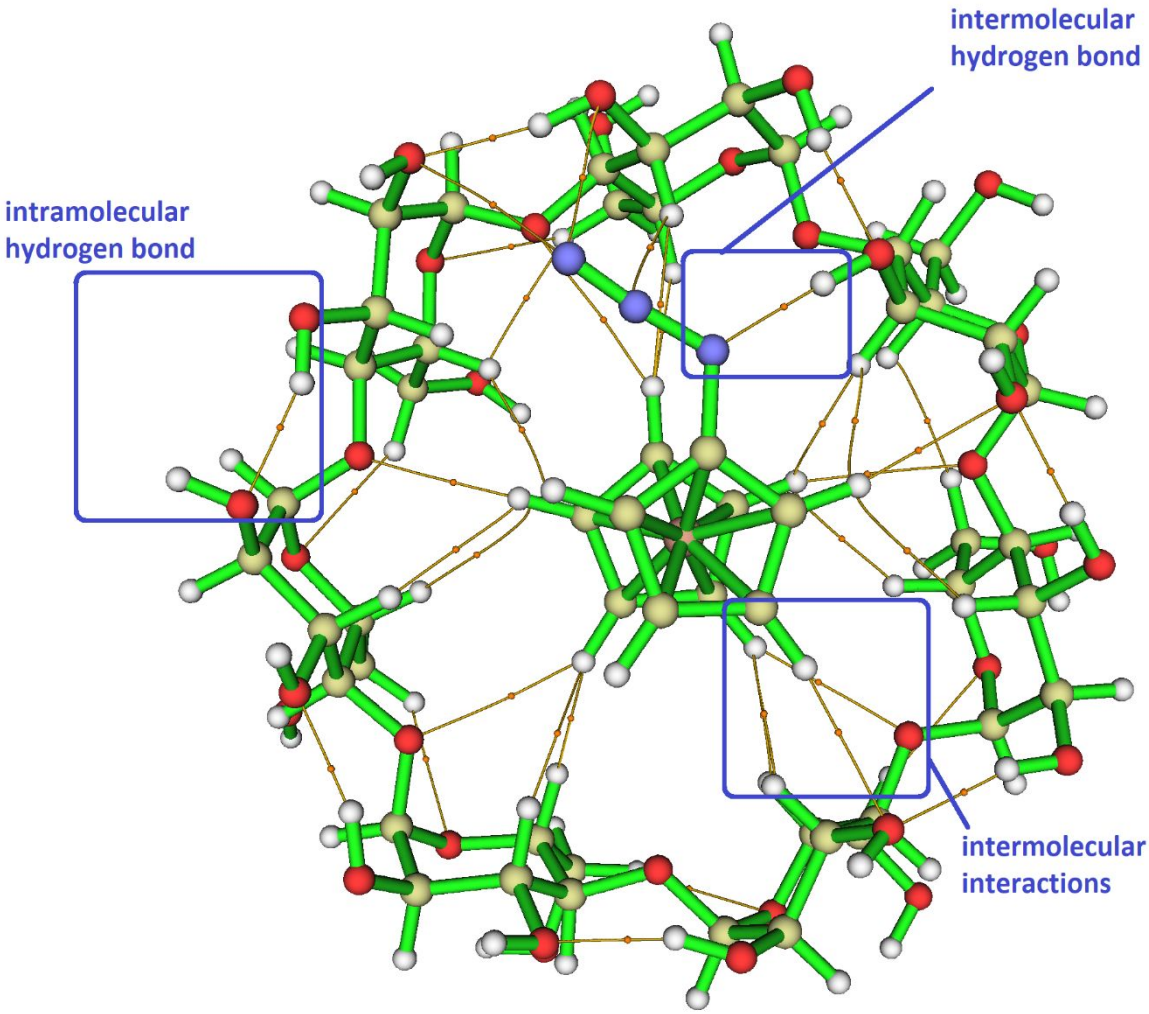

**Figure S2**. QTAIM molecular graph at B3LYP/6-31G(d) level of theory for 2' Fc@CB[7]. Lines represent different stabilizing interactions. Points represent (3,-1) critical points.

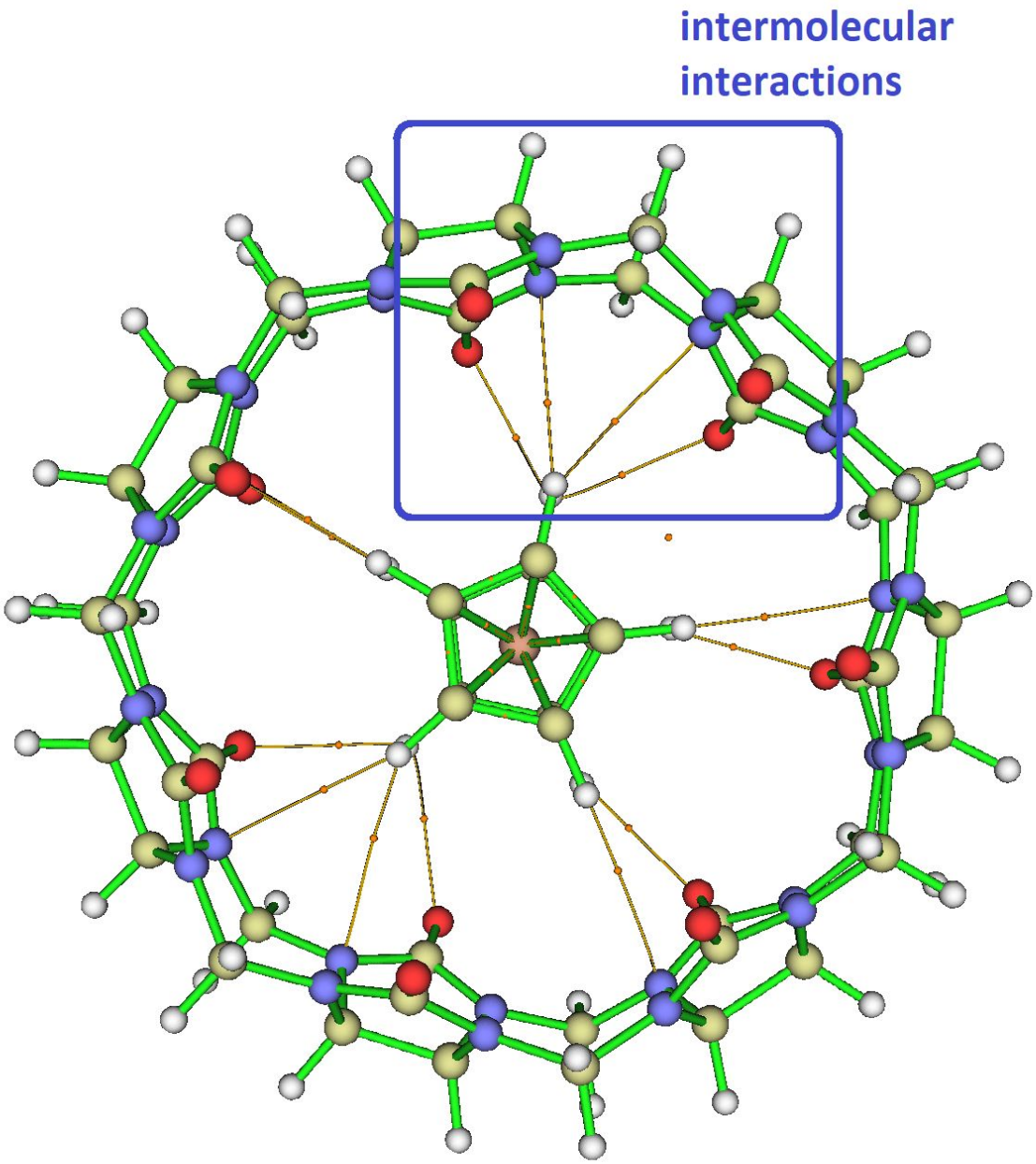

**Table S1**. Topological parameters for 7' $FcN_3$@βCD calculated by the quantum theory of atoms in molecules (QTAIM). All values are in atomic units.

| Description | CP | $\rho(r)$ | $\nabla^2\rho(r)$ | $H(r)$ |
|---|---|---|---|---|
| Intermolecular HB | N2...H68-O67 (CP362) | 0.02768 | 0.08016 | -0.00520 |
| βCD intramolecular HB | O41...H52-O51 (CP193) | 0.02648 | 0.07860 | -0.00155 |
| βCD intramolecular HB | O43...H36-O35 (CP218) | 0.02802 | 0.08528 | -0.00133 |
| βCD intramolecular HB | O37...H25-O24 (CP318) | 0.02854 | 0.08532 | -0.00151 |
| βCD intramolecular HB | O26...H74-O73 (CP430) | 0.02351 | 0.07457 | -0.00079 |
| βCD intramolecular HB | O65...H76-O75 (CP449) | 0.02740 | 0.08816 | -0.00084 |
| βCD intramolecular HB | O49...H60-O59 (CP250) | 0.02440 | 0.07324 | -0.00124 |
| βCD intramolecular HB | O67...H58-O57 (CP379) | 0.02753 | 0.07844 | -0.00185 |
| Intermolecular H...H | H92...H21 (CP347) | 0.00374 | 0.01189 | +0.00083 |
| Intermolecular H...H | H88...H21 (CP352) | 0.00409 | 0.01479 | +0.00099 |
| Intermolecular $R_2O$...H | $R_2O$28...H21 (CP368) | 0.00498 | 0.01915 | +0.00095 |
| Covalent (βCD) | C149-C147 (CP422) | 0.25911 | -0,62894 | -0.21378 |
| Covalent (βCD) | C147-O65 (CP436) | 0.25274 | -0.45332 | -0.35555 |
| Covalent (βCD) | O65-H66 (CP439) | 0.34060 | -1.79181 | -0.50836 |
| Covalent ($FcN_3$) | H19-C18 (CP284) | 0.27789 | -0.97895 | -0.27928 |
| Covalent ($FcN_3$) | C5-C6 (CP329) | 0.28921 | -0.69917 | -0.27249 |
| Covalent ($FcN_3$) | C5-N2 (CP342) | 0.27477 | -0.78859 | -0.37556 |
| Covalent ($FcN_3$) | N2-N3 (CP331) | 0.43444 | -0.89231 | -0.56531 |
| Iron...Carbon ($FcN_3$) | C18-Fe1 (CP309) | 0.08679 | 0.27079 | -0.02700 |
| Iron...Carbon ($FcN_3$) | Fe1-C5 (CP334) | 0.08776 | 0.27317 | -0.02779 |

$\rho(r)$: electron density; $\nabla^2\rho(r)$: Laplacian; $H(r)$: Total electron density; HB: hydrogen bond

**Table S2**. Topological parameters for 2' FcN@CB[7] calculated by the quantum theory of atoms in molecules (QTAIM). All values are in atomic units.

| Description | CP | $\rho(r)$ | $\nabla^2\rho(r)$ | $H(r)$ |
|---|---|---|---|---|
| Intermolecular (included ring) | C93...H13 (CP255) | 0.00292 | 0.01131 | +0.00076 |
| Intermolecular (included ring) | N51...H15 (CP201) | 0.00387 | 0.01271 | +0.00062 |
| Intermolecular (included ring) | N54...H15 (CP198) | 0.00287 | 0.01021 | +0.00057 |
| Intermolecular (included ring) | N58...H17 (CP230) | 0.00390 | 0.01278 | +0.00063 |
| Intermolecular (included ring) | N63...H19 (CP322) | 0.00390 | 0.01277 | +0.00063 |
| Intermolecular (included ring) | N39...H21 (CP346) | 0.00288 | 0.01021 | +0.00057 |
| Intermolecular (included ring) | N42...H21 (CP335) | 0.00383 | 0.01260 | +0.00062 |
| Intermolecular (outside ring) | O29...H9 (CP221) | 0.00796 | 0.02939 | +0.00099 |
| Intermolecular (outside ring) | O31...H9 (CP218) | 0.00581 | 0.02306 | +0.00107 |
| Intermolecular (outside ring) | O27...H11 (CP277) | 0.00965 | 0.03355 | +0.00077 |
| Intermolecular (outside ring) | O23...H3 (CP354) | 0.00574 | 0.02283 | +0.00107 |
| Intermolecular (outside ring) | O25...H3 (CP341) | 0.00797 | 0.02941 | +0.00098 |
| Intermolecular (outside ring) | O35...H5 (CP330) | 0.00918 | 0.03246 | +0.00084 |
| Intermolecular (outside ring) | O33...H7 (CP253) | 0.00921 | 0.03253 | +0.00083 |

$\rho(r)$: electron density; $\nabla^2\rho(r)$: Laplacian; $H(r)$: Total electron density

**Figure S3**. NCI Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for 2' Fc@CB[7] (left) and 7' $FcN_3$@Bcd (right).

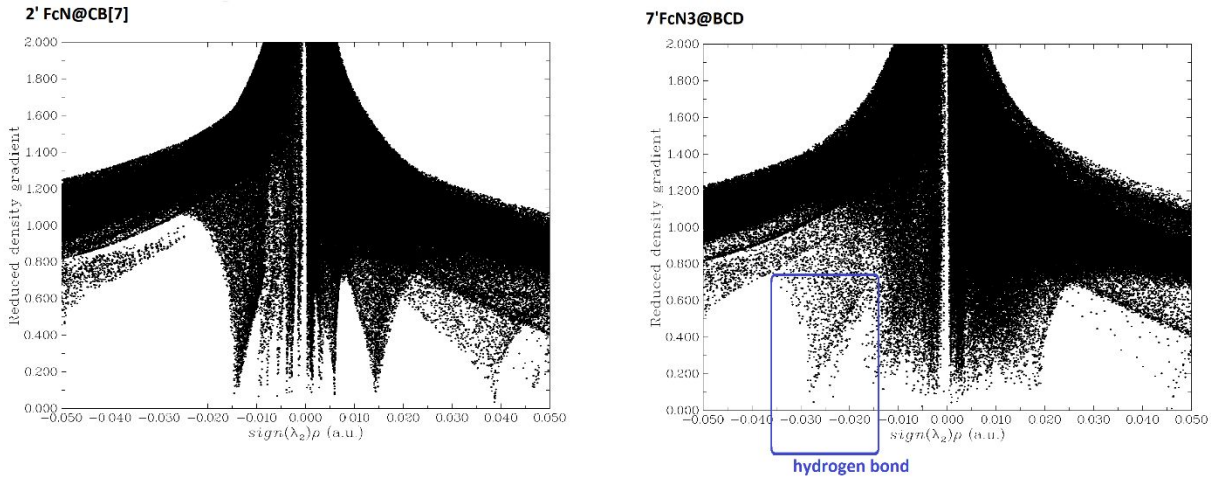

**Table S3**. Second-Order Perturbation Theory Analysis of Fock Matrix in NBO Basis. Electron-donor orbitals, electron-acceptor orbitals, corresponding energies, and distances.

| Donor | Acceptor | $E^{(2)}$ (kcal.mol$^{-1}$) [r in Å] |
|---|---|---|
| Intermolecular hydrogen bond | | |
| LP N2 (guest) | $\sigma^*$O67–H68 (βCD) | 14.27 [1.97] |
| Intramolecular βCD hydrogen bond | | |
| LP O41 | $\sigma^*$O51–H52 | 3.18 [1.97] |
| LP O43 | $\sigma^*$O35–H36 | 2.34 [1.92] |
| LP O37 | $\sigma^*$O24–H25 | 1.96 [1.92] |
| LP O26 | $\sigma^*$O73–H74 | 0.98 [1.99] |
| LP O65 | $\sigma^*$O75–H76 | 4.79 [1.92] |
| LP O49 | $\sigma^*$O59–H60 | 2.84 [1.98] |
| LP O67 | $\sigma^*$O57–H58 | 10.47 [1.96] |

**Table S4**. Bond Energy (BE) predicted by ρ(r) (QTAIM) at BCP for neutral complexes according to Tian Lu and collaborators* for 7' $FcN_3$@βCD. Level of theory: B3LYP/6-31G(d).

| Description | BCP | ρ(rBCP) | BE (kcal.mol$^{-1}$) [-223.08 x $\rho(r_{BCP})$/au +0.7423]* |
|---|---|---|---|
| Intermolecular HB | N2...H68-O67 (CP362) | 0.02768 | -5,43 |
| βCD intramolecular HB | O41...H52-O51 (CP193) | 0.02648 | -5.16 |
| βCD intramolecular HB | O43...H36-O35 (CP218) | 0.02802 | -5.51 |
| βCD intramolecular HB | O37...H25-O24 (CP318) | 0.02854 | -5.62 |
| βCD intramolecular HB | O26...H74-O73 (CP430) | 0.02351 | -4.50 |
| βCD intramolecular HB | O65...H76-O75 (CP449) | 0.02740 | -5.37 |
| βCD intramolecular HB | O49...H60-O59 (CP250) | 0.02440 | -4.70 |
| βCD intramolecular HB | O67...H58-O57 (CP379) | 0.02753 | -5.40 |

ρ(r): electron density; HB: hydrogen bond; *J. Comput. Chem., 40, 2868 (2019)

**Figure S4**. Superposition of the X-Ray Crystallographic geometries of the free CB[7] and the CB[7] hosts in the Fc@CB[7] experimental inclusion compounds.