

SUPPORTING INFORMATION FOR:

**Efficient structural and energetic screening of fullerene encapsulation in a large
supramolecular double decker macrocycle**

Fabian Bohle and Stefan Grimme*

GFN2-xTB:

Version 6.1 of GFN2-xTB¹ was used, as implemented in the *xtb* code. All GFN2-xTB calculations were carried out with the GBSA implicit solvation model and CHCl₃ as solvent. For all calculations (optimizations and hessian calculations) the ‘*very tight*’ settings were used (verytight: E_{conv}(energy convergence) = 1 · 10⁻⁷ E_h; G_{conv}(gradient convergence) = 2 · 10⁻⁴ E_h · α⁻¹; accuracy(for integral cutoffs and SCF criteria) = 0.05). Vibrational frequencies were calculated for thermostistical correction to free energy and to verify that the optimized geometries are indeed minimum structures on the electronic potential hypersurface (check for no imaginary modes). The thermostistical contributions to free energy are calculated in the rigid-rotor-harmonic-oscillator approach (RRHO)² and include zero point vibrational energies at 298.15 K. To reduce the error of the harmonic approximation for low-lying vibrational frequencies as well as numerical noise in the calculations, the RRHO-scheme (an interpolation between the rigid-rotor (RR)- to the harmonic oscillator (HO) is applied at low-lying frequencies (every vibrational mode below 50 cm⁻¹).

xTB-IFF:

The intermolecular forcefield xTB-IFF³ is implemented in a standalone code called *xtbiff* and is generated from ‘*low cost*’ quantum mechanical (QM) input data (atomic partial charges, localized molecular orbitals and frontier orbital energies and densities have to be provided), here generated by GFN2-xTB(GBSA(CHCl₃)). The QM data from each fragment is used to dock the intermolecular fragments and generate the best docking position. The docking itself is run in gas phase, but the provided QM input data is generated within the GBSA implicit solvation model. xTB-IFF returns the intermolecular interaction energy and several docking geometries sorted by their interaction energies. Since only rigid fragments are docked, the best xTB-IFF geometry has to be optimized once more by GFN2-xTB(GBSA).

B97-3c/COSMO reference calculations:

B97-3c/COSMO(ε=4.8)⁴ reference single-point calculations were performed with the TURBOMOLE.7.2.1 program package⁵. The resolution-of-identity (RI) approximation for Coulomb integrals was generally applied⁶ using the matching default auxiliary basis sets⁷. The integration of the exchange-correlation contribution was performed on the numerical quadrature grids *m4*. The default convergence criteria for single-points [10⁻⁷ E_h] was applied. To be able to compare to the GFN2-xTB(GBSA) calculations the implicit solvent model COSMO was applied.

Reaction path calculation:

The reaction path is calculated to get a good guess on the transition state structure. To start from reasonable geometries reactants and products are optimized with GFN2-xTB(GBSA(CHCl₃)). The reaction path is then calculated with the growing string method GSM⁸ using GFN2-

xTB(GBSA(CHCl₃)) as the underlying electronic structure method. The reaction path was calculated with 20 nodes on the reaction string. Geometries close to the estimated transition state were picked and Hessians were calculated to find the imaginary mode of the transition state. On the examined reaction path no transition state could be obtained (no single imaginary mode was obtainable).

TABLE I: Lowest lying fullerene isomers determined by GFN2-xTB(GBSA(CHCl₃) free energy:

Fullerene isomer name within the manuscript:	Fullerene name from Tomanek's ⁹ ESI:
C ₆₀	C ₆₀
C ₇₀	C ₇₀
C ₇₂	C ₇₂ -D6d
C ₇₄	C ₇₄ -D3h
C ₇₆	C ₇₆ -D2
C ₇₈	C ₇₈ -C2v-3
C ₈₀	C ₈₀ -D5h-6
C ₈₄	C ₈₄ -D2-22
C ₉₀	C ₉₀ -C2-45
C ₉₆	C ₉₆ -D2-183
C ₁₀₀	C ₁₀₀ -D2-449

REFERENCES:

1. C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* 15 (2019) 1652 (<https://dx.doi.org/10.1021/acs.jctc.8b01176>)
2. S. Grimme, *Chem. Eur. J.* 18 (2012) 9955 (<https://dx.doi.org/10.1002/chem.201200497>)
3. S. Grimme, C. Bannwarth, E. Caldeweyher, J. Pisarek, A. Hansen, *J. Chem. Phys.* 147 (2017) 161708 (<https://dx.doi.org/10.1063/1.4991798>)
4. J. G. Brandenburg, C. Bannwarth, A. Hansen, S. Grimme, *J. Chem. Phys.* 148 (2018) 064104 (<https://dx.doi.org/10.1063/1.5012601>)
5. TURBOMOLE V7.2.1 2017, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
6. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 242 (1995) 652 ([https://dx.doi.org/10.1016/0009-2614\(95\)00838-U](https://dx.doi.org/10.1016/0009-2614(95)00838-U))
7. F. Weigend, *Phys. Chem. Chem. Phys.* 8 (2006) 1057 (<https://dx.doi.org/10.1039/b515623h>)
8. P. M. Zimmerman, *J. Chem. Phys.* 138 (2013) 184102 (<https://dx.doi.org/10.1063/1.4804162>)
9. David Tománek, *Guide Through the Nanocarbon Jungle*, Morgan & Claypool Publishers, San Rafael, USA, 2014 (<http://dx.doi.org/10.1088/978-1-627-05273-3>)