

SUPPORTING INFORMATION

Steric Clash In Real Space: Biphenyl Revisited

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Computational Details and inclusion of dispersion forces

Electronic structure calculations were carried out at the B3LYP/def2-VTZP level of theory using the Gaussian 16 software package [1] for all partial optimizations (the dihedral angle is constrained from 0° to 90°). Minima and transition states of the potential energy surface are characterized by the corresponding frequency. Molecular graphs within the QTAIM framework were obtained using the AIMAll program (version 16.10.09) [2]. The NCIPLOT program (version 3.0) was used for the study of the reduced density gradient behavior [3, 4]. The Electron Localization Function (ELF) measures the probability of finding electron pairs and provides a Lewis picture of the molecule [5,6], allowing the identification of core electrons, bonds and lone pairs. The TopMod code was used to obtain the ELF values [7].

It is well known that B3LYP might provide wrong results in systems where noncovalent interactions play a significant role. For this reason, we carried out dispersion-corrected calculations at the B3LYP-D3BJ/def2-TZVP level of theory (see Figure S1 below).

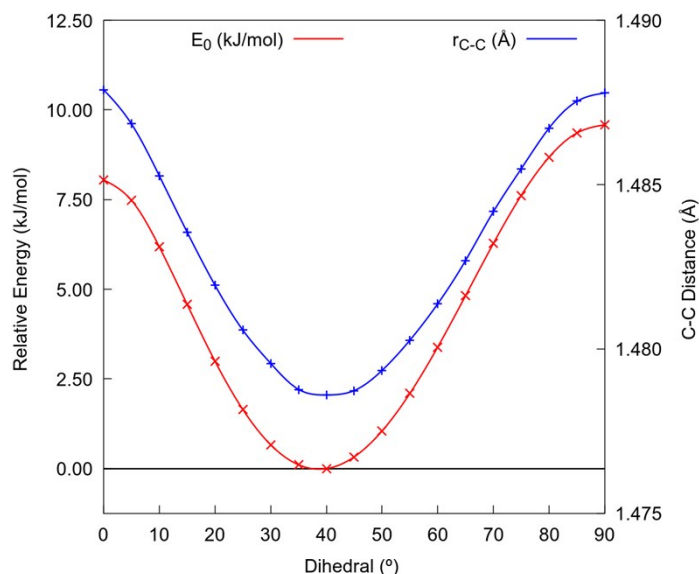


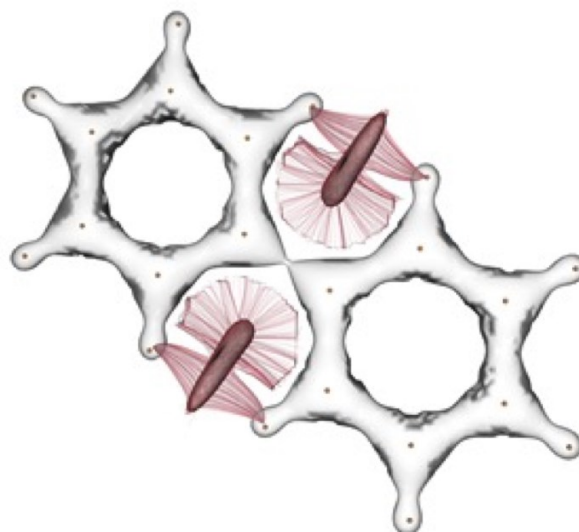
Figure S1. Relative energy profile at the B3LYP-D3BJ/def2-TZVP level of theory.

The B3LYP-D3BJ/def2-TZVP profile is very similar to the B3LYP profile. However, the 90° barrier is now significantly larger than the 0° one in comparison with the B3LYP profile. This trend is not appropriated, since both barriers should be essentially equal. A second aspect to be noticed is that the electron density at the critical point of the CC bridge changes by approx. 0.002 a.u. (0.27435 a.u. vs 0.27231 a.u.), meaning that the properties extracted would have not changed by including dispersion forces. Regarding

the geometry of the equilibrium structure, B3LYP is found at a dihedral angle of 39.380° whereas B3LYP-D3BJ is found at 38.688° (experimental reference: 44,4°).

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Figure S2. Density gradient lines from the NCI region for the planar biphenyl structure.



To analyse which atoms are contributing to the steric clash, we follow the density gradient lines shown in the figure above. Whereas a bundle connects the *ortho* hydrogens through the (3,-1) BCP point, the (3,+1) RCP interaction clearly relates to the rest of the pseudo-ring (*ortho* carbons and carbons from the bridge). This result would mean that the H-H interaction is stabilizing, whereas the carbon atoms are forced by the structure.

Figure S3. Volume of the *ortho* and *para* hydrogen ELF basins upon rotation of biphenyl.

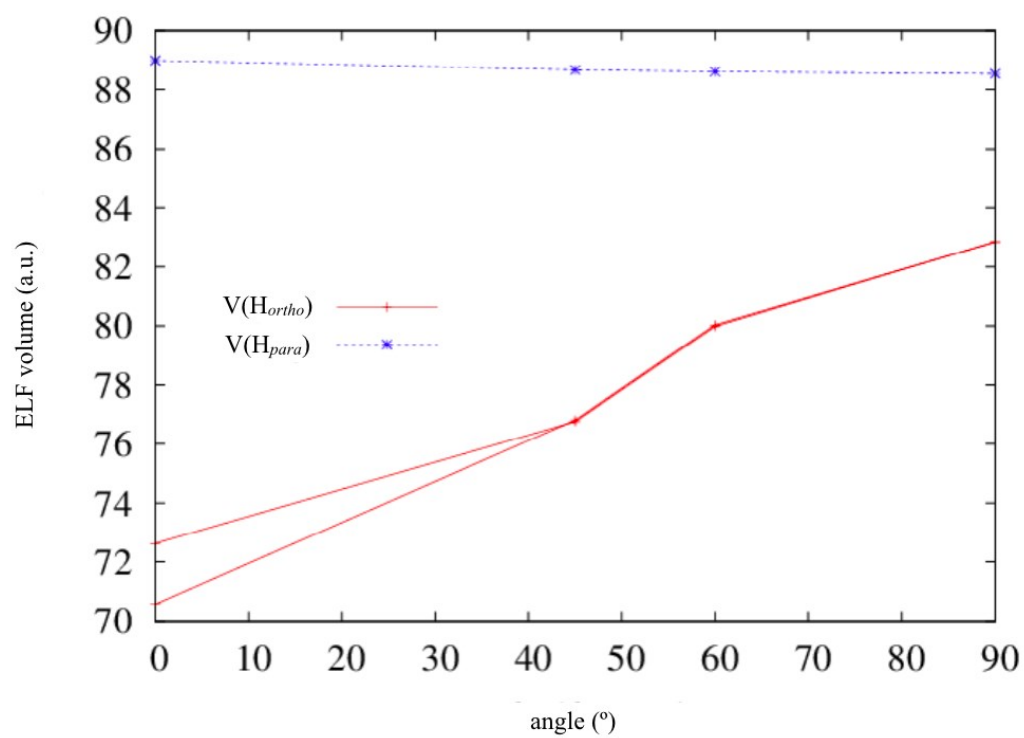
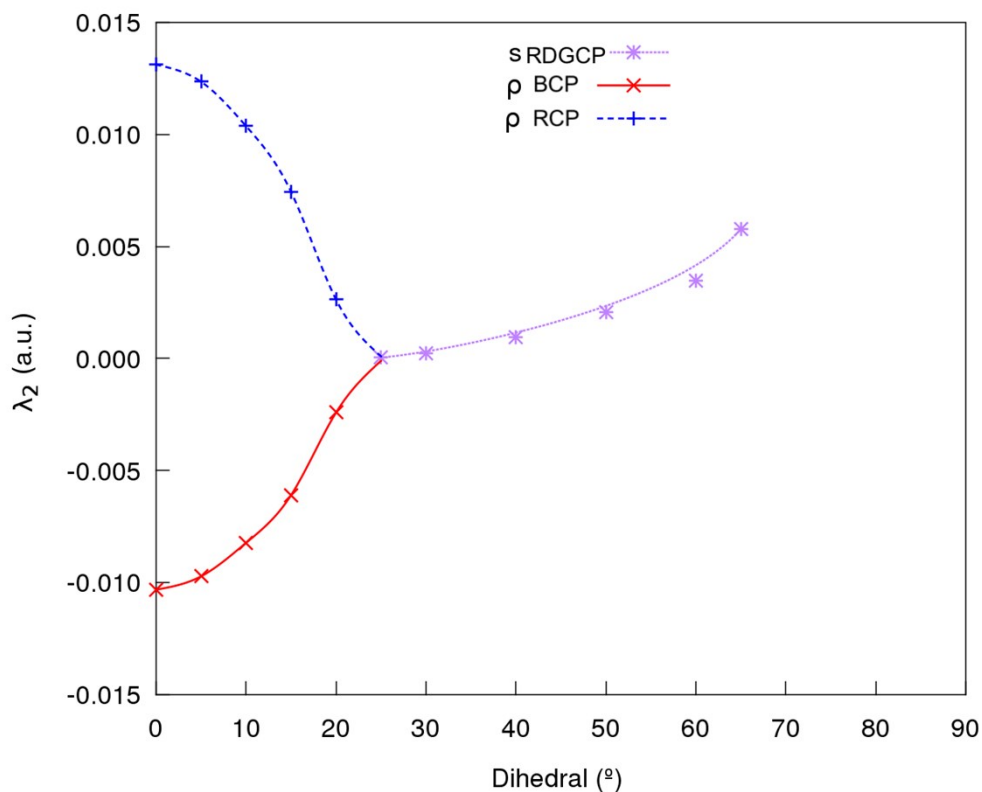


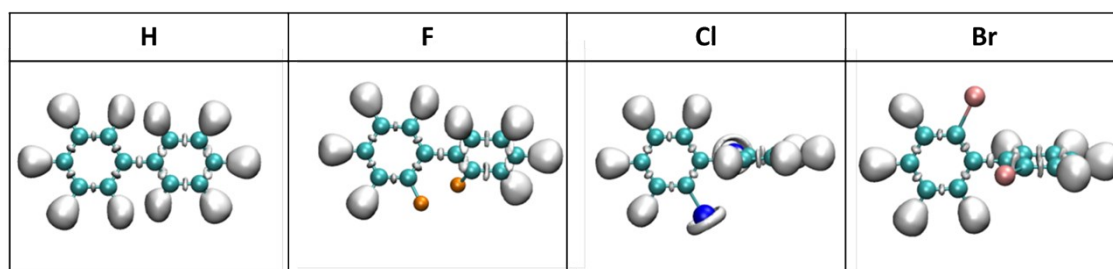
Figure S4. Scanning of λ_2 values at the BCP (red x marks), RCP (blue cross marks) and RDGCP (reduced density gradient critical point, lilac star marks) between benzene rings versus the dihedral angle for the biphenyl molecule.



The locality of the compression can be retrieved from the trends of the λ_2 values at the corresponding BCP, RCP and reduced density gradient critical point (RDGCP) of the interpenetrating region upon variation of the dihedral angle, as shown in Figure 6. The curvature of the electron density is connected with the inverse of λ_2 : large values of λ_2 occur in regions where the electron density changes abruptly. This behavior is related to the concept of locality.

All in all, the NCI method results are in very good harmony with the ELF and λ_2 results: at small angles it allows to smoothly follow the evolution of interaction interplays beyond QTAIM critical point collapse in a very intuitive way.

Figure S5. 2,2'-difluorobiphenyl, 2,2'-dichlorobiphenyl and 2,2'-dibromobiphenyl ELF basins at their equilibrium geometries.



F. Lerroux [see ref. 22 in the manuscript] studied the effect of replacing the *ortho* hydrogens by halogen atoms on the biphenyl structure. We show here the ELF basins for the H, F, Cl and Br substituted biphenyl structures at the equilibrium geometries. Dihedral angles reported by Lerroux are 42.5° (H), 45.1° (F), 59.9° (Cl) and 63.6° (Br) at the B3LYP/6-311+G* level of theory. A very similar increase is also observed for the halogen-substituted crystalline structures [22].