Torsional motion of biphenyl and derivatives — theory and strong laser pulses

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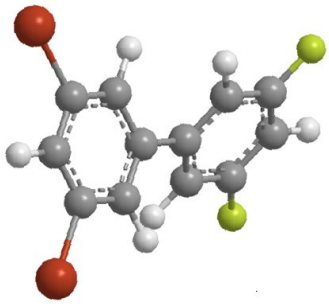
Abstract

From an electronic structure point of view, biphenyl is a surprisingly challenging molecule. Especially pinpointing the energetics of the internal rotation around the central C–C bond connecting the two benzene units has proven problematic; *ab initio* quantum chemical methods tend to give too high barriers, especially for the rotation around the planar conformation. Here, it will be shown that the experimental barriers *can* be reproduced, finally reconciling theory with experiment. For this, extrapolations of both the basis set toward the basis set limit and electron correlation toward the full configuration-interaction limit are needed, with CCSD(T)/aug-cc-pVQZ (1420 basis functions) calculations a prerequisite. Further, the minimum of the torsional angle is significantly increased by free energy corrections, which are needed to reach an agreement with experiment.

For biphenyl, the density functional B3LYP approach is found to perform well compared to the highest level *ab initio* calculations and experiment. This allows for a reliable study of biphenyl derivatives, main characters in the second act of this talk. It will be shown that torsional motion can be induced in suitably substituted biphenyls using strong laser pulses. A nanosecond laser pulse spatially aligns the C–C bond axis that connects the phenyl rings. This allows a perpendicularly polarized, intense femtosecond pulse to initiate torsional motion, accompanied by an overall rotation. The induced torsional motion opens up the possibility for various future applications. Examples include control of conductivity *via* the manipulation of the torsion angle, and time-resolved studies of de-racemication.



[1] M.P. Johansson, J. Olsen, "**Torsional Barriers and Equilibrium Angle of Biphenyl: Reconciling Theory with Experiment**", *J. Chem. Theory Comput.* **4** (2008) 1460–1471.

[2] C.B. Madsen, L.B. Madsen, S.S. Viftrup, M.P. Johansson, T.B. Poulsen, L. Holmegaard, V. Kumarappan, K.A. Jørgensen, H. Stapelfeldt, "**Manipulating the torsion of molecules by strong laser pulses**", *Phys. Rev. Lett.* (accepted)