Reply to Comment on “Distinctive Normal Harmonic Vibrations of [2.2]Paracyclophane[1]”

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Regarding calculations of the equilibrium structure of [2.2]-paracyclophane, the primary complaint of the commentors seems to lie ultimately in who calculated a D_2 minimum structure first. Henseler and Hohlneicher take exception first with the level of agreement with experiment which we reported and secondly with our reported energy difference between the D_2 and D_{2h} conformers. Henseler and Hohlneicher (HH) continue with the claim that a paper reporting MP2 energies for the benzene dimer[2] supports their allegation that the MP2 method they used to calculate energies for [2.2]paracyclophane is superior to the B3LYP hybrid Hartree−Fock/density functional method which we used.[3]

In regards to HH’s first point, our reported agreement with experiment: (1) HH object to our definition of the twist angle and our comparison with the angle derived from experiment. The angle we chose to represent the twist has been used in other publications[4,5] and is more straightforward to visualize and to extract from the data. We regret, and appreciate their observation, that we were actually comparing with a “half-twist” angle. Reanalysis of our data shows the calculated half-twist angle, as defined by the crystallographers,[6] to be 1.2°, in comparison with the experimental value of 3.2°. Within the limits of compational methods, this is still excellent agreement for a very low-energy torsion, especially when comparing to a solid state structure. (2) Neither here nor in the original paper do we claim that the calculated twist angle is *the* exact twist angle for the equilibrium conformation of [2.2]paracyclophane. We simply claimed to have the best calculated angle in the literature to that date. (3) Overall, we asserted and still maintain that this method provides “very good” agreement with the X-ray crystallographic structure.

In regards to HH’s second point, our reported energy difference for D_2 and D_{2h} conformers: (1) We are fully aware of the uncertainty of the very small energy difference between the two conformers. We state in the paper in question that, “This energy difference is so near the limitations of the method as to be inconclusive regarding the equilibrium structure.” Agreement with experiment on as many data points as possible is a much better test. Our calculated vibrational frequencies and *intensities* for the D_2 structure are in excellent overall agreement with the experimental IR spectrum. This agreement was much better than that from vibrations of the D_{2h} structure. Thus we concluded that including electron correlation and polarization functions in the theoretical chemistry more correctly models the minimum energy conformation than prior Hartree−Fock calculations.[7,8] (2) The reference provided by a reviewer of HH’s comment discusses integration grid problems for B3LYP in calculations on the pseudorotation of tetrahydrofuran.[9] Implications that this same problem is present in our calculations are total speculation. Without a dedicated multinode supercomputer with gigabytes of memory, the calculations which were necessary to isolate this aberration are practically infeasible for [2.2]paracyclophane. Deviation between our calculated twist angle and the experimentally derived angle may simply be a matter of having not reached basis set convergence. A basis set with diffuse functions, or at least more diffuse polarization functions, will likely improve the accuracy considerably.[2]

Finally, in regards to HH’s third point, the improved suitability of their MP2/6-31G calculations over our B3LYP/4-31G* calculations: (1) Reference by Henseler and Hohlneicher to a computational study of benzene dimer[2] as supporting the use of MP2/6-31G for [2.2]paracyclophane is deceptive. The referenced, intensive comparison of MP2, MP4, and CCSD(T) with many large basis sets by Hobza, Selzle, and Schlag actually states, *in the abstract*, “MP2 strongly overestimates the stabilization energy and leads to incorrect global minimum.[2]” In the basis set comparison, Hobza, Selzle, and Schlag find that not only are polarization functions inescapable for finding the correct minimum but *diffuse* polarization functions are critical for accuracy.[2] Hobza, Selzle, and Schlag also found that even when using a split-valence basis set similar to 6-31G but including polarization functions, the results were inadequate.[2] Thus accepting the implication by HH that the benzene dimer results point to an optimum theoretical chemistry for the interactions in [2.2]paracyclophane, the combination of MP2 with the split-valence 6-31G basis set which has *no* polarization functions is one of the worst possible choices for [2.2]paracyclophane. (2) The polarization functions omitted from the basis set utilized by HH are likely to be especially important for [2.2]paracyclophane because they allow adjustments of the electron density to follow the torsions, including the one questioned in their first point. (3) HH imply that the “correlation effects” will be better accounted for by MP2 over B3LYP. When first approached with this comment, we resisted being drawn into a “my method is better than your method” argument. Extensive literature exists demonstrating that density functional theory methods in general and B3LYP in particular are at least as good as, and in most cases better than, MP2.[3,10] The fact remains, however, that both of these methods do better with dynamical correlation than nondynamical correlation.[11,12] The nondynamical correlation could be important in [2.2]paracyclophane because of low-lying and near-degenerate excited states.[7,13,14] Thus these two methods share similar possible deficiencies for [2.2]paracyclophane. These deficiencies are likely to be exacerbated by the small basis sets necessary for this large molecule.

In conclusion, experiment is the final arbiter; our original argument for the first computational evidence of D_2 ground-state geometry is based on excellent agreement with experimentally measured vibrational frequencies and intensities. This vibrational data, either to confirm even a local minimum or to show acceptable accuracy when compared with experiment, are not provided in the comment by Henseler and Hohlneicher. In light of the findings regarding diffuse functions for benzene dimer, the agreement which either of us report for the cyclophane twist angle is potentially fortuitous. In the absence of a definitive, gas-phase, experiment for an exact angle, a better method with a much larger basis set will be necessary for precise characterization of [2.2]paracyclophane. The vibrational assignments reported in “Distinctive Normal Harmonic Vibrations of [2.2]Paracyclophane” can still be useful for experimentalists studying this fascinating family of molecules.

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References and Notes

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(14) See ref 1 for more references related to the structure and properties of [2.2]paracyclophane.