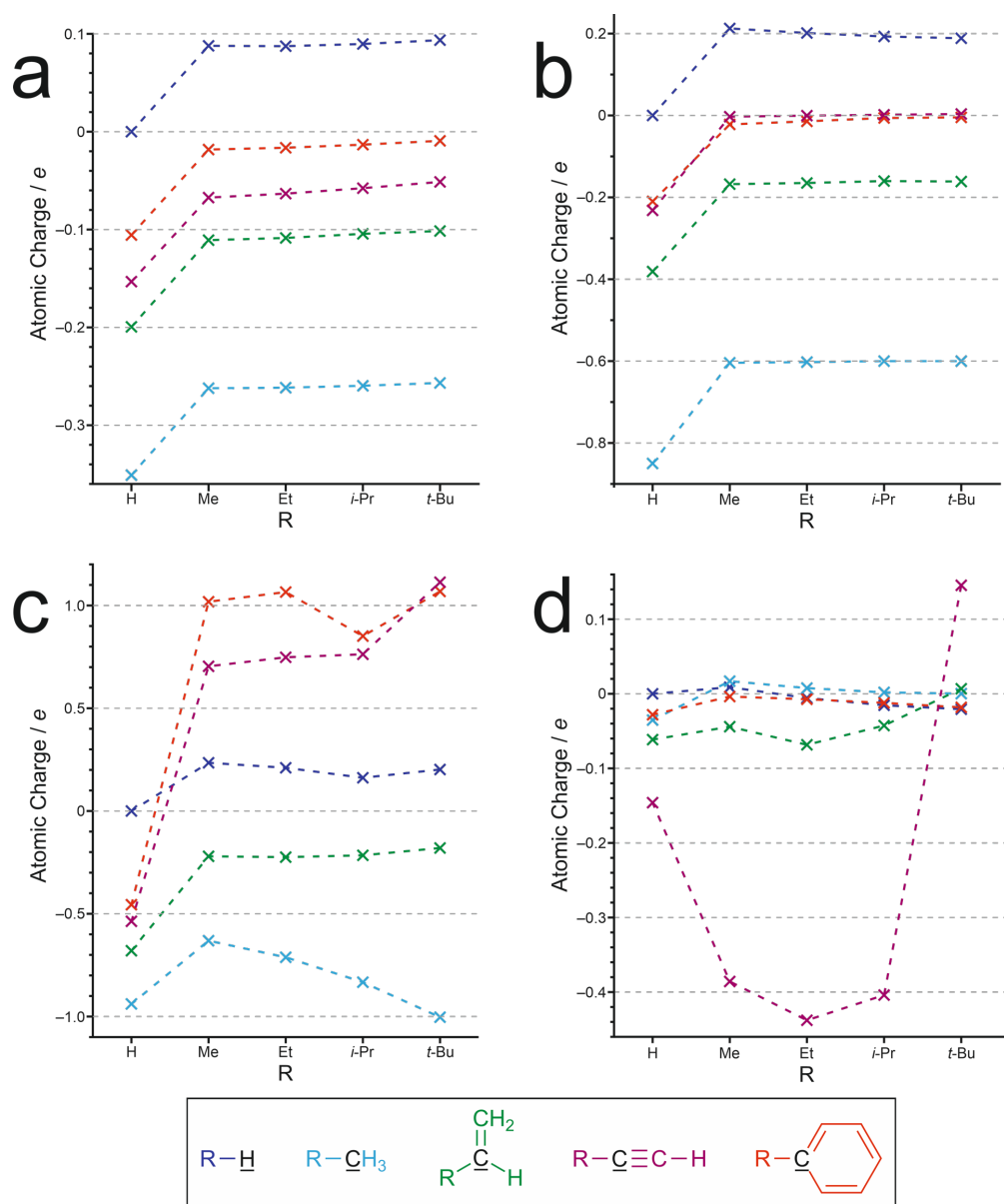


## Alkyl Groups in Organic Molecules are NOT Inductively Electron-Releasing

Mark C. Elliott, Colan E. Hughes, Peter J. Knowles and Benjamin D. Ward

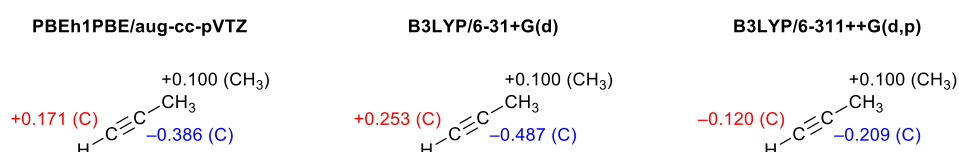
It was noted in the manuscript that the conclusions we have reached are identical when the other charge models (CM5, NBO, Mulliken, QTAIM) are used. We provide additional data in support of this statement.

**Figure 3. Comparison of Alkyl Groups to Hydrogen. (a) CM5, (b) NBO, (c) Mulliken and (d) QTAIM.**

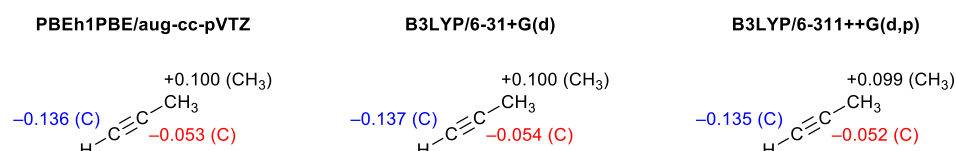


CM5 and NBO charges show exactly the same as the Hirshfeld charges discussed in the main manuscript, although the numbers are larger in magnitude in both cases. This does not affect our conclusions. Mulliken charges show the same, apart from alkyl groups attached to methyl. There is a significant trend within the alkyl groups such that *t*-Bu is electron-donating compared to hydrogen. Mulliken charges are known to be problematic,<sup>1</sup> but even here we find the general trend that alkyl groups are electron-withdrawing when compared to hydrogen.

The QTAIM charges for alkynes are problematic for several reasons. Firstly, they fail our benchmarking process as they do not reproduce the dipole moment calculated from the overall density. Secondly, the QTAIM charges are extremely sensitive to the approximations (functional, basis set) in the DFT calculation. QTAIM charges based on DFT calculations with three different ansätze are shown below (red = less electron-rich, blue = more electron-rich).



The Hirshfeld calculations are remarkably consistent across the three ansätze.



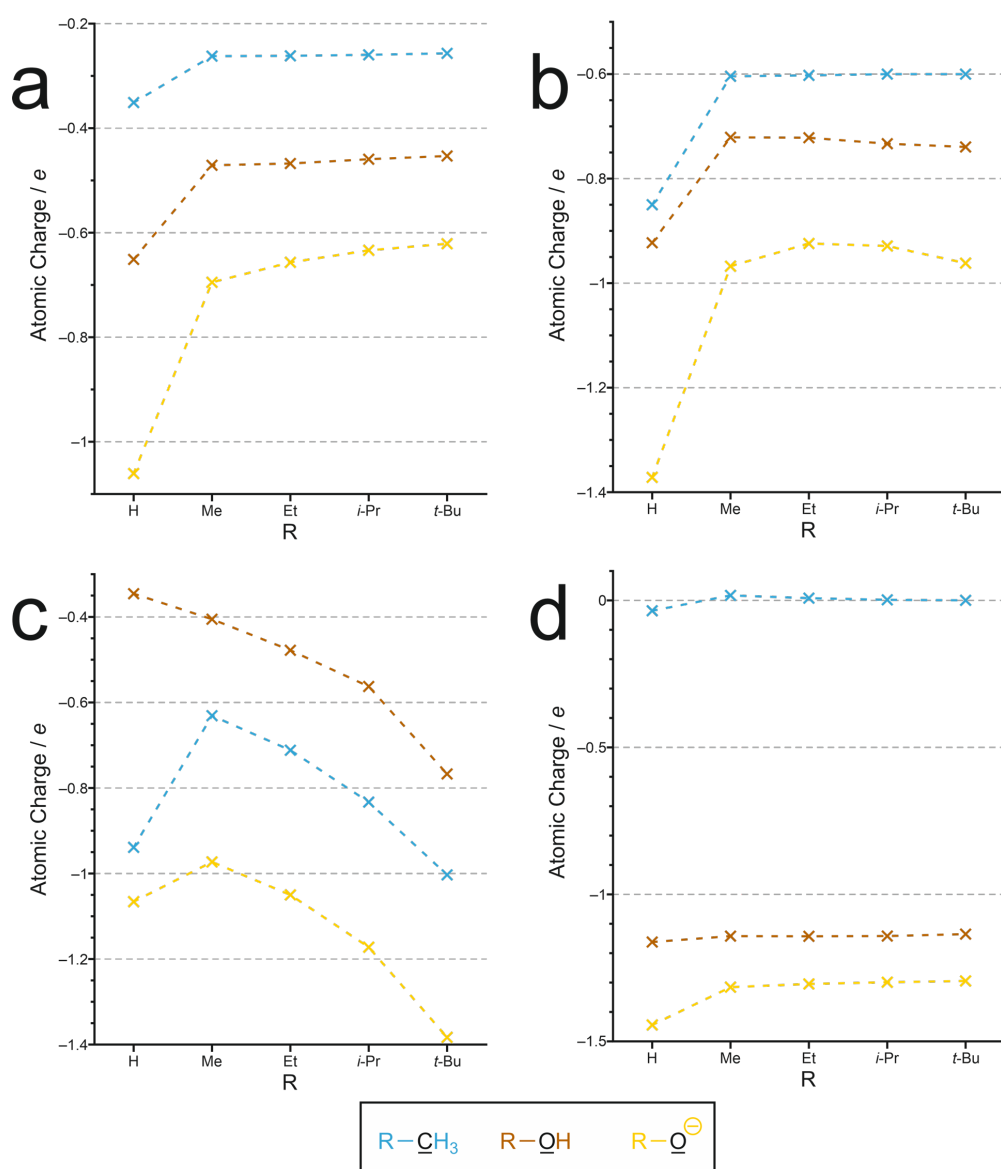
Finally, although of lesser importance, the QTAIM charges are inconsistent with our chemical intuition. We expect (as found with the other charge partitioning models), the methyl group in propyne to exert an electron-donating hyperconjugation effect towards C1, whereas two of the three QTAIM calculations find a significant electron-withdrawing effect from this position. The QTAIM charges for propyne have been noted before.<sup>2</sup> Jabłoński and Krygowski have provided us with further unpublished data that show similar results.<sup>3</sup> We see similar problems for the alkene QTAIM calculations but to a lesser extent.

1. B. Wang, S. L. Li and D. G. Truhlar, *J. Chem. Theory Comput.*, 2014, **10**, 5640-5650.

2. G. R. S. de Freitas and C. L. Firme, *J. Mol. Model.*, 2013, **19**, 5267-5276.

3. M. Jabłoński, personal communication; M. Jabłoński and J. Krygowski, *Struct. Chem.*, 2021, **32**, 285-296.

Figure 7. (a) CM5, (b) NBO, (c) Mulliken and (d) QTAIM.



We have already highlighted the problems with Mulliken charges. The idea that an alcohol oxygen atom is less negatively charged than an alkane carbon atom is further evidence that we cannot compare these charges in any meaningful way across different series of compounds. The CM5, NBO and QTAIM charges are consistent with the Hirshfeld charges in the main manuscript in predicting an alkyl group electron-withdrawing inductive effect for the alkanes and alcohols, which is supported/dominated by a polarizability effect in the alkoxides.

In short, our conclusions are supported by calculations using five different charge partitioning models, although we note the poor quality of Mulliken calculations and the poor performance of QTAIM calculations for the alkynes, and to a lesser extent the alkenes.