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Correction: Not antiaromaticity gain, but increased asynchronicity enhances the Diels–Alder reactivity of tropone

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Correction for 'Not antiaromaticity gain, but increased asynchronicity enhances the Diels–Alder reactivity of tropone' by Eveline H. Tiekink *et al.*, *Chem. Commun.*, 2023, **59**, 3703–3706, <https://doi.org/10.1039/D3CC00512G>.

In the original paper, the reactivity of tropone and its neutral and deprotonated hydrazone analogs was studied using the generalized gradient approximation functional BP86-D3(BJ) for geometries and the range-separated hybrid functional ω B97X-D for energies. The authors have since identified a technical issue in the implementation of the ω B97X-D functional in the ADF software package, specifically the dispersion correction. Therefore, they have recomputed all energetic values (the optimized geometries remain the same as in the original manuscript due to using BP86) with ZORA- ω B97X-D4/TZ2P and prepared new tables (Tables 1 and 2) and figures (Fig. 1 and 2) from these results.

The conclusions are congruent with the original ZORA- ω B97X-D/TZ2P results, while the absolute energy values have changed, and the relative energy of all stationary points are stabilized. The updated results are reported below.

All analyses are performed at the ZORA- ω B97X-D4/TZ2P¹ level of theory on the geometries optimized by ZORA-BP86-D3(BJ)/TZ2P. The results included in this correction act as an update to those previously given in the original publication. Please see the original publication for further details related to the methodology. The associated electronic supplementary information has also been updated with additional data for the calculations reported here.

Results

Table 1 Electronic energies (ΔE) of the stationary points (in kcal mol^{−1}) for the Diels–Alder reactions between **M** and **1**, **2-prot**, **2**, **3-prot**, and **3**^{ab}

Diene	RC	TS1	INT	TS2	P
1	−8.7	20.8			−38.5
2-prot	−9.0	21.1			−41.0
3-prot	−9.1	23.0			−37.0
2	−17.9	−7.8	−22.6	−18.8	−48.0
3	−8.6	7.2			−45.8

^a Computed at ZORA- ω B97X-D4/TZ2P//ZORA-BP86-D3(BJ)/TZ2P. ^b See Fig. S1 and Table S1 for the transition state structures and Gibbs free energies (ESI).

Table 2 Energy decomposition analysis terms (in kcal mol^{−1}) of the Diels–Alder reactions between **M** and **1** and **2**^a

Diene	ΔE	ΔE_{strain}	ΔE_{int}	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi}	ΔE_{disp}
1	19.9	33.8	−13.9	−49.8	94.1	−56.7	−1.6
2	−6.9	21.4	−28.3	−52.8	79.9	−53.9	−1.6

^a Computed at consistent TS-like geometries ($C_{\text{M}} \cdots C_{\text{diene}} = 2.160 \text{ \AA}$) at ZORA- ω B97X-D4/TZ2P//ZORA-BP86-D3(BJ)/TZ2P.

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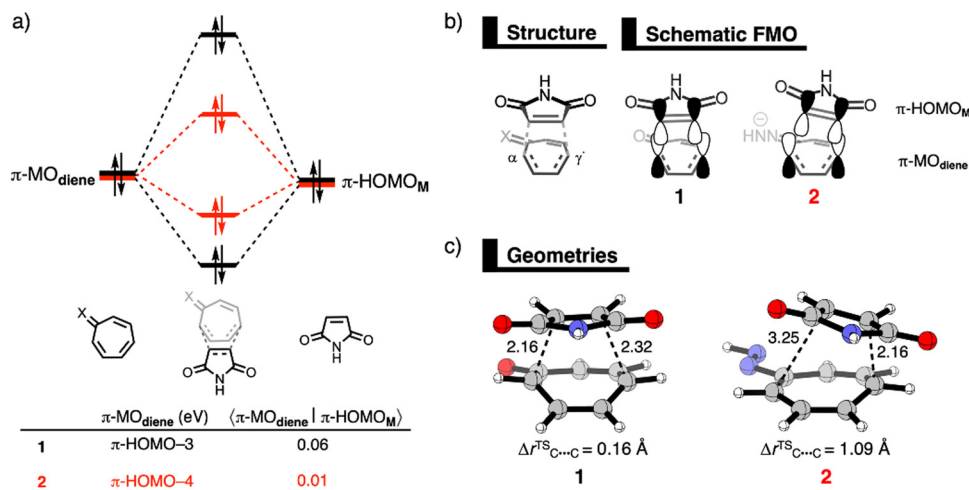


Fig. 1 (a) Molecular orbital diagram with the most significant occupied orbital overlaps; (b) key occupied orbitals; and (c) the structures with key structural information (in Å) of the Diels-Alder reactions between **M** and diene **1** and **2**, computed at consistent TS-like geometries ($C_M \cdots C_{diene} = 2.160 \text{ \AA}$) at ZORA- ω B97X-D4/TZ2P//ZORA-BP86-D3(BJ)/TZ2P.

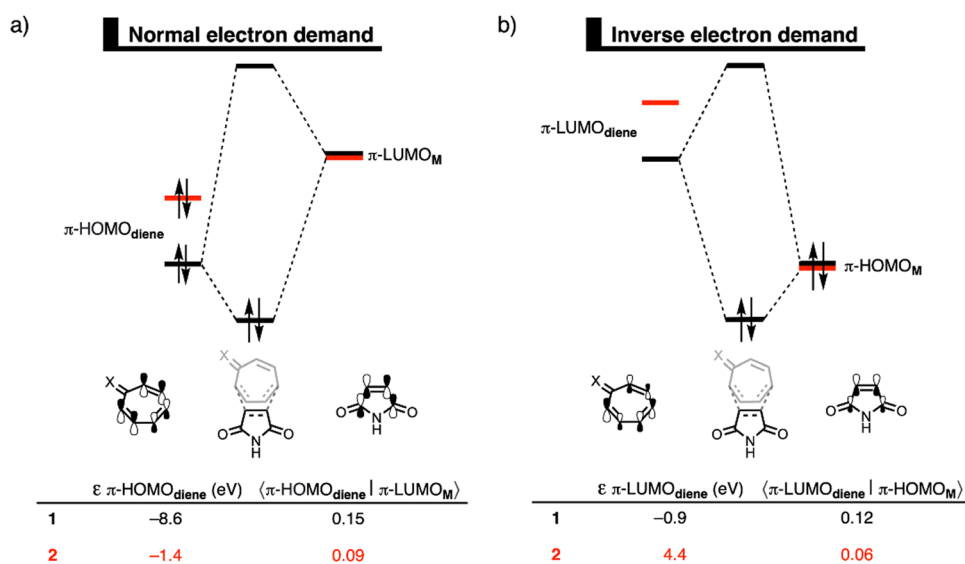


Fig. 2 Kohn-Sham molecular orbital diagrams with orbital energy levels and overlaps for (a) the normal electron demand π -HOMO_{diene}– π -LUMO_M; and (b) the inverse electron demand π -LUMO_{diene}– π -HOMO_M of the Diels-Alder reactions between **M** and diene **1** and **2**, computed at consistent TS-like geometries ($C_M \cdots C_{diene} = 2.160 \text{ \AA}$) at ZORA- ω B97X-D4/TZ2P//ZORA-BP86-D3(BJ)/TZ2P.

These updated energies, orbital overlaps, and orbital energy levels are provided to show that the major conclusions in the original publication remain, despite the aforementioned technical issues.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

References

- (a) J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 084106; (b) E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J. Chem. Phys.*, 2019, **150**, 154122.

