Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information
accompanying:

Intramolecular π-hole interactions with nitro aromatics

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Contents

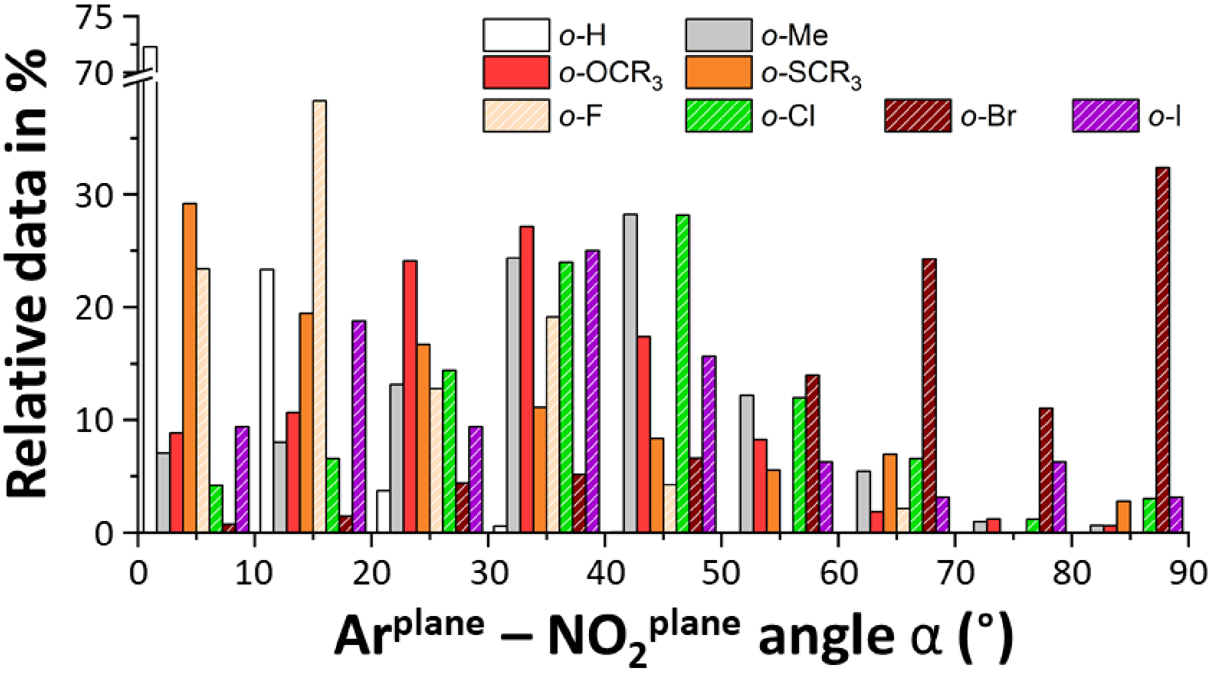

Figure S1. Bar diagrams of the relative amount of data as a function of the aryl plane – NO_2 plane angle (α) for the structures considered in query a in Figure 1, further detailed in Table 1.

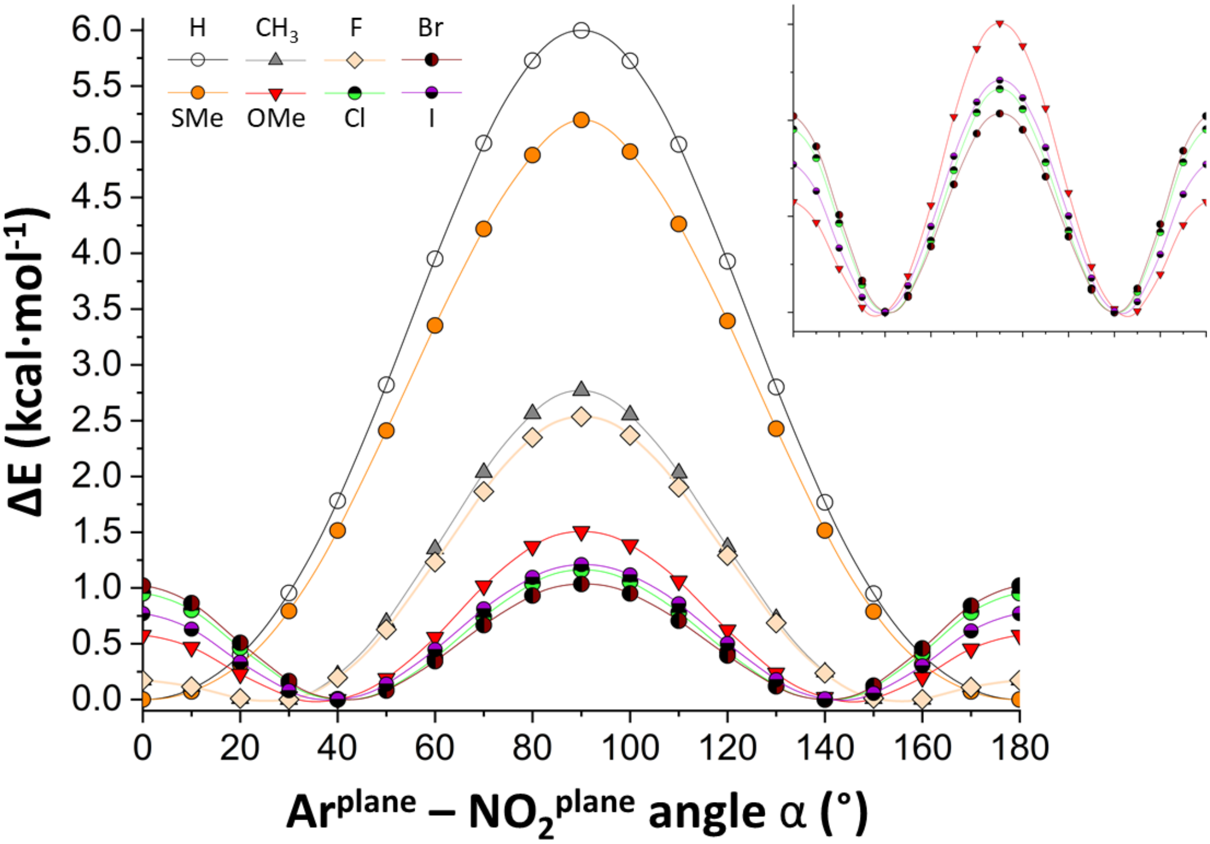

Figure S2. Energy profiles for (*o*-H) nitro arenes with indicated *ortho*-substitution as a function of the aryl plane – NO_2 plane angle (α). Computations were performed at the DFT/PBE0-D3/def2-TZVP level of theory (see also Table 1).

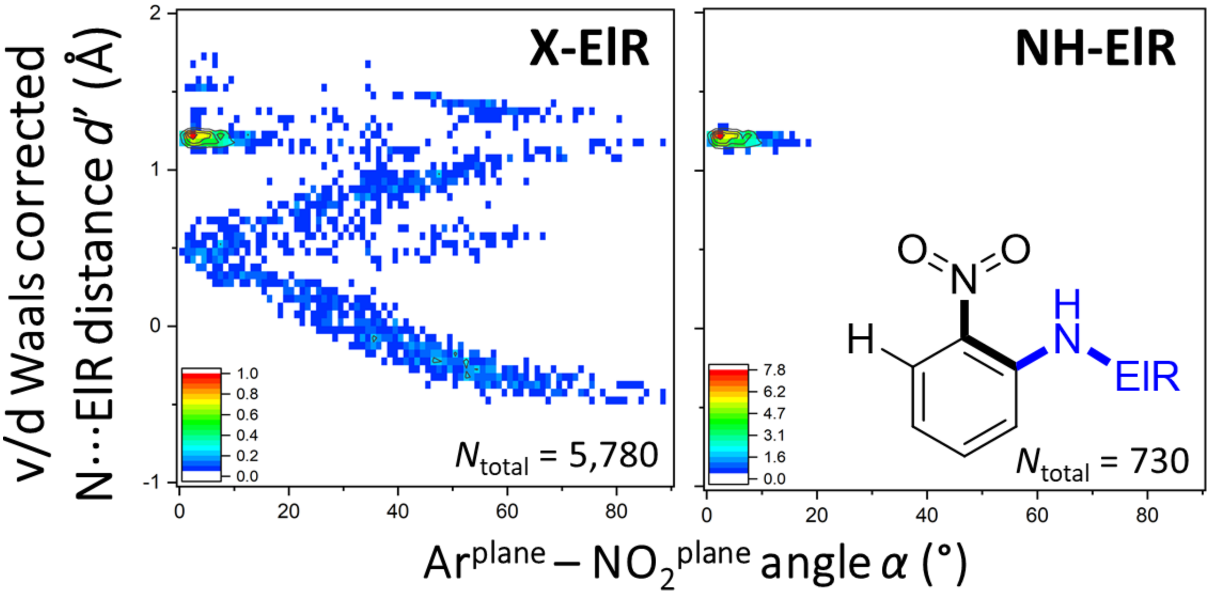

Figure S3. *d′*(α) heat plots for data obtained with query b in Figure 1 (left, 5,780 hits) and a similar query where X = NH (right, 730 hits). From this comparison it is evident that the feature at *d′* ≈ 1.2 Å and β ≈ 5° is nearly entirely due to *o*-NH-ElR structures. The planarity and relatively large distance *d′* is caused by intramolecular NO_2···H–N hydrogen bonding interactions.

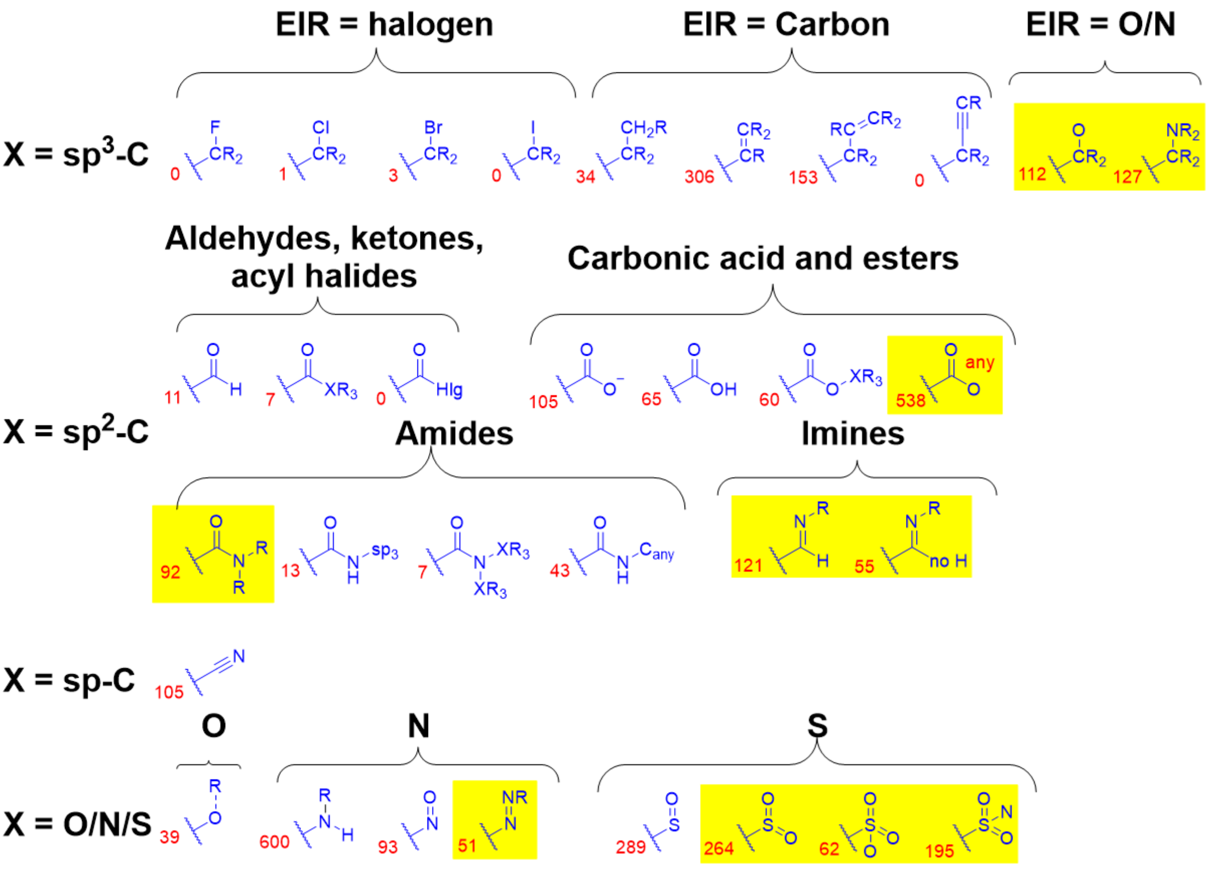

Figure S4. Overview of specific structures considered to elucidate the nature of X and EIR (see query b in Figure 1). The amount of CIFs found with each structure is indicated in red. The remaining data (not containing any of the shown structures) involved small datasets (> 30 CIFs) and were not considered further. The structures highlighted in yellow were inspected further by means of *d'*(α) plots and DFT calculations (see Figure 4 and Figure S5 for details).

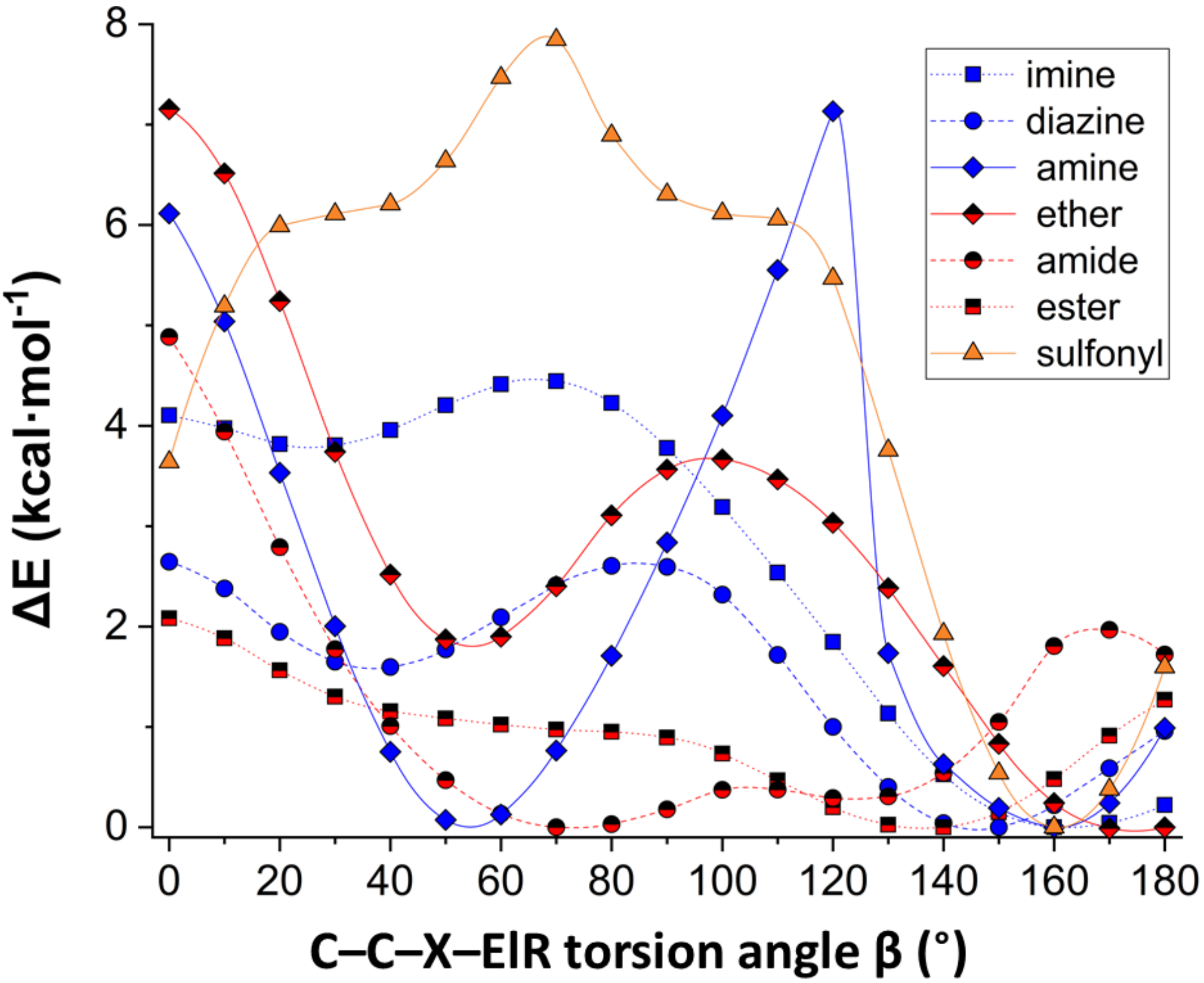

Figure S5. Energy profiles for nitro arenes with indicated *ortho*-substitution as a function of C-C-X-ElR torsion angle (β). Computations were performed at the DFT/PBE0-D3/def2-TZVP level of theory. X and **ElR** are as follows: imine: -C=**N**H, diazine: -N=**N**H, amine: -CH$_2$**N**(CH$_3$)$_2$, ether: -CH$_2$**O**CH$_3$, amide: -C(**O**)NHCH$_3$, ester: -C(**O**)OCH$_3$, sulfonyl: -S**O**$_2$.

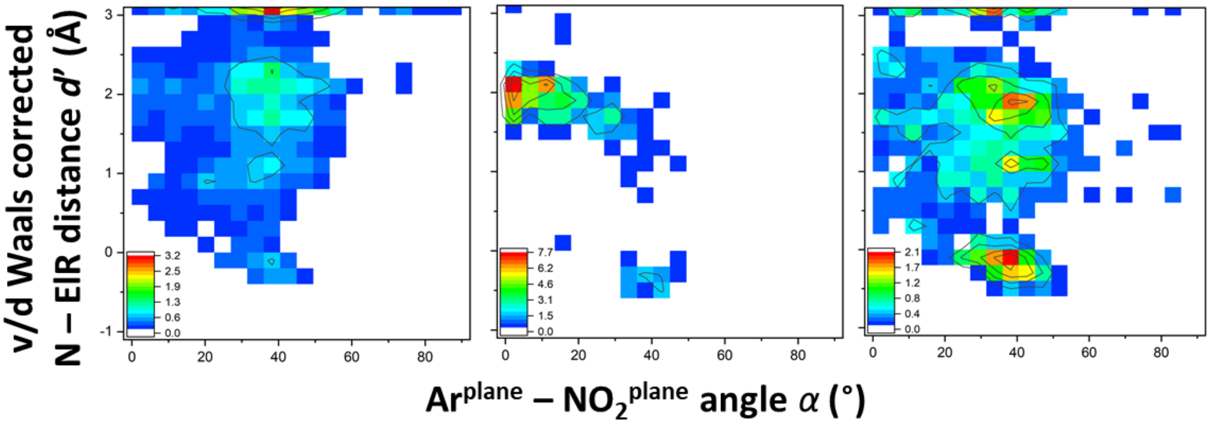

Figure S6. $d'(\alpha)$ heat plots for data obtained with query c in Figure 1 with $n = 1$ (left, 8,528 hits), a similar search but including only *o*-NH structures (middle, 401 hits) and a similar search excluding o-NH structures and structured with a metal atom (right, 2,377 structures). These plots reveal that the features at [2,10] and [3,40] in the most broadly defined dataset (left) are caused by *o*-NH and metal structures respectively. The latter was found –on manual inspection– to be due to metals acting as X to bridge ElR and the nitroarene and these data were thus omitted in the $d'(\alpha)$ heat plot shown in Figure 5.

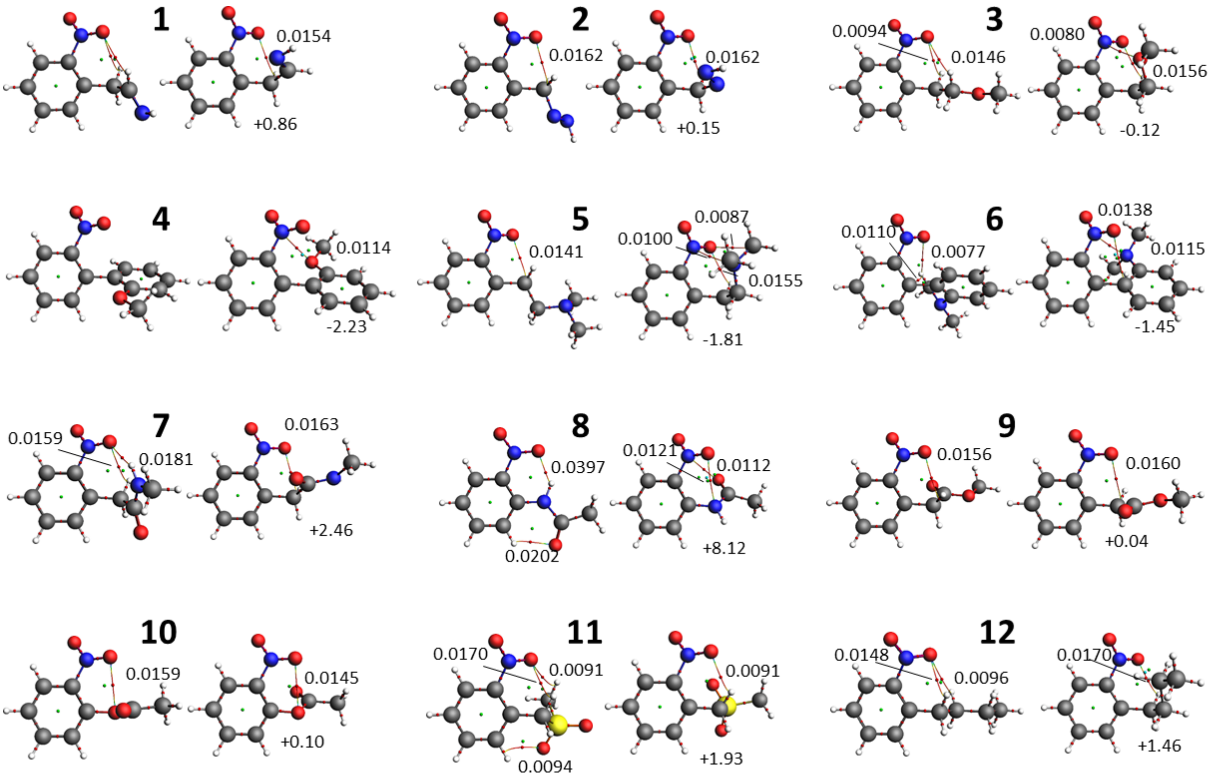

Figure S7. Overview of geometry optimized conformers of nitro aromatics **1** – **12** (see also Figure 5) and accompanying 'atoms in molecules' analysis (bond paths in thin red lines and bond critical points in small red spheres with density values in arbitrary units). The structures on the left hand side were always obtained starting from a geometry that had the potentially interacting atom as far away from the nitro group as possible; the geometry on the right was always obtained starting from close contact N/O→N^{NO_2} geometries. The calculations were performed at the DFT/B3LYP-D3/def2-TZ2P level of theory and relative energies of the two conformers is given in kcal·mol^{-1}.

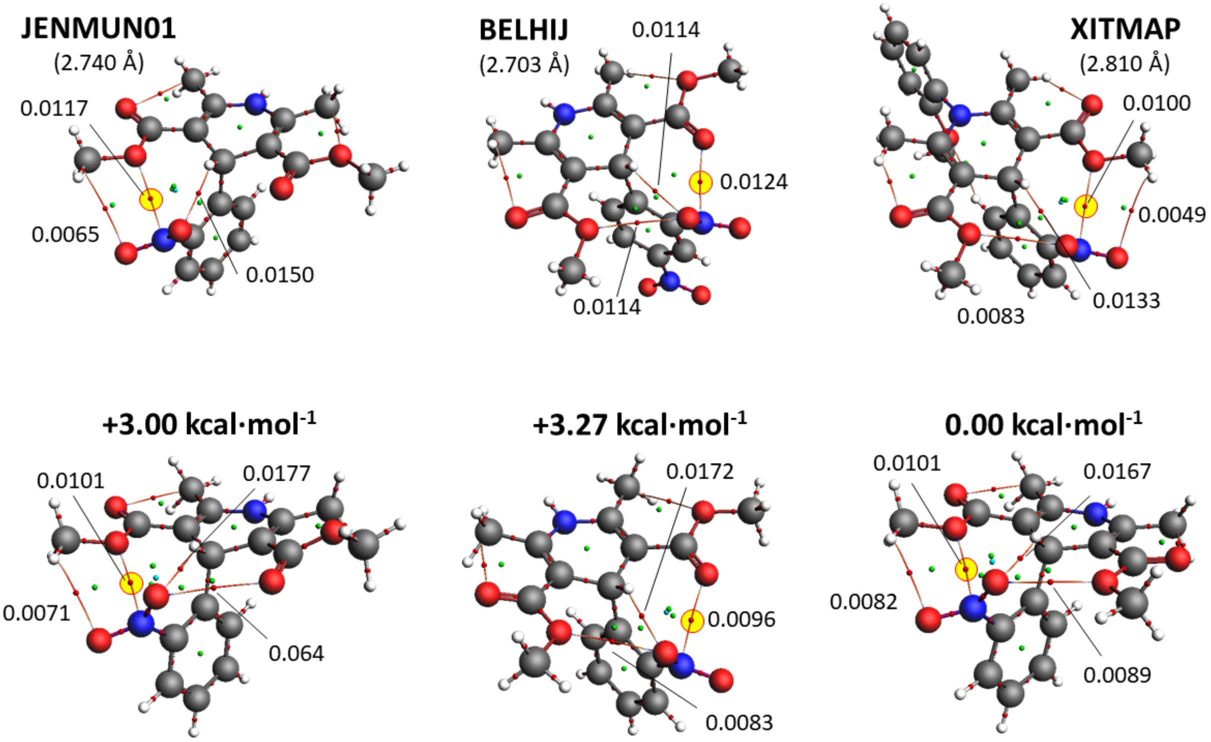

Figure S8. Top: Overview of an AIM analysis of three structural isomers of dihydropyridines with an *o*-nitrobenzene as found within JENMUN01, BELHIJ and ZITMAP. Bottom: Geometries of energy optimized isomers that and their AIM analyses. The energy of the conformational isomer with both carbonyl O-atoms pointing towards the nitro aromatic (not shown) is +6.55 kcal·mol^{-1} (not observed in the CSD or the PDB). The ^{NO_2}N···O bcp's are all about ρ = 0.01 a.u. and all calculations were run at the DFT/B3LYP-D3/def2-TZ2P level of theory. See also Figure 6.