Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Initial Decomposition Pathways of 1,1-Diamino-2,2-Dinitroethylene (α-FOX-7) in the Condensed Phase

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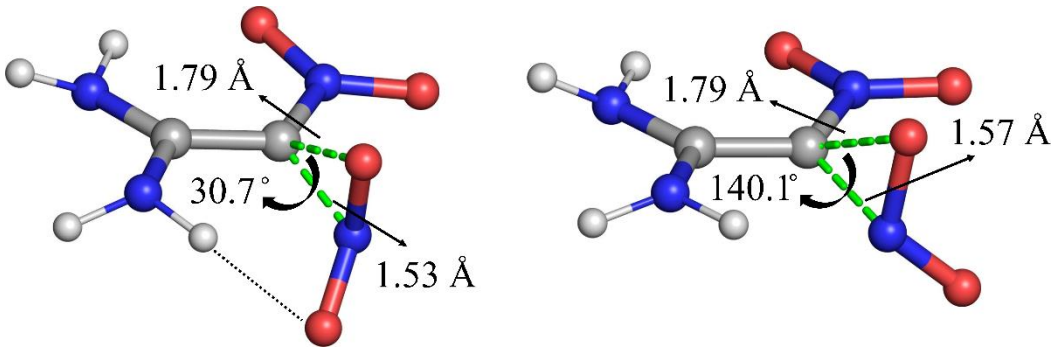


Figure S1: Representative figure showing two different isomers **ts1** and **ts1′** (r_{CO}, r_{CN}, and ∠CCNO) for the nitro to nitrite isomerization transition state, with important geometrical parameters. The black dotted line represents intramolecular H-bond between the oxygen of isomerizing -NO_2 group and the hydrogen atom of neighbouring -NH_2 group.

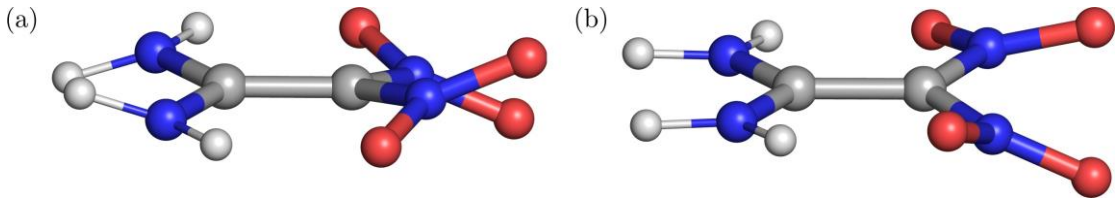


Figure S2: Representative figure showing optimized structures of FOX-7 in (a) gas-phase and (b) on a sheet.

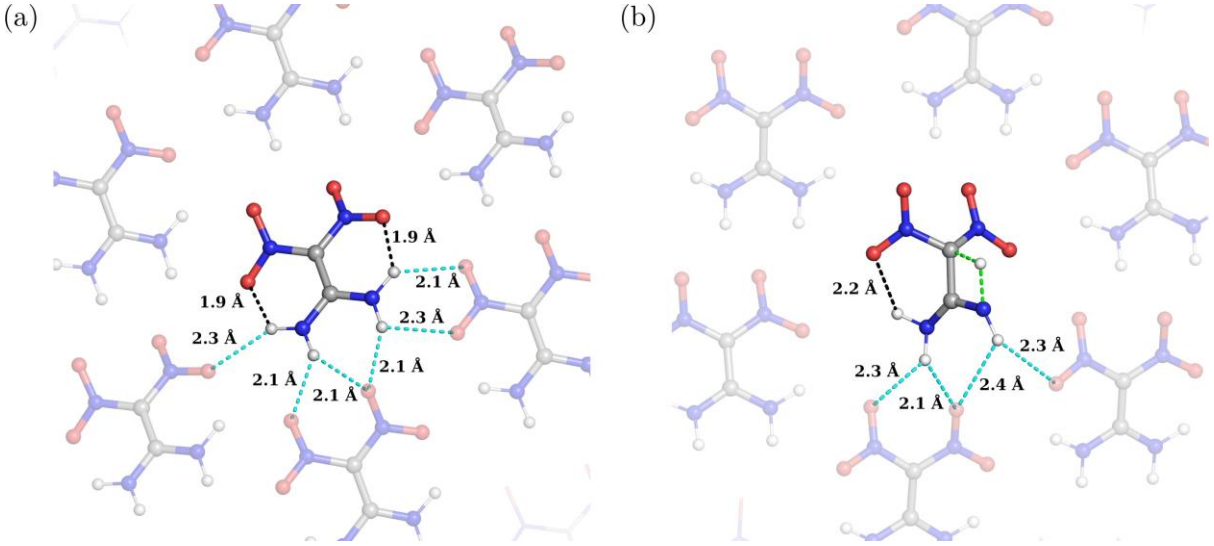


Figure S3: Representative figure showing optimized structures of (a) FOX-7 and (b) **ts3** in the sheet. The intra- and intermolecular H-bonds are denoted by black and cyan dashed lines respectively.

(a)

(b)

(c)

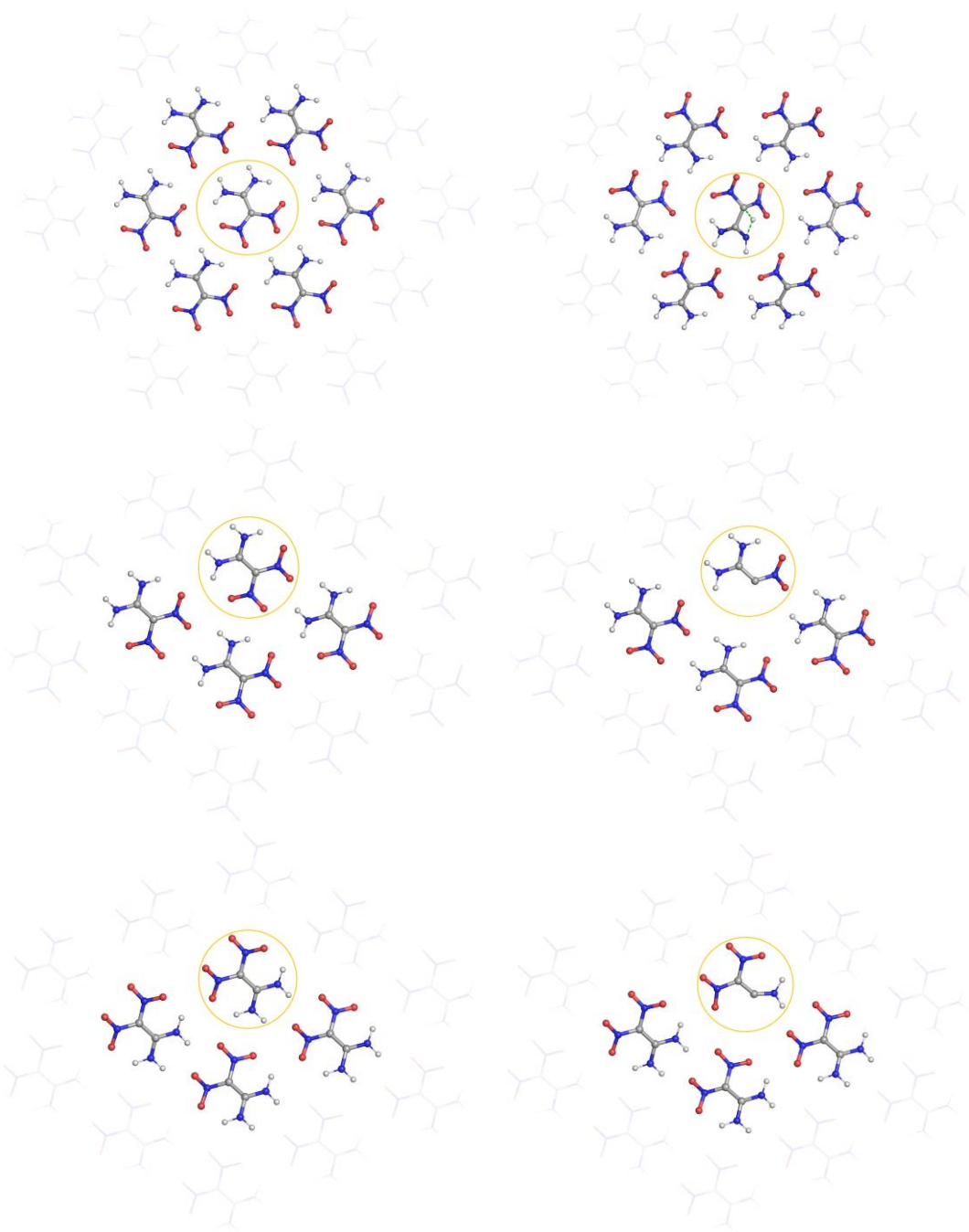


Figure S4: Representative figures showing the choice of neighbouring molecules used to study (a) H-atom transfer via **ts3**, (b) -C-NO_2 dissociation forming intermediate **int6** + NO_2, and (c) -C-NH_2 dissociation forming **int7** + NH_2, on a sheet structure.

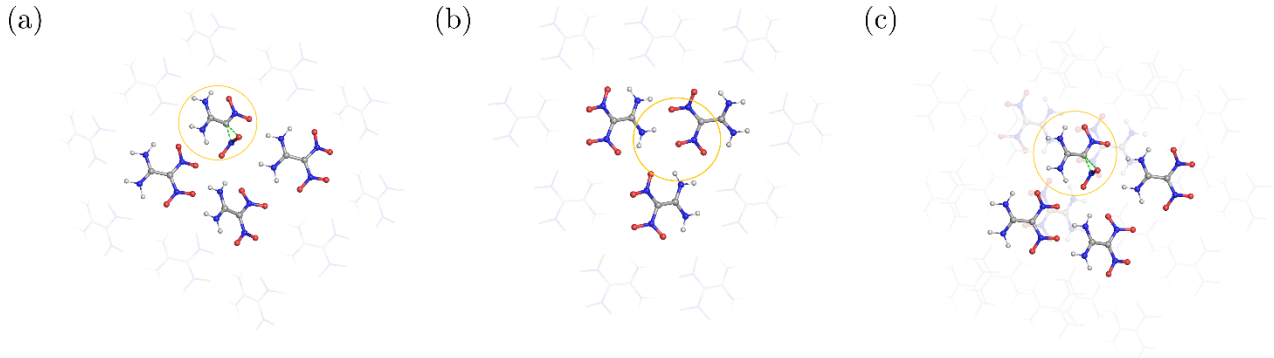
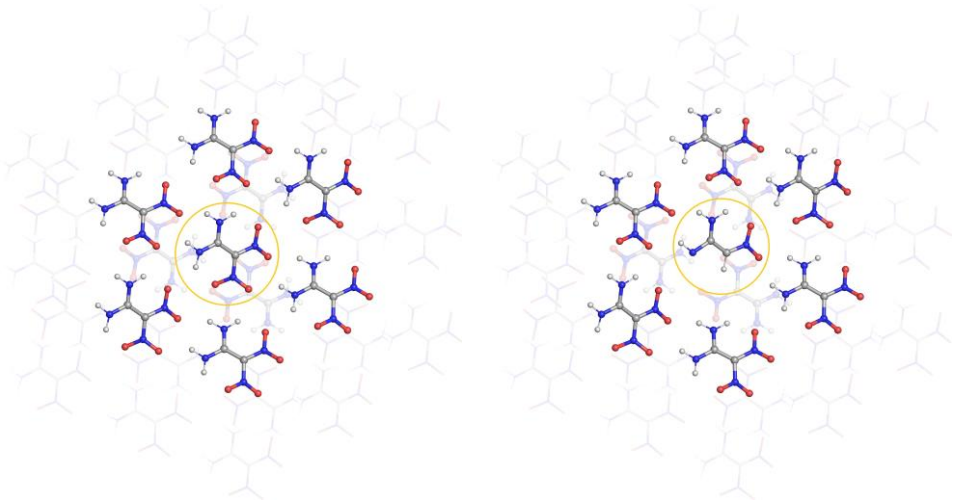
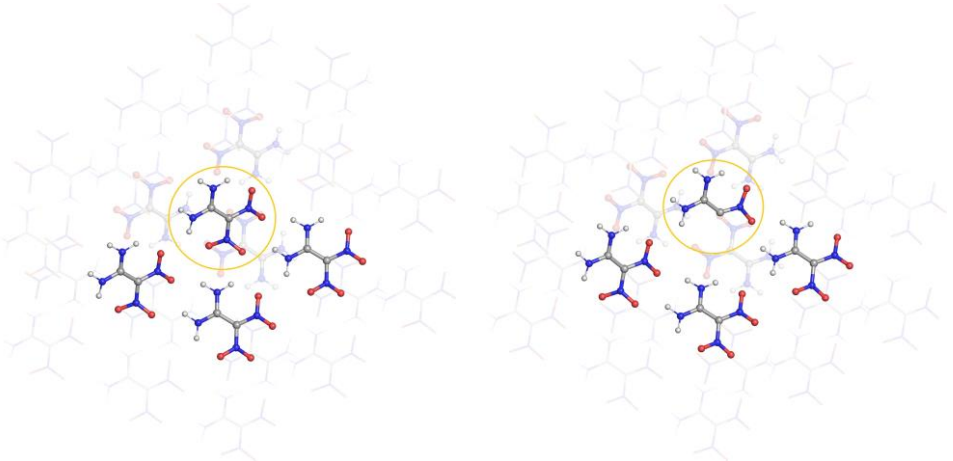


Figure S5: Representative figure showing (a) the top layer, (b) the bottom layer, and (c) full surface modelled for the -NO_2 to -ONO isomerization pathway (**ts1**). The molecules with a ball-and-stick representation are allowed to relax during a geometry optimization, whereas the rests are held fixed. The orange circle denotes the position of the reactive molecule ((a) and (c)) and the projection to the layer beneath (b).

(a)



(b)



(c)

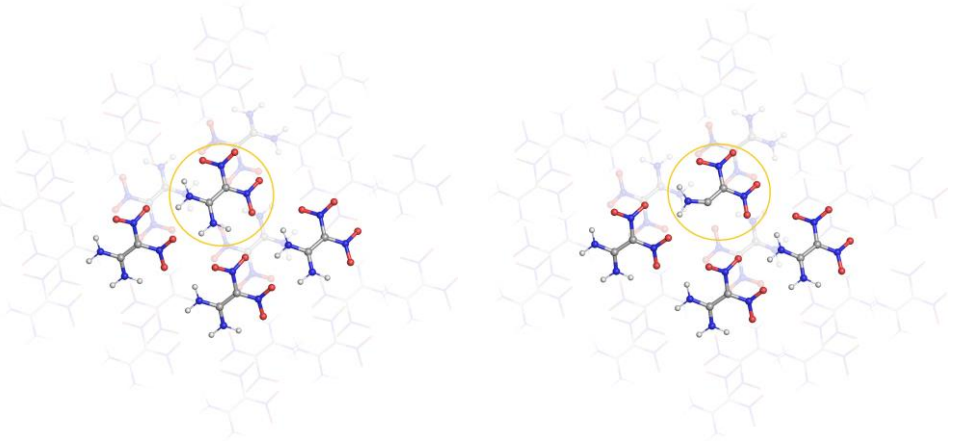


Figure S6: Representative figures showing the choice of neighbouring molecules used to study (a) H-atom transfer eventually forming **int5** + NO_2, (b) -C-NO_2 dissociation forming intermediate **int6** + NO_2, and (c) -C-NH_2 dissociation forming **int7** + NH_2, on a surface.

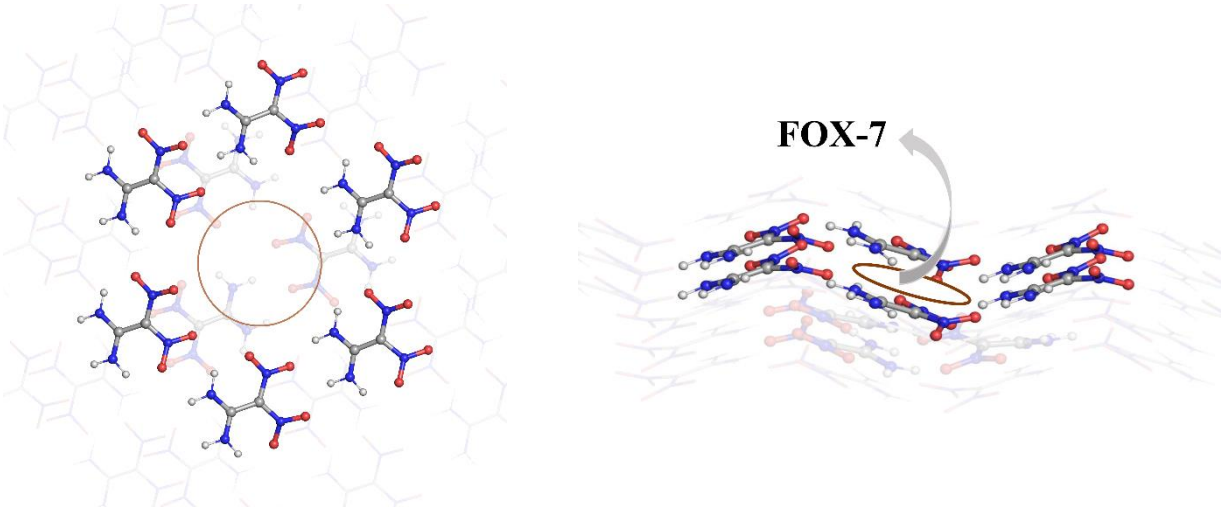


Figure S7: Representative figures showing desorption of one FOX-7 molecule from the surface. The brown circle represents the vacant site created after desorption of the FOX-7 molecule.

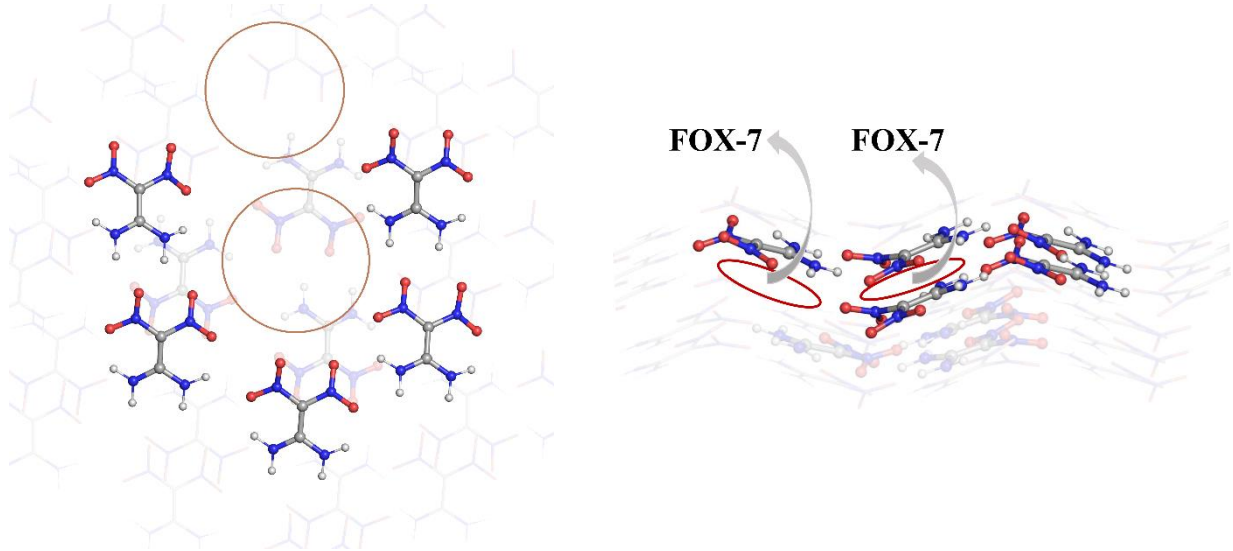


Figure S8: Representative figures showing desorption of two FOX-7 molecules from the surface. The brown circles represent the vacant sites created after desorption of the FOX-7 molecules.