

## ?-Holes promote the concertedness in nucleophilic aromatic substitution reactions of nitroarenes

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The mechanism of the S<sub>N</sub>Ar reactions between 1-halo-2,4-dinitrobenzenes and amines was revisited by means of DFT calculations. Remarkably and contrary to the traditional text-book perspective, the dehalogenation of 1-X-2,4-dinitrobenzenes bearing good leaving groups (X = Cl, Br and I) by soft nucleophiles involves a single-step mechanism passing through a barrierless C-X bond cleavage step. Solely the reaction of 1-fluoro-2,4-dinitrobenzene follows the traditional addition-elimination pathway. The analysis of the charge transfer patterns along the reaction path for the whole systems studied suggests that for those nitroarenes exhibiting ?-holes the dehalogenation mechanism occurs through a single-step. Nucleophile effects on the reaction rates were also discussed.