Computational Study of Substituent Effects on the Decomposition of 2H-Tetrazoles

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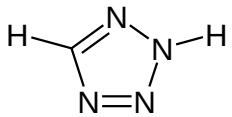
2H-Tetrazoles allow for the photochemical and thermal release of N_2 to generate nitrilimines, R^1–CNN–R^2. Our long-term aim is to generate nitrilimines with large carbene-character; for experimental purposes, it is thus useful to establish first computationally which substituents lead to a well-defined decomposition (neither explosive nor energetically inaccessible). It has been suggested that N-substitution is the determining factor for this. In addition, in disubstituted 2H-tetrazoles, we have shown previously that C-substitution might be responsible for a switch from concerted (electron donating groups) to stepwise (electron withdrawing groups) decomposition, yet a clear trend was not observed. In the stepwise decomposition, the N–N bond breaks first, with TS1 as the corresponding transition state. By following the decomposition of selected monosubstituted 2H-tetrazoles, we have now found several linear relations with Hammett σ^+ constants. This systematic approach has shown the larger the Hammett σ^+ constant, the larger the difference in relative energy between TS1 and the concerted TS, with this effect more pronounced for C-substitution.



Parent 2H-tetrazol, showing positions for C and N substitution.