

Hydrogen Abstraction-Induced Ring Opening In Thiazolo[5,4-d]thiazole, Benzthiazole, and Thiazole

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The deprotonation of thiazole rings is a common method to achieve further modification of their structure. Attempts to perform this reaction on thiazolo[5,4-d]thiazole however, resulted in decomposition. The decomposition has raised questions as to why this structure breaks its ring structure while other thiazoles, such as benzthiazole and thiazole, form stable anionic intermediates. The hypothesis is that this reaction fails for thiazolo[5,4-d]thiazole due to rapid ring-opening decomposition of one of the thiazole rings upon deprotonation. To test this hypothesis the activation energy for ring openings of thiazolo[5,4-d]thiazole, benzthiazole, and thiazole itself have been calculated at the MP2/6-31+G** level of theory. The anion and isonitrile for all three species were optimized and their structures were confirmed with a frequency calculation. In order to find the transition states, coordinates of the optimized anion and isonitrile were used in QST2 Synchronous Transit-Guided Quasi-Newton (STQN) Method calculations. Frequency calculations confirmed that the structures were minima or maxima along the reaction path. Internal Reaction Coordinates (IRC) calculations were run to confirm that each transition state was on the reaction path. These calculations indicated that the activation energy for ring opening of benzthiazole and thiazole are similar and slightly larger than that of thiazolo[5,4-d]thiazole.

