

Substituent and Solvent Effects on the N₂-N₃ Hindered Rotation in *cis*-Triazenes

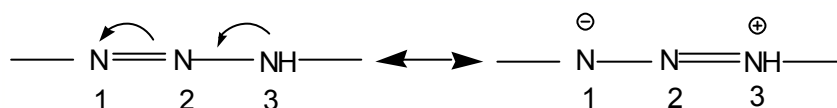
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Triazenes contain a diazoamino group and are photochromic materials that can reversibly change their configuration from *trans* to *cis* when excited. Due to their photochromic nature, they have been used as molecular switches in optical memory materials. Other applications for triazenes are widespread spanning the industrial and medicinal fields. They have been used in organic synthesis, the synthesis of dyestuffs, and in anti-cancer therapy.

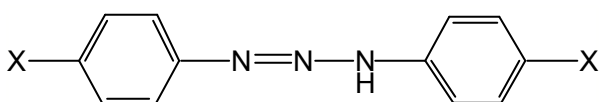
Based on a previous study from our group, it was determined that the thermal isomerisation process (*cis* to *trans*) in aqueous basic solution involves two steps:

- 1) a hindered rotation about the N₂-N₃ bond; and
- 2) a tautomerisation

The rotation about the N₂-N₃ bond is hindered due to its partial double bond character attributed to the delocalisation of the electrons shown below:



In this study, laser flash photolysis was used to determine the solvent effects on the N₂-N₃ hindered rotation in *cis*-1,3-diphenyltriazenes. The substituent effects on the rotation were also investigated for the symmetrically *p,p'*-disubstituted *cis*-1,3-diphenyltriazenes.



X = MeO, Me, H, Cl, CF₃

The rate constants for the restricted rotation were determined at various temperatures and the activation parameters (ΔH^\ddagger and ΔS^\ddagger) were found by plotting $\ln(k/T)$ vs. $1/T$ (Eyring equation).

It was seen that as the solvent polarity increased, the rate constants increased as well. Thus, the corresponding decrease in the energy of activation as the solvent became increasingly polar suggests the involvement of a polar transition state.

Regarding the substituent effects, as the functional group became increasingly electron-withdrawing, the ΔH^\ddagger increased. This can be rationalised by the increased double bond character of the N₂-N₃ bond attributed to predominant conjugation of the phenyl ring at the N₁ position.