JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 1057–1060
Published online 27 July 2004 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.824

Substituent and solvent effects on the N-2—N-3 hindered rotation of *cis*-1,3-diphenyltriazenes†

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Received 4 August 2003; revised 6 January 2004; accepted 14 January 2004

ABSTRACT: Laser-flash photolysis techniques were applied to investigate the dependence of the rotational barrier about the N-2—N-3 bond of symmetrically 4,4′-disubstituted *cis*-1,3-diphenyltriazenes on substituents and solvents. The increase in the rotational barrier with increasing ability of the 4-substituent to withdraw electrons implies the intramolecular process to be more susceptible to the electronic character of the aryl group attached to N-1 than of that bonded to N-3. Furthermore, the increase in the rotational barrier with decreasing solvent polarity implies an increase in dipole moment on rotation from the ground state to the transition state. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: triazenes; restricted rotation; rotational isomerism; rotational barrier; substituent effects; solvent effects

INTRODUCTION

Unsaturated compounds able to undergo reversible changes in double-bond configurations are subjects of interest for potential applications, among others, in molecular electronic devices.[1] Recent investigations from our laboratory have focused on the (reversible) isomerization mechanism of symmetrically 4,4′-disubstituted 1,3-diphenyltriazenes. Laser excitation of *trans*-1,3-diphenyltriazenes in aqueous media has been shown to lead to the instantaneous formation (i.e. within the time response of the nanosecond laser-flash photolysis system used) of the corresponding *cis*-1,3-diphenyltriazenes, which subsequently revert to the thermodynamically more stable *trans*-forms.[2,3] The thermal *cis*-to-*trans* isomerization is found to be catalyzed by general acids and general bases (Scheme 1). Acid catalysis (attributed to rate-limiting proton transfer to N-1) becomes more predominant as the electron-donating character of the aryl group increases, while base catalysis (attributed to rate-limiting base-promoted ionization of N-3) becomes dominant as the electron-withdrawing character of the aryl group increases.[3] The photoinduced *trans*-to-*cis* isomerization renders indeed a non-equilibrium mixture of *s-cis* and *s-trans* conformers of the corresponding *cis*-1,3-diphenyltriazene. Interestingly, the process ascribed to hindered rotation about the N-2—N-3 bond in *cis*-1,3-diphenyltriazenes (i.e. *s-cis* to *s-trans* conversion in Scheme 1) becomes rate controlling when working in aqueous NaOH solutions,[2,3] and preliminary kinetic data seem to indicate an increase in the rotational barrier with increasingly stronger electron-withdrawing aryl groups, and with decreasing solvent polarity.[3]

Restricted rotation about the N-2—N-3 bond of the triazeno (diazoamino) group is attributed to its partial double-bond character, as represented by the two resonance forms shown in Scheme 2. Hindered rotation of triazenes has been the subject of both experimental and theoretical studies.[4–12] However, with the exception of one theoretical study of triazene (H_2NNNH) and its methyl derivatives in the gas phase,[12] these conformational studies refer exclusively to restricted rotation in *trans*-triazenes; experimental data on hindered rotation in *cis*-triazenes were indeed unprecedented prior to our investigations. In the present paper, we report the results of a study of the influence of substituents and solvents on the energy barrier corresponding to the hindered rotation in *cis*-1,3-di(4-X-phenyl)triazenes (X = CH_3O, CH_3, H, Cl or CF_3) dissolved in aqueous media.

RESULTS AND DISCUSSION

Rate constants for hindered rotation in *cis*-1,3-di(4-X-phenyl)triazenes were determined upon laser excitation (at $\lambda = 355$ nm) of *trans*-1,3-di(4-X-phenyl)triazenes in aqueous NaOH solutions. In agreement with previous preliminary data, rate constants for hindered rotation are found to diminish (i) as the electron-withdrawing character of the 4-substituent increases, (ii) with decreasing polarity/hydrogen-bond donor (HBD) ability of the

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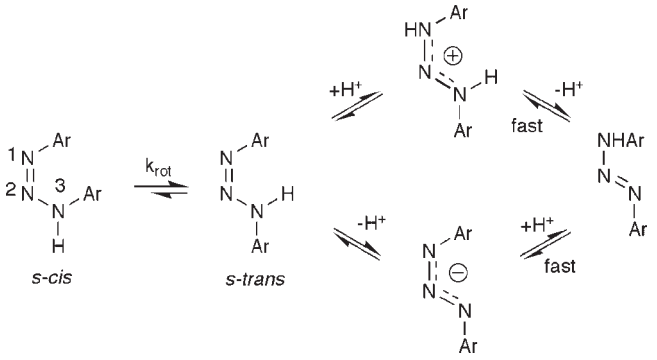
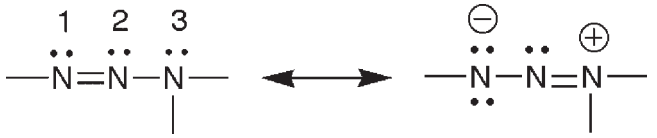
†Paper presented at the 9th European Symposium on Organic Reactivity, 12–17 July 2003, Oslo, Norway.
Contract/grant sponsor: Natural Sciences and Engineering Research Council of Canada.



Scheme 1



Scheme 2

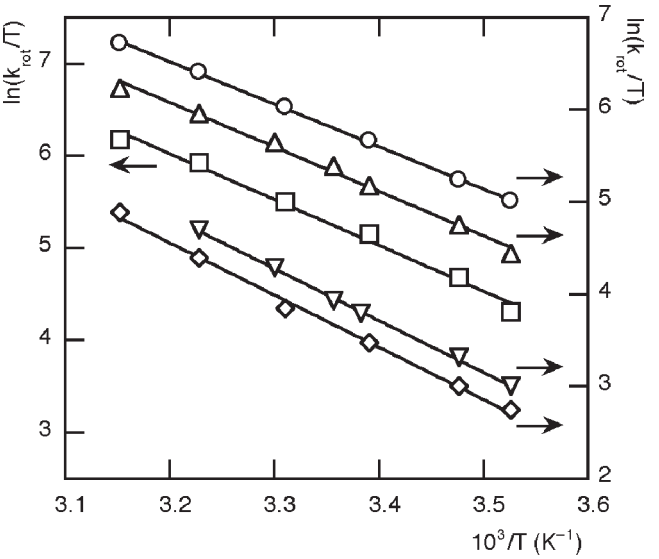


Figure 1. Eyring plot for N-2—N-3 restricted rotation in *cis*-1,3-di(4-X-phenyl)triazene in 30% THF–H_2O solution [X = CH_3O (O), CH_3 (Δ), H (□), Cl (▽), and CF_3 (◇)]

organic co-solvent and (iii) with increasing co-solvent concentration (Table 1).

In order to obtain the activation parameters corresponding to N-2—N-3 restricted rotation, rate constants for hindered rotation were determined at different temperatures. From the data shown in Fig. 1 for 30% THF–H_2O solutions, it is found that the activation free energy and activation enthalpy both increase with increasing electron-withdrawing character of the 4-substituent (Table 2). While no study exists on the effects of disubstitution at N-1 and N-3 in *trans*-triazenes, a progressive decrease in the rate of hindered rotation for a number of *trans*-1-aryl-3,3-dialkyltriazenes with increasing electron withdrawal of the aryl group has indeed been reported.[4,10a] With respect to solvent effects on hindered rotation, from the data displayed in Fig. 2 for THF–H_2O solutions of 1,3-diphenyltriazene (i.e. X = H) of different co-solvent composition, it is found that the activation free energy and activation enthalpy both increase with increasing organic co-solvent concentration (Table 3, first three entries). Likewise, for a given co-solvent percentage (i.e. 30% v/v), the activation free energy is found to decrease with increasing solvent polarity (Fig. 2 and Table 3, last three entries), although the dependence of activation enthalpy on the type of solvent is not clear. It should be pointed out here that a similar solvent effect (i.e. increase in activation energy with decreasing solvent polarity) has been reported for a number of *trans*-1-aryl-3,3-dialkyltriazenes; values for $\Delta G^{\ddagger}$ in $CDCl_3$ are found to be smaller than in CS_2.[6] Finally, the activation entropy (if at all significant) is in all cases consistently small (Tables 2 and 3), indicating that the rotation process is not associated with considerable entropy changes between the transition state and the ground state in any case.

The increase in activation free energy and in activation enthalpy, observed experimentally with increasingly stronger electron-withdrawing groups, correlates very well with the shortening of the N-2—N-3 bond of the *s-cis* conformer predicted by means of AM1 semiempirical

Table 1. Rate constants for N-2—N-3 restricted rotation in *cis*-1,3-di(4-X-phenyl)triazene in aqueous solutions of different co-solvent composition

	k_{rot} (10^5 s^{-1})[a]				
Substituent	MeOH	DMSO	AN	2-PrOH	THF
CH_3O[b]	4.4 ± 0.1	2.94 ± 0.08	2.8 ± 0.1	2.54 ± 0.08	1.00 ± 0.02
H[b]	3.4 ± 0.2	1.94 ± 0.09	1.62 ± 0.04	1.59 ± 0.06	0.56 ± 0.02
H[c,d]	n/a	2.5 ± 0.1	2.25 ± 0.06	2.44 ± 0.09	1.26 ± 0.08
H[c,e]	3.54 ± 0.07	2.8 ± 0.1	2.8 ± 0.1	3.0 ± 0.1	2.7 ± 0.2
CF_3[c]	0.54 ± 0.05	0.31 ± 0.01	0.28 ± 0.01	0.166 ± 0.002	0.098 ± 0.006

[a] Values correspond to averages from at least five independent kinetic runs. Aqueous solution contains 30% organic co-solvent, unless indicated otherwise; $T = 21\,^{\circ}C$; $\mu = 0.5$ M (NaCl).
[b] Values taken from Ref. 3.
[c] This work.
[d] Aqueous solution contains 20% organic co-solvent.
[e] Aqueous solution contains 10% organic co-solvent.

Table 2. Activation parameters for N-2—N-3 restricted rotation in *cis*-1,3-di(4-X-phenyl)triazene in 30% THF–H_2O solution,[a] and N-2—N-3 bond lengths calculated by AM1

Substituent	$\Delta H^{\ddagger}$ (kcal mol^{-1})[b]	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ (kcal mol^{-1})[c]	Bond length (pm)[d]
CH_3O	9.1 ± 0.1	-5.0 ± 0.4	10.6 ± 0.1	134.8 (139.8, 138.1)
CH_3	9.6 ± 0.4	-5 ± 1	11.1 ± 0.3	134.3 (139.7, 138.4)
H	9.9 ± 0.5	-4 ± 2	11.1 ± 0.8	134.2 (139.7, 138.1)
Cl	11.2 ± 0.2	-1.8 ± 0.7	11.7 ± 0.2	134.0 (139.7, 138.1)
CF_3	11.3 ± 0.4	-2 ± 1	11.9 ± 0.3	133.4 (139.6, 137.9)

[a] $\mu = 0.5$ M (NaCl).
[b] 1 kcal = 4.184 kJ.
[c] 21 °C.
[d] Bond length for *s-cis* conformer. Values in parentheses correspond to TS1 and TS2, respectively.

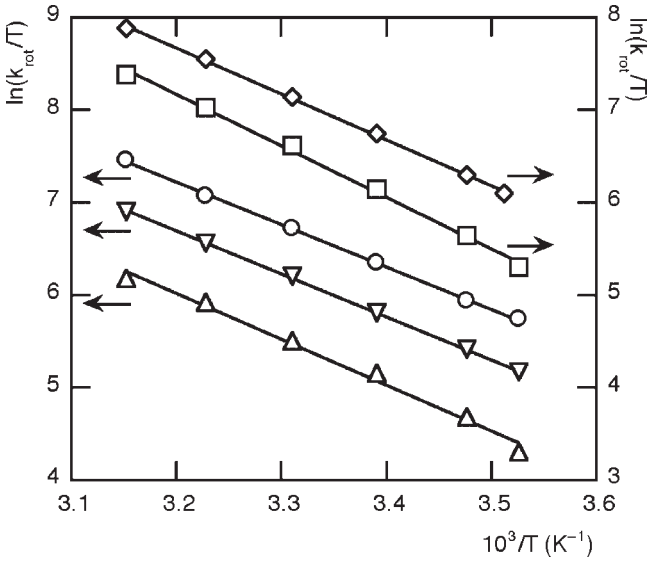


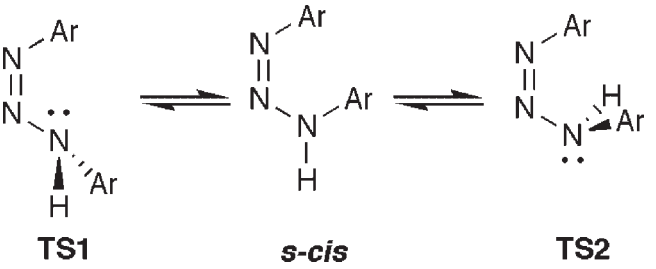
Figure 2. Eyring plot for N-2—N-3 restricted rotation in *cis*-1,3-diphenyltriazene in aqueous solutions of different co-solvent composition: 30% MeOH (◇), 30% AN (□), 15% THF (O), 20% THF (▽), and 30% THF (Δ)

Table 3. Activation parameters for N-2—N-3 restricted rotation in *cis*-1,3-diphenyltriazene in aqueous solution[a]

Co-solvent	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ (kcal mol^{-1})[b]
15% THF	9.1 ± 0.1	-3.6 ± 0.4	10.2 ± 0.2
20% THF	9.2 ± 0.1	-4.4 ± 0.3	10.5 ± 0.1
30% THF	9.9 ± 0.5	-4 ± 2	11.1 ± 0.8
30% AN	11.1 ± 0.3	2 ± 1	10.5 ± 0.4
30% MeOH	9.9 ± 0.4	-0.6 ± 0.5	10.1 ± 0.4

[a] $\mu = 0.5$ M (NaCl).
[b] 21 °C.

calculations (Table 2). Two *ab initio* studies of conformations of triazene (H_2NNNH) in the gas phase reported two possible transition states for rotation around the N-2—N-3 bond.[8,12] In these structures the hydrogens on N-3 are bisected by the symmetry plane, and the lone pair on N-3 is either *anti* or *syn* to the N-1═N-2 double bond. Similarly, AM1 semiempirical calculations predict two possible transition states for rotation about the N-2—N-3 bond of the *s-cis* conformer of *cis*-1,3-diphenyltriazene, i.e. the unshared pair of electrons at N-3 being *syn* (TS1)



Scheme 3

or *anti* (TS2) to the diazo group (Scheme 3). As shown in Table 2, essentially no change in the N-2—N-3 bond length in TS is predicted with 4-substitution at the AM1 level, thus changes in the rotational barrier with 4-substitution reflect a change in the N-2—N-3 bond length in the *s-cis* conformer.

The increase in activation energy observed experimentally with decreasing polarity/HBD ability of the organic co-solvent, and with increasing organic co-solvent concentration, clearly indicates the involvement of a transition state more polar than the ground state *s-cis* conformer. A theoretical study on amide transition states has shown a general correlation between dipole moment and solvation,[13] and differential solvation has been invoked to interpret the increase in the rotational barrier of amides with solvent polarity,[14] and the lack of solvent effects in the rotational barrier of carbamates.[15] Future theoretical (*ab initio*) studies will be aimed at describing the solvation effects on hindered rotation in *cis*-1,3-phenyltriazenes.

In summary, this is the first documented example of a systematic study on the influence of medium and structure on the rotational barrier of *cis*-1,3-di(4-X-phenyl)-triazenes. The increase in the rotational barrier about the N-2—N-3 bond observed experimentally with increasingly stronger electron-withdrawing groups implies the intramolecular isomerization process to be more susceptible to the electronic character of the aryl group attached to N-1 than of that bonded to N-3. Furthermore, the increase in the rotational barrier about the N-2—N-3 bond observed experimentally with decreasing polarity/HBD ability of the organic co-solvent, and with increasing organic co-solvent concentration, clearly indicates an

increase in dipole moment on rotation from the ground state *s-cis* conformer to the transition state.

EXPERIMENTAL

Symmetrically 4,4′-disubstituted *trans*-1,3-diphenyltriazenes employed were existing samples from a previous study.[3] Kinetic studies were carried out in aqueous NaOH solutions (typical NaOH concentrations ranged from 0.01 to 0.2 M) having an organic co-solvent; the ionic strength of these solutions was kept constant at 0.5 M using NaCl as the compensating electrolyte. Solutions were prepared using analytical-reagent grade salts, water purified in a Millipore apparatus, and spectrophotometric grade organic solvents (EM Science, Omnisolv grade).

Laser experiments were carried out using a Nd:YAG laser (Continuum, Surelite I-10) operated at $\lambda = 355$ nm (4–6 ns pulses, <15 mJ per pulse) for excitation. Samples were contained in quartz cells constructed of 7×7 mm^2 Suprasil tubing. Further details on the time-resolved laser-flash photolysis system employed in this study are reported elsewhere.[16] All measurements were carried out at 21 ± 1 °C.

Observed rate constants were obtained by first-order fittings using the general curve-fitting procedure of Kaleidagraph 3.0.5 software from Abelbeck Software. Molecular modeling calculations were carried out using the AM1 method as implemented in the Gaussian 03M program.[17]

Acknowledgment

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Thanks are due to Professor A. Pierini and Mr. S. Allende (Universidad Nacional de Córdoba) for valuable discussions and assistance regarding AM1 calculations.

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