NMR STUDY OF HINDERED ROTATION IN 1-ARYL-3,3-DIMETHYLTRIAZENES

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Abstract—Temperature dependent NMR spectra have been observed for a series of para-substituted 1-aryl-3,3-dimethyltriazenes, 3. The temperature dependence has been interpreted in terms of restricted internal rotation about the N₂,N₃ bond of these triazenes and activation parameters ΔF^4 , ΔH^4 , and ΔS^4 have been calculated from the spectral data. The origin of the rotational barrier is considered to lie in partial double bond formation between N₂ and N₃ due to the contribution of 1,3-dipolar resonance hybrids to the ground states of these triazenes. This interpretation is supported by a sizable substituent effect $\rho = -2.1$ for the rotational process in the series studied. Chemical shift data at low temperatures indicates a stereospecific association of benzene with the triazenes studied which places the benzene ring closer to the *trans* N-Me group in the 1,3-dipolar resonance hybrid.

AMINE derivatives which possess π -conjugative systems directly attached to nitrogen (1) exist partially as the 1,3-dipolar resonance structures 2 and may be represented as 3. An observable effect of such resonance hybridization is an increase in the

$$\begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ -\underline{Y} \\ \times -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ -\underline{Y} \\ \times -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ -\underline{Y} \\ \times -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ -\underline{Y} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times} \\ \underbrace{\times} \\ -\underline{N} \\ \end{array} \xrightarrow{} \begin{array}{c} \stackrel{|}{\xrightarrow{}} \\ \underbrace{\times} \\ \underbrace{\times}$$

effective barrier to rotation about the X—N bond. This occurs to an appreciable extent in derivatives in which the dipolar resonance structures 2 are stabilized by the presence of electronegative elements or substituents at the position of Y. Amine derivatives such as amides¹ (X = C, Y = O), nitrosamines² (X = N, Y = O), enamines³ (X = Y = C), hydrazones³ (X = N, Y = C), and amidines⁴ (X = C, Y = N) exist to a sufficient extent in the 1,3-dipolar structure, 2, to cause the barrier to rotation about the X—N bond to be measurable by NMR techniques.

We have found that 1-aryl-3,3-dimethyl triazenes (4) produced upon the coupling of aryl diazonium salts with dimethyl amine⁵ are excellent models for the study of the 1-+2 resonance hybridization. Each of the *para*-substituted triazenes listed in Table 1 exhibited temperature variable NMR spectra which were interpretable in terms of hindered internal rotation about the N₂, N₃ bond of 4. The N-Me signals in the NMR spectra of the triazenes studied (see Table 1) appeared as a single peak at room temperature. At lower temperatures the signals broadened and eventually emerged as two distinct signals of equal intensity. This type of temperature dependence may be described, *vide infra*, as a case of hydrogen exchange between two sites with equal populations and lifetimes. The temperature dependence was examined

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TABLE 1 CHEMICAL SHIFTS AND COALESENCE TEMPERATURES OF TRIAZENE N-METHYL HYDROGENS

para-Substituent	Tc _{CDCI} ,	δ vs TMS Room Temp (37°)			δ vs TMS (-56°)			
		CDCl ₃	C2D3OD	C₅H₅	CDCl,	C2D,OD	C°H°	
OCH,	-44°	192-0	192	172	207·5 188	201 184		
СН3	- 31.5	192-0	192	172	205-5 186-5	200-5 189-5		
н	-23.5	193	190	170	206 187	198-5 181-5		
Cl	-13	195	193	169	208-5 188-5	208 * 191*	168-5° 163-5°	
NO ₂	+37°	205	214	166	216 ⁶ 196 ⁶		165-8 ⁴ 158-5 ⁴	

▲ At - 20°

▶ At -5°

' At -3.5° (signals not well resolved)

4 At 6°

by the line width method above and below the coalesence temperatures. The rates of the exchange process were estimated above the coalesence temperatures using Eq. 1.^{2,6} In this equation Δv is the separation of the N-Me signals when the rate

$$k = \pi \Delta v^2 / 2W \tag{1}$$

process is slow and W is the exchange broadening, i.e. the width of the Me signals at half height. When it was apparent that the separation of the Me signals varied with temperature, Δv was plotted as a function of temperature and Δv was obtained at each temperature from the plot. The observed exchange broadening was corrected for natural line width by subtracting from it the line width of the TMS signal at the same temperature. Since at high temperature (where exchange is rapid) the width of the N-Me signals approached the width of the TMS signals at the same temperature, no correction was necessary for broadening of the N-Me signals by unresolved long range coupling. At the coalescence temperatures the rates of exchange were calculated from Eq. 2 and below the coalescence temperature k was calculated using Eq. 3.^{2, 6} The exchange broadening term W in Eq. 3 was corrected as described for the high temperature determinations. Although this method of obtaining exchange rates from the NMR spectra is not as accurate as complete line-shape matching, we feel the rates obtained by this method are sufficiently precise for the present study.

$$k = \pi \Delta v / \sqrt{2} \tag{2}$$

$$k = \pi W \tag{3}$$

If the present N-Me interchange is treated as a typical rate process, the temperature dependence of the rate constant, k for the interchange may be expressed by the Eyring rate Eq. 4.

$$k = \frac{KfT_e}{h} - \exp\left(-\Delta F^{\ddagger}/RT\right)$$
(4)

The transmission coefficient (f) in this equation is assumed to be unity since the transition state for the interconversion represents the conformation about the N₂, N₃ bond in which any *p*-orbital overlap between these atoms is minimal. This conformation thus represents the energy maximum in the potential energy curve for the N₂-N₃ rotation.^{7,8} Substitution of numerical constants and f = 1 into Eq. 4 followed by rearrangement gives Eq. 5. Since $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, Eq. 4 may be expanded to Eq. 6.

$$\Delta F^{\ddagger} = 4.58 \ T(10.32 + \log_{10} T/k) \tag{5}$$

$$\log_{10} k/T = 10.32 + \frac{\Delta S^{*}}{2.3 R} - \frac{\Delta H^{*}}{2.3 RT}$$
(6)

For the purposes of comparison of different triazenes the free energy of activation (ΔF^{\ddagger}) was calculated (Eq. 5) at a single temperature (298° A) for all triazenes. Plots of log k/T vs 1/T yielded straight lines (Fig. 1) from which the activation enthalpy ΔH^{\ddagger} and activation entropy ΔS^{\ddagger} were calculated (Eq. 6). Errors in these determinations were estimated by drawing lines of maximum and minimum slope containing between them all the experimental points. The values for ΔF^{\ddagger} , ΔH^{\ddagger} , and ΔS^{\ddagger} reported in Table 2 are the means of the values calculated in this manner.

DISCUSSION

Triazenes of type 4 are azo derivatives and as such may undergo *cis-trans* isomerization about the azo linkage. This process would produce NMR spectra in which the N-Me hydrogens resonate at different magnetic fields. Furthermore, this process would be expected to be temperature dependent. We feel that this process is not the origin of the temperature dependence in the NMR spectra of triazenes because the exchange process which is observed involves exchange of the N-Me hydrogens between two equally probable sites with equal lifetimes. This would not be the case if *cis-trans* isomerization of 4 were being observed since the sterically less hindered *trans* isomers of 4 (shown) are the more stable.⁹ In support of this conclusion are X-ray crystallographic studies of p,p'-dibromodiazoaminobenzene which show it to be *trans* in the solid state.¹⁰ Finally, the observation that the signals



FIG. 1 Plots of log k/Tvs 1/T for 4, $X = NO_2 (O)$, X = H(+) and $X = OCH_3(\times) CDCl_3$ solution.

due to the aromatic hydrogens are not temperature dependent indicates the rate process is not *cis-trans* isomerization about the azo linkage.

The observed temperature dependence of the NMR spectra of the triazenes studied is most easily interpreted in terms of hindered internal rotation about the N_2 , N_3 bonds of these compounds. This process would give rise to temperature dependent spectra resulting from variation in the rate of transposition of the N-methyls about the azo linkage of 5. Furthermore, this process would be expected to involve interchange of the N-Me hydrogens between two equally probable sites with equal lifetimes as was observed.

At a given temperature the observed differences in the rates of internal rotation about the N₂, N₃ bonds of the *para*-substituted triazenes studied are interpreted in terms of the ability of the *para*-substituents to stabilize the 1,3-dipolar form 5 of these compounds.* This form represents the ground state for the rotation process whereas the transition state is represented by the conformation about the N₂, N₃ bond in which the *p*-orbitals on these atoms are perpendicular and they are thus singly bonded. The chemical shift of the N-Me signals of the substituted triazenes when rotation is fast (room temp) gives an indication of the transmission of inductive effects of the substituents through the N₂, N₃ single bond. The data in Table 1 reveals these effects to be rather small.

Transition state theory considers the transition state in a rate process as being in equilibrium with the ground state. Thus estimates of rate constants in the present

^{*} The dipole moments of the triazenes studied increases markedly as the aryl ring is substituted with electron withdrawing groups. This increase has also been ascribed to the increased contribution of the 1,3-dipolar form 5 to the ground state of these compounds upon such substitution (Ref. 9).

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para-Substituent	$\Delta F^{1_{296}}$ (kcal/mole)	ΔH ¹ (kcal/mole)	ΔS ¹ (eu)	ΔF^{1}_{298} (kcal/mole)	ΔH^{t} (kcal/mole)	ΔS [‡] (eu)	ΔF [‡] 296 (kcal/mole)	ΔH [‡] (kcal/mole)	ΔS [‡] (eu)
OCH,	12·7±04	7:4±0.5	- 16·1±2·3	13-1±0-3	6-5±0-5	-21·6±2·5			
сн,	130±03	9-4±0-5	-11.5±2.3						
H	13·7±03	8:7±0-5	-16.8±2.3	13-6±0-4	9-7±0-7	-12:2±4:6			
ס	13-9±0-2	7.8±0.5	-21·2±2·8	14.6 ± 0.2	14-0+3-7	-104 + 0.9			
NO1	15.7±02	11-7±1-1	-12·7±4·1				16·1±0-3	13·1±0-9	-9.4±1.6

case are equivalent to estimates of free energy differences between the various species considered above. Accordingly the present rate process exhibits a linear Hammett relationship with a clear retardation of the process by electron-withdrawing substituents (Fig. 2).¹¹



FIG. 2 Correlation of log k_x/k_H and σ_x for the N-methyl interchange in triazenes of type 4.

The N-Me hydrogens which resonate at higher magnetic field in each of the substituted triazenes studied are assigned to the position in the 1,3-dipolar form 5 cis to the N atom bearing the negative charge.¹² These hydrogens appear about 0.3 ppm higher field than those N-Me hydrogens trans to this N when the low temperature spectra are observed in deuterochloroform (Table 1). Dilution of deuterochloroform solutions of the *p*-nitrophenyl and *p*-chlorophenyltriazenes with benzene caused the resonances assigned to the trans N-Me hydrogens to shift to higher field more rapidly than those of the corresponding cis (Fig. 3). The high coalesence temperature of the p-nitrophenyltriazene allowed determination of the chemical shift difference between the two N-Me signals in benzene solution. Inspection of the NMR spectrum of this derivative in benzene solution at 0° revealed the trans-N-Me hydrogens shifted upfield by 0.9 ppm whereas the cis-N-Me hydrogens were shifted by 0.6 ppm. Such a change is consistent with stereospecific association of benzene with the triazenes in such a manner as to place the benzene ring closer to the trans than to the *cis* hydrogens. Such a situation is depicted in $\mathbf{6}$ and has been elegantly employed by Karabatsos and Taller to account for analogous solvent shifts in the NMR spectra of N,N-dialkyl nitrosamines.¹² Similar effects have been observed in the NMR spectra of amides.¹³



FIG. 3 Plot of Δv for the N-methyl signals of 4, $X=NO_2$ (C) at 0°C and X=CI (Δ) at -28°C, as a function of mole per cent C_6H_6 in CDCl₃.

EXPERIMENTAL

Mps were obtained on a Fisher-Johns m.p. block and are uncorrected. UV spectra were measured with a Cary 14 spectrometer. Analyses were performed by Alfred Bernhardt Microanalytical Laboratory in Mulheim, West Germany.

NMR spectra. NMR spectra were determined on a Varian A 56/60 spectrometer equipped with a variabletemp accessory. The temps were determined with the aid of the Varian methanol and glycol sample and shift-temp correlation charts and are accurate to within $\pm 2^{\circ}$ in their absolute values.

Preparation of 1-aryl-3,3-dimethyltriazenes. The 1-aryl-3,3-dimethyltriazenes studied were prepared by coupling variously substituted aryl diazonium salts with Me_2NH in buffered aqueous soln according to Procedure F of ref. 5. The yield in these coupling reactions ranged from 75–90%. Each triazene was extracted in ether soln and purified according to its properties, i.e. distillation under vacuum or crystallization from ether-petrol soln. Relevant data are recorded below in Table 3.

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		$\lambda \max(\log_{10} s)$ hexane		Ana Calc.		alyses Found	
Ar	M.P. (b.p./mm)	[Lit. ⁹ λ _{max} (log ₁₀ ε) ethanol]	Formula	С	Н	С	н
p-anisyl	(59/0-75) Lit. [•] (174–177/29)	286 (4·24), 322 (4·17) [288 (4·12), 324 (4·17)]	C ₉ H ₁₃ N ₃ O	60-32	7.31	59 ·74	7.37
p-tolyl	46·5-47·5° Lit. ¹⁴ 50-51°	286 (4·17), 322 (4·17) [285 (4·15), 324 (4·07)]	C ₉ H ₁₃ N ₃	66·23	8-03	66·55	8·39
phenyl	(125°/8) Lit. ¹⁵ (125–127/19)	286 (4·15), 303 (4.11) [285 (4·14), 308 (4·11)]	C ₈ H ₁₁ N ₃	64·40	7.43	63·60	7∙46
p-chloro- phenyl	55–56° Lit. ⁹ (164–166/27)	286 (4·18), 311 (4·10) [287 (4·18), 314 (4·15)]	C ₈ H ₁₀ ClN ₃	52·26	5.49	52·49	5.83
<i>p</i> -nitro- phenyl	143144° Lit. ¹⁵ 144145°		C ₈ H ₁₀ N ₄ O ₂	49·48	5.19	49· 4 6	5 ∙30

TABLE 3 PROPERTIES OF TRIAZENES $Ar - N = N - N < CH_3$

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