# The Effect of Electron-withdrawing Substituents on the Tautomerism between 1-Aryl-3-Methyltriazenes and 3-Aryl-1-methyltriazenes

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Variable-temperature n.m.r. spectroscopic studies show that 1-aryl-3-methyltriazenes with strongly electron withdrawing *para*-substituents exist in a state of tautomeric equilibrium, $ArN=N \cdot NHMe \rightleftharpoons ArNH \cdot N=NMe$. Similar study of 3-methyl-1-*p*-tolyltriazene shows the presence of only the conjugated tautomer, $p\text{-}MeC_6H_4 \cdot N=N \cdot NHMe$, whereas arylmethyltriazenes with strongly electron-withdrawing *ortho*-substituents exist as the non-conjugated tautomer, $ArNH \cdot N=NMe$.

IN a previous communication,[1] the formation of 1-aryl-3-methyltriazenes by coupling of arenediazonium salts with methylamine was found to be affected by the nature of the substituent in the aryl group. Here we report a more detailed study of the spectral characteristics of these 1-aryl-3-methyltriazenes, which suggests that the nature, and position of the substituent in the aryl group also has an effect on the tautomeric equilibrium,

$$ArN=N \cdot NHMe \rightleftharpoons ArNH \cdot N=NMe$$
$$\text{(I)} \qquad\qquad \text{(II)}$$
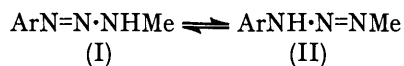
Hadzi and Jan [2] studied the NH stretching bands in the i.r. spectra of several 3-alkyl-1-aryltriazenes and concluded that the tautomeric equilibrium was shifted in favour of the unconjugated tautomer (II) by the presence of electron-withdrawing substituents. Similar observations have been recorded for the diaryltriazenes (III)/(IV). In these the presence of a $-I, -M$ group in the *para*-

position of one aryl group favours tautomer (III) whereas $+M$ groups, whether *meta*- or *para*- to the triazene bridge, favour tautomer (IV).[3] More recently, Isaacs

$$XC_6H_4 \cdot NH \cdot N=NPh \rightleftharpoons XC_6H_4 \cdot N=N \cdot NHPh$$
$$\text{(III)} \qquad\qquad\qquad \text{(IV)}$$
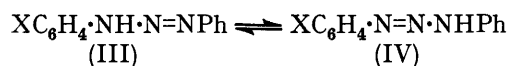
and Rannala [4] have suggested that 3-methyl-1-*p*-tolyltriazene (VIIa) exists in a state of rapid tautomeric equilibrium at room temperature, but conclude from low-temperature n.m.r. measurement that the conjugated tautomer, $p\text{-}MeC_6H_4 \cdot N=N \cdot NHMe$, is the more stable form.

## RESULTS AND DISCUSSION

Assignment of chemical shifts in the tautomers (I) and (II) should be greatly facilitated by comparison with the model compounds (V) and (VI) respectively, in which the location of the N=N group is fixed by the trisubstitution pattern. 3,3-Dialkyl-1-aryltriazenes (V) are readily

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[1] T. P. Ahern and K. Vaughan, *J.C.S. Chem. Comm.*, 1973, 701.

[2] D. Hadzi and J. Jan, *Spectroscopy Letters*, 1968, **1** (3), 139—143.

[3] T. Mitsuhashi and O. Simamura, *Chem. and Ind.*, 1964, 578; S. Weckherlin and W. Leuttke, *Tetrahedron Letters*, 1964, 711; Rodd's 'Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier Publishing Co., Amsterdam, 1973, vol. IIIc, p. 92.

[4] N. S. Isaacs and E. Rannala, *J.C.S. Perkin II*, 1974, 899.

available from the reaction of diazonium salts with secondary amines.[5] 1-$p$-Bromophenyl-3,3-dimethyltriazene [6] displayed sharp $N$-methyl proton resonance at δ 3.25, in
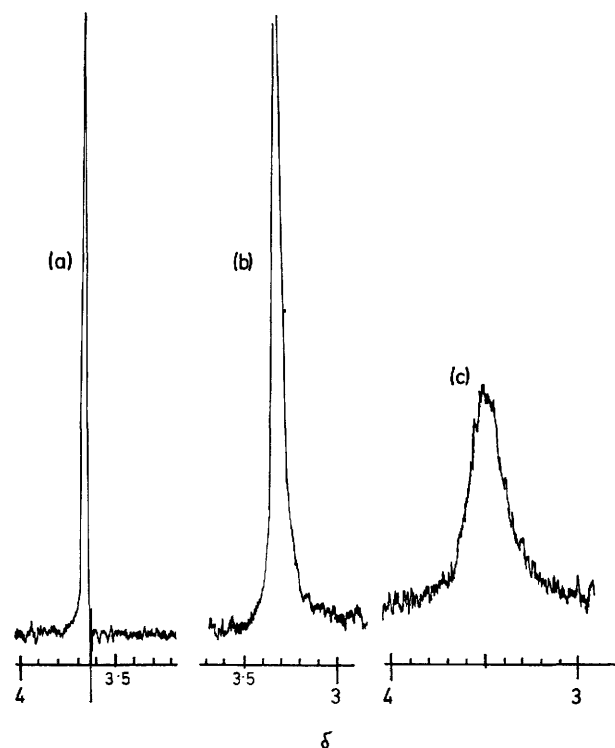


FIGURE 1  $N$-Methyl proton magnetic resonance spectra of (a) 1-methyl-3-($o$-nitrophenyl)triazene, (b) 3-methyl-1-($m$-nitrophenyl)triazene, and (c) 3-methyl-1-($p$-nitrophenyl)-triazene at ambient temperature in deuteriochloroform (saturated solutions)

close agreement with the value reported [7] for 1-phenyl-3,3-dimethyltriazene (δ 3.23). By contrast, model compounds of type (VI), 1-alkyl-3,3-disubstituted triazenes, are unknown.

$$ArN=N-NMe_2 \qquad ArNR-N=NMe$$
$$(V) \qquad\qquad (VI)$$
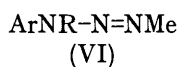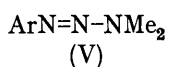
The $para$-substituted 1-aryl-3-methyltriazenes (VIIb—e) display $N$-methyl-proton resonances in the range δ 3.4—3.5 (Table), which are substantially broadened at room temperature (e.g. Figure 1c). The $meta$-nitrophenyltriazene (VIIf) also displays broad $N$-methyl proton resonance (Figure 1b). The $N$-methyl proton resonance in the $ortho$-substituted triazenes (VIIg—j) are significantly further downfield, ca. δ 3.6 than those of the $para$-isomers. Moreover, the $N$-methyl proton resonances of the $ortho$-derivatives are sharp (e.g. Figure 1a), being comparable in line width to that observed for the $p$-tolyltriazene (VIIa) and the 3,3-dimethyltriazene (V).

The broadness of the $N$-methyl proton resonance in the $meta$- and $para$-substituted triazenes (VIIb—f) strongly suggests that these triazenes are in a state of rapid tauto-

[5] A. Baeyer and C. Jaeger, Ber., 1875, **8**, 149.
[6] L. Hunter, J. Chem. Soc., 1937, 320.
[7] Sadtler Index of N.M.R. Spectra, 1968, # 4499M.

meric equilibrium at room temperature, giving rise to chemical shifts intermediate between the $N$-methyl proton resonances expected for tautomers (I) and (II). Evidence for this hypothesis is seen in the n.m.r. spectrum of the $p$-cyano-derivative (VIIb) in the region of $N$-methyl proton resonance (3—4 p.p.m.), which changes

Spectral characteristics of the 1-aryl-3-methyltriazenes
$$XC_6H_4 \cdot N=N \cdot NHMe \text{ (VII)}$$

| Substituent (X) | N—Me proton resonance (δ, room temp.) | I.r. absorption (cm$^{-1}$) (1 400—1 500 cm$^{-1}$ range) |
|---|---|---|
| (a) $p$-Me | 3.17 (sharp) * | 1 410w, 1 435s |
| (b) $p$-CN | 3.40 (broad) † | 1 415w, 1 482s |
| (c) $p$-Ac | 3.43 (broad) † | 1 420m, 1 485w |
| (d) $p$-CO$_2$Me | 3.38 (broad) † | 1 430s, 1 480w |
| (e) $p$-NO$_2$ | 3.50 (broad) † | 1 480m |
| (f) $m$-NO$_2$ | 3.31 (broad) ‡ | 1 430s, 1 470s |
| (g) $o$-NO$_2$ | 3.65 (sharp) * | 1 405w, 1 490s |
| (h) $o$-CO$_2$Et | 3.57 (sharp) * | 1 410w, 1 495s |
| (j) $o$-Ac | 3.63 (sharp) * | 1 490m |

* Line width in range 1—1.5 Hz.  † Line width in range 3.5—12 Hz.  ‡ Line width 3 Hz.

dramatically as the temperature is lowered (see Figure 2). At +20 °C two distinct signals of approximately equal intensity are evident, and at −30 °C the downfield signal sharpens to a singlet (δ 3.62) whereas the upfield signal shows as a distinct doublet (δ 3.22).

These observations demonstrate conclusively the presence of both tautomers of the $p$-cyano-derivative. The singlet methyl at δ 3.62 must be that of the non-conjugated tautomer (II) whereas the methyl signal of tautomer (I) appears at δ 3.22 as a doublet, owing to coupling with the adjacent NH proton. The NH proton resonances of the tautomers become distinct at δ 8.4 and 9.8 at
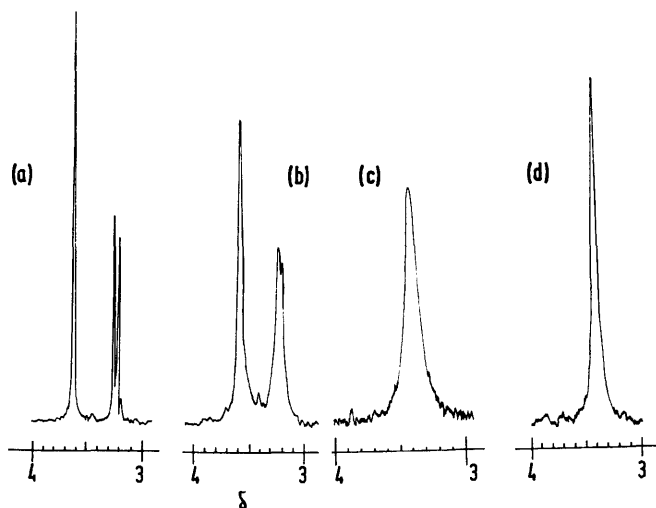


FIGURE 2  $N$-Methyl proton magnetic resonance spectra of 1-($p$-cyanophenyl)-3-methyltriazene at (a) −30 °C, (b) +20 °C, (c) room temperature, and (d) +55 °C

−30 °C; however, both signals are broadened to the extent that the multiplicity is hidden. Above room temperature, the N—Me proton resonance of (VIIb) sharpens considerably (Figure 2), indicating an increase in the rate of the tautomeric equilibrium.

The absence of line-broadening of the $N$-methyl proton resonance in the n.m.r. spectra of the *ortho*-substituted triazenes (VIIg—j) clearly suggests that each of these triazenes exist as a single tautomer.  Moreover the chemical shift for the $N$-methyl protons (*ca.* $\delta$ 3.6) is very close to that observed here for the non-conjugated tautomer of the $p$-cyano-derivative (VIIb) and is shifted downfield by approximately 0.4 p.p.m. relative to the 3,3-dialkyltriazenes (V).  This observation suggests that the preference in the triazenes (VIIg—j) is for the non-conjugated tautomer (II) exclusively.  Definite confirmation of this hypothesis is obtained from variable-temperature n.m.r. measurement with 1-methyl-3-(*o*-ethoxycarbonylphenyl)triazene (VIIh).  The singlet $N$-methyl proton resonance of (VIIh) shows no change in line width or chemical shift between $-30$ and $+60$ °C; the NH proton resonance of (VIIh) sharpens substantially at the lower temperature, presumably because of a change in the rate of proton exchange, but retains the singlet characteristic expected for the tautomer ArNH·N=NMe.

The n.m.r. spectrum of the $p$-tolyltriazene (VIIa) at $-55$ °C is consistent only with the presence of the conjugated tautomer $p$-MeC$_6$H$_4$·N=N–NHMe.  The $N$-methyl proton resonance becomes a doublet at low temperature, while the NH proton resonance becomes identifiable as a quartet, consistent with the splitting and chemical shift expected for tautomer (I).  However, the presence of the unconjugated tautomer of (VIIa) is not indicated by the n.m.r. spectrum, and therefore (VIIa) does not appear to be in a state of tautomeric equilibrium.  The absence of coupling in the room-temperature n.m.r. spectrum of (VIIa) could well be a consequence of rapid proton exchange, rather than rapid tautomerisation as suggested by Isaacs and Rannala.[4, *]

These conclusions are partially substantiated by the i.r. spectral data of the triazenes in the region of azogroup (N=N) absorption (Table).† The N=N stretching frequency of 1-aryl-3,3-dialkyltriazenes (V) has been identified with absorption at 1 410—1 415 cm$^{-1}$ in the i.r. region.[8]  Absorption in the region *ca.* 1 410 cm$^{-1}$ in the i.r. spectra of the *ortho*-nitro- and *ortho*-ethoxycarbonylphenyltriazenes (VIIg and h) is very weak, whereas strong absorption at 1 490—1 495 cm$^{-1}$ for these compounds most likely arises from the nonconjugated azogroup in the preferred tautomer (II).[9]  The i.r. spectra of the *para*-substituted triazenes (VIIb—e) exhibit two principal bands in this region, with variable intensity, at 1 415—1 430 and 1 480—1 485 cm$^{-1}$.  Although assignment of these bands is uncertain, it is possible that they arise from the N=N stretching vibration in the tautomers (I) and (II), thereby supporting the conclusion that these triazenes exist in a state of tautomeric equilibrium.

* *Note added in proof:* The unconjugated tautomer of (VIIIa) has recently been detected by low-temperature $^{13}$C n.m.r. spectroscopy (K. Albert, H. Iwamura, and A. Rieker, *Tetrahedron Letters*, 1976, 2627).  However the conclusions drawn in this paper are based on extremely weak n.m.r. signals and are thus open to question.

† Hadzi and Jan [2] studied only the NH stretching vibration region in the i.r. spectra of some of these compounds; they did not report any observations of the N=N stretching vibration.

Hadzi and Jan [2] also concluded, from i.r. data, that *para*-substituted 1-aryl-3-alkyltriazenes exist as tautomeric mixtures.  The i.r. spectrum of the $p$-tolyltriazene (VIIa) exhibits the absorption at 1 410 cm$^{-1}$ expected for the conjugated tautomer.

Thus, it is clear that the equilibrium (I) $\rightleftharpoons$ (II) is shifted in favour of the unconjugated tautomer (II) by the presence of electron-withdrawing substituents in the aryl-group, and that the preference for tautomer (II) is total when the substituent is in the *ortho*-position.  These observations correlate closely with the previously reported effect of substituents on the tautomerism of diaryltriazenes.[3]  The apparent stability of the non-conjugated tautomer could be attributed to the resonance effect of the substituent, delocalising the electron lone-pair on the N-1 atom:
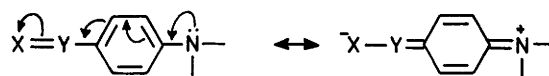


The stabilisation energy gained from this resonance could compensate for the loss of resonance energy caused by unconjugation of the N=N azo-group.  However, the total preference for the non-conjugated tautomer in the *ortho*-substituted triazenes can best be explained by the presence of a strong intramolecular hydrogen bond, as shown here for the *ortho*-ethoxycarbonyl-derivative (VIIh):
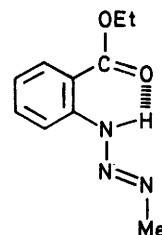


Intramolecular hydrogen bonding is much less likely in the conjugated tautomer of (VIIh) and, of course, is not possible in the *meta*- and *para*-derivatives.  The *ortho*-substituted phenyl-triazenes (VIIg—j) may represent the only known examples of triazenes that can truly be described as 1-alkyltriazenes, *i.e.* (VI).

## EXPERIMENTAL

The 1-aryl-3-methyltriazenes (VIIb—h) were prepared by coupling the arenediazonium salt with methylamine, as described previously.[1,9]  3-Methyl-1-$p$-tolyltriazene (VIIa) was obtained commercially (Eastman).  The reaction of methylamine with the diazonium salt derived from *o*-aminoacetophenone is described elsewhere.[10]  I.r. spectra were recorded in Nujol mulls with a Perkin-Elmer 467 grating spectrophotometer.  N.m.r. spectra were recorded at room temperature with a Varian A-60-A spectrometer using tetramethylsilane as internal standard in deuteriochloroform (saturated solutions); line widths (full width at half maximum height)

[8] ' Open-Chain Nitrogen Compounds,' P. A. S. Smith, Benjamin, New York, 1966, vol. II, p. 336.

[9] R. J. LeBlanc and K. Vaughan, *Canad. J. Chem.*, 1972, **50**, 2544.

[10] H. Fong and K. Vaughan, *Canad. J. Chem.*, 1975, **53**, 3714—3719.

were measured at 500 Hz sweep width, at a sweep time of 500 s. N.m.r. spectra were recorded at temperatures above and below ambient with a Varian HA100 spectrometer and a Varian V6040 variable temperature controller.

1-p-*Bromophenyl*-3,3-*dimethyltriazene*.— *p*-Bromoaniline was diazotised at 0 °C in hydrochloric acid with sodium nitrite and coupled with dimethylamine to afford 1-*p*-bromophenyl-3,3-dimethyltriazene (yield quantitative), m.p. 61.5—62 °C (lit.,[6] 62.5 °C).